#### PART 1

#### DIPOSITIVE CARBONIUM IONS

#### PART 11

SYNTHESIS AND REACTIONS OF TETRAMETHYLBENZOCYCLOBUTENE DERIVATIVES

Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY Richard Wayne Fish 1960 THESIS

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### PART I

### DIPOSITIVE CARBONIUM IONS

### PART II

### SYNTHESIS AND REACTIONS OF TETRAMETHYLBENZOCYCLOBUTENE DERIVATIVES

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Richard Wayne Fish

#### AN ABSTRACT

Submitted to the School of Advanced Graduate Studies of Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1960

Approved

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#### ABSTRACT

The primary purpose of this investigation was to determine the structure of the species responsible for the intense red color observed when trichloromethylpentamethylbenzene was added to 100% sulfuric acid. Cryoscopic measurements showed that five particles were produced in the reaction. Two of these, swept from the solution with dry nitrogen, were hydrogen chloride. Conductance measurements on the original and the hydrogen chloride-free solutions showed that two bisulfate ions were produced. Hydrolysis of the original solution gave a nearly quantitative yield of pentamethylbenzoic acid. The hydrogen chloride-free solution gave a nearly quantitative yield of pentamethylbenzoic acid and approximately one mole of chloride ion per mole of trichloromethylpentamethylbenzene when hydrolyzed. The best explanation for these data is that the fifth particle must be a stable dipositively charged carbonium ion (II).



This is believed to be the first reported example of a dipositive carbonium ion.

The structure of the dipositive ion was investigated by ultraviolet, visible and proton magnetic resonance spectroscopy. These spectra are compared with spectra of compounds with similar structures. The dication was also produced when trichloromethylpentamethylbenzene was dissolved in trifluoroacetic acid which had been saturated with boron trifluoride. Evaporation of the solvent from the solution gave a dark red, almost crystalline residue. A colorless liquid, formed when this residue was heated under reduced pressure, was ultimately converted to pentamethylbenzoic anhydride. The mechanism of this reaction is discussed.

The aluminum chloride-catalyzed reaction of carbon tetrachloride with pentamethylbenzene, which gave excellent yields of trichloromethylpentamethylbenzene, was extended to the preparation of trichloromethyl-2, 3, 4, 5-tetramethylbenzene and trichloromethyl-2, 4, 6-trimethylbenzene. These compounds also form dipositive carbonium ions in 100% sulfuric acid and in trifluoroacetic acid saturated with boron trifluoride.

An investigation of the thermal stability of trichloromethylpentamethylbenzene showed that when it is heated at 110-125<sup>°</sup>, it undergoes an intramolecular cyclization with a loss of one mole of hydrogen chloride. The product is a, a-dichlorotetramethylbenzocyclobutene, isolated in 89% yield. Hydrolysis of the dichloro compound gave a quantitative yield of tetramethylbenzocyclobutenone.

Tetramethylbenzocyclobutenone was refluxed with deuteroethanol to determine its ability to enolize to a tetramethylbenzocyclobutadienolate anion. Although two experiments gave a ketone with the same melting point, and an infrared spectrum showing a carbon-deuterium absorption, attempts to repeat the exchange were not successful.

By means of a variety of reduction procedures, it was possible to convert tetramethylbenzocyclobutenone to the corresponding alcohol, hydrocarbon, or hexamethylbenzene, each in good yield. Refluxing with alcoholic sodium hydroxide converted tetramethylbenzocyclobutenone to pentamethylbenzoic acid.

iii

### PART I

### DIPOSITIVE CARBONIUM IONS

### PART II

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By

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v

## TABLE OF CONTENTS

## Page

## PART I

## DIPOSITIVE CARBONIUM IONS

INTRODUCTION	1
RESULTS AND DISCUSSION	6
Cryoscopic Measurements	6
Conductance Measurements	12
Interpretation	14
Driving Forces for the Formation of Dipositive Ions	18
Other Trichloromethylpolymethylbenzenes	25
Ultraviolet and Visible Spectra	32
Proton Magnetic Resonance Spectra	42
Miscellaneous Experiments	50
	50
EXPERIMENTAL	59
A. Syntheses $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	59
Trichloromethylpentamethylbenzene	59
Trichloromethyl-2, 3, 4, 5-tetramethylbenzene.	60
Trichloromethyl-2, 4, 6-trimethylbenzene.	64
Bromodurene	65
Durenecarboxylic acid	67
Prehnitene (1, 2, 3, 4-tetramethylbenzene)	68
(a) Decarboxylation of 2, 3, 4, 5-tetra-	
methylbenzoic acid	68
(b) Jacobson rearrangement of durene	70
Methyl 2, 3, 5, 6-tetramethylbenzoate	71
Methyl 2, 3, 4, 5-tetramethylbenzoate	73
Methyl 2, 4, 6-trimethylbenzoate	75
Pentamethylbenzoic anhydride	75
(a) Mixed anhydride intermediate	78
(b) Reduction of pentamethylbenzoic	
anhydride	79
2, 3, 4, 5, 6-Pentamethylbenzophenone	79
Pentamethylbenzophenone dichloride	82
Pentamethylbenzaldehyde	85
a, a-Dichloromethylpentamethylbenzene	86
Chloromethylpentamethylbenzene	89

B. Structure Proof of the Trichloromethyl Compounds. 90

## TABLE OF CONTENTS - Continued

Reaction of trichloromethylpentamethylbenzene-	
100% sulfuric acid	90
(a) With water	90
(b) With methanol	90
Solvolysis of trichloromethylpentamethylbenzene.	93
(a) With aqueous acetone	93
(b) With methanol	93
Reaction of trichloromethyl-2, 3, 4, 5-tetramethyl-	
benzene-100% sulfuric acid	95
(a) With water $\ldots$ $\ldots$ $\ldots$ $\ldots$	95
(b) With methanol	95
Solvolysis of trichloromethyltetramethylbenzene.	97
(a) With aqueous acetone	97
(b) With methanol	97
Reaction of trichloromethyl-2, 4, 6-trimethyl-	
benzene-100% sulfuric acid	99
(a) With water $\ldots$	99
(b) With methanol	99
Solvolysis of trichloromethyl-2, 4, 6-trimethyl-	
benzene	101
(a) With aqueous acetone	101
(b) With methanol	101
C. Reaction of trichloromethylpentamethylbenzene with	
trifluoroacetic acid saturated with boron tri-	
fluoride	103
D. Reaction of benzoyl chloride with phosphorus penta-	
chloride	105
E. Reaction of benzotrichloride with 100% sulfuric acid	
in the presence of several aromatic hydrocarbons	106
F. Cryoscopic Measurements	107
$\mathbf{App}$ paratus	107
Procedure	108
Stock sulfuric acid	110
G. Conductance Measurements	110
Apparatus	110
Procedure	111
H. Quantitative Determination of Hydrogen Chloride	
from Dissolution of Trichloromethyl Compounds	
in Sulfuric Acid	111
Apparatus	111
Procedure	114

### TABLE OF CONTENTS - Continued

### Page

Ultraviolet an	nd visible .		• •	• •	•	•	 •	•
Proton Magne	etic Resona	.nce .			•	•	 •	•
Infrared								•

### PART II

## SYNTHESIS AND REACTIONS OF TETRAMETHYL-BENZOCYCLOBUTENE DERIVATIVES

INTRODUCTION	119
<b>RESULTS AND DISCUSSION.</b>	122
EXPERIMENTAL	137
A. Syntheses	137
a, a-Dichlorotetramethylbenzocyclobutene	137
Tetramethylbenzocyclobutenone	139
Tetramethylbenzocyclobutenol	141
butenone	141
tetrahydrofuran	141
chloride in diglyme	141
3. Sodium borohydride in diglyme	142
Tetramethylbenzocyclobutene	143
with maleic anhydride	145
C. Stability of Tetramethylbenzocyclobutenone	147
1. To ethanolic 1 N hydrochloric acid	147
2. To ethanolic 0.1 N sodium hydroxide	148
3. To 0.1 M sodium methoxide	149
D. Reactions of Tetramethylbenzocyclobutenone	149
Deuterium exchange studies	149

## TABLE OF CONTENTS - Continued

## Page

Oxidation $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	52
l. Selenium dioxide	152
2. Nitrous acid	152
Catalytic hydrogenation	153
l. Platinum oxide	153
2. Copper chromite	153
E. Miscellaneous Experiments	155
SUMMARY	157
LITERATURE CITED	16 <b>0</b>
<b>APPENDIX</b>	166

## LIST OF TABLES

TABL	Ξ	Page
I	Freezing Point Data	7
II	Stoichiometry with Respect to Hydrogen Chloride	9
III	Determination of the Third Chloride Ion after Hydro- lyzing the Hydrogen Chloride-Free Trichloromethyl Compound-100% Sulfuric Acid Solutions	11
IV	Molar Conductivities in 100% Sulfuric Acid at 25 $^{\circ}$	13
v	Recovery of Hydrogen Chloride from Chlorosulfonic- Sulfuric Acid Solutions.	16
VI	Relative Rates of Solvolysis of Benzyl Halides in $50\%$ Aqueous Acetone at $30^{\circ}$	19
VII	Solvolysis of Substituted Benzylic Chlorides in $50\%$ Ethanol at $35^{\circ}$	19a
VIII	Solvolysis of Substituted a-Phenethyl Chlorides in Absolute Ethanol at 35 <sup>0</sup>	20
IX	Freezing Point Data	30
x	Ultraviolet Absorption of Polymethyl Compounds in Cyclohexane	43
XI	Visible and Ultraviolet Absorption of Polymethyl Compounds in 100% Sulfuric Acid	44
XII	Chemical Shifts of Some Carbonium Ions	49
XIII	Conductance Data in 100% Sulfuric Acid at 25°	112
XIV	Equivalent Conductance Values for 100% Sulfuric Acid for a One Year Period	113
xv	Determination of Chloride Ion in the Presence of Sulfate Ion by Fajans' Method at pH 8	115

## LIST OF FIGURES

FIGURE Pag	çe
<ol> <li>Comparison of the ultraviolet spectra of trichloro- methylpentamethylbenzene, dichloromethylpenta- methylbenzene, chloromethylpentamethylbenzene and hexamethylbenzene in cyclohexane</li></ol>	35
<ol> <li>Comparison of the ultraviolet spectra of trichloro- methylpentamethylbenzene, trichloromethylprehnitene, trichloromethylmesitylene and benzotrichloride in cyclohexane.</li> <li>3</li> </ol>	36
3. Comparison of the ultraviolet spectrum of trichloro- methylpentamethylbenzene with the ultraviolet spectrum of pentamethylbenzene and benzotrichloride in cyclo- hexane	37
4. Comparison of the ultraviolet-visible spectra of the dipositive carbonium ions, II, XI and XIII with benzo-trichloride in 100% sulfuric acid	39
<ul> <li>5. Comparison of the ultraviolet-visible spectra of penta- methylphenylchlorodicarbonium ion in 100% sulfuric,</li> <li>1, 1, 2, 3, 4, 5, 6-heptamethylbenzenonium ion in concen- trated hydrochloric acid and pentamethylbenzoyl cation in 100% sulfuric acid</li></ul>	ŧ0
<ul> <li>6. Effect of pentamethylbenzoyl cation on the ultraviolet- visible spectrum of pentamethylphenylchlorodi- carbonium ion (in 100% sulfuric acid)</li></ul>	11
<ol> <li>Proton magnetic resonance spectra of 2M trichloro- methylpentamethylbenzene in carbon tetrachloride and 2M pentamethylphenylchlorodicarbonium ion in 100% sulfuric acid</li></ol>	16
8. Proton magnetic resonance spectra of pentamethyl- benzoic acid in chloroform and pentamethylbenzoyl cation in 100% sulfuric acid	17

## LIST OF FIGURES - Continued

FIGURE	Page
9. Infrared spectrum of trichloromethylpentamethyl- benzene	61
10. Infrared spectrum of trichloromethyl-2, 3, 4, 5-tetra- methylbenzene	63
<pre>11. Infrared spectrum of trichloromethyl-2,4,6-tri- methylbenzene</pre>	66
12. Infrared spectrum of durenecarboxylic acid	69
<pre>13. Infrared spectrum of 1, 2, 3, 4-tetramethylbenzene (prehnitene)</pre>	72
14. Infrared spectrum of methyl 2, 3, 5, 6-tetramethyl- benzoate	74
<pre>15. Infrared spectrum of methyl 2, 3, 4, 5-tetramethyl- benzoate</pre>	76
16. Infrared spectrum of methyl 2, 4, 6-trimethylbenzoate.	. 77
17. Infrared spectrum of pentamethylbenzoic anhydride	80
18. Infrared spectrum of pentamethylbenzyl alcohol	81
19. Infrared spectrum of 2, 3, 4, 5, 6-pentamethylbenzo- phenone	83
20. Infrared spectrum of pentamethylbenzaldehyde	87
21. Infrared spectrum of a, a-dichloromethylpentamethyl- benzene	88
22. Infrared spectrum of chloromethylpentamethyl- benzene	91
23. Infrared spectrum of pentamethylbenzoic acid	92
24. Infrared spectrum of methyl pentamethylbenzoate	94
25. Infrared spectrum of 2, 3, 4, 5-tetramethylbenzoic acid	96

# LIST OF FIGURES - Continued

•

FIGURE Pag	e
<ul> <li>26. Infrared spectrum of an equimolar mixture of methyl-</li> <li>2, 3, 4, 5-tetramethylbenzoate and methyl 2, 3, 5, 6-</li> <li>tetramethylbenzoate</li></ul>	8
27. Infrared spectrum of 2, 4, 6-trimethylbenzoic acid 10	0
28. Infrared spectrum of product from methanolysis of trichloromethylmesitylene	12
29. Visible spectrum of trichloromethylpentamethyl- benzene in trifluoroacetic acid saturated with boron trifluoride	)4
30. Proton magnetic resonance spectrum of trichloro- methylpentamethylbenzene in trifluoroacetic acid- boron trifluoride solvent	)4
31. Diagram of freezing-point apparatus 10	19
32. Comparison of the ultraviolet spectra of a, a-dichloro- tetramethylbenzocyclobutene and trichloromethyl- pentamethylbenzene in cyclohexane	:3
33. Ultraviolet spectrum of tetramethylbenzocyclo- butenone in absolute ethanol	:4
34. Proton magnetic resonance spectrum of a, a-dichloro- tetramethylbenzocyclobutene	:6
35. Proton magnetic resonance spectrum of tetramethyl- benzocyclobutenone 12	:7
36. Proton magnetic resonance spectrum of deuterated tetramethylbenzocyclobutenone 13	2
37. Infrared spectrum of a, a-dichlorotetramethylbenzo- cyclobutene	8
38. Infrared spectrum of tetramethylbenzocyclobutenone. 14	0
39. Infrared spectrum of tetramethylbenzocyclobutenol 14	4

## LIST OF FIGURES - Continued

FIGURE	Page
40. Comparison of the infrared spectra of tetramethyl- benzocyclobutene and hexamethylbenzene	146
41. Infrared spectrum of deuterated tetramethylbenzo- cyclobutenone	151
42. Infrared spectrum of 1, 1-dichloro-4, 6-dimethyl- benzocyclobutene	166
43. Infrared spectrum of hexamethylbenzene	167
44. Infrared spectrum of pentamethylbenzene	168
45. Infrared spectrum of 1, 2, 4, 5-tetramethylbenzene (durene)	169
46. Infrared spectrum of the second vapor chromato- graphic fraction from the decarboxylation of 2, 3, 4, 5- tetramethylbenzoic acid	170

## PART I

## DIPOSITIVE CARBONIUM IONS

INTRODUCTION

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#### INTRODUCTION

Carbonium ion theory has been invaluable in interpreting many organic reactions, and numerous types of carbonium ions have been discovered or postulated. Garbonium ions are generally thought to be transient entities of rather high energy; evidence for their intervention in reactions is largely kinetic and stereochemical. But some have been unequivocally established through the isolation of crystalline salts (1, 2, 3, 4, 5). Carbonium ions studied thus far bear a single positive charge, with the exception of ions produced in a mass spectrometer or by other high energy means (6). Even though multicharged cations are well-known in inorganic chemistry, this possibility has been ignored in the past by the organic chemist. Perhaps the reason is that carbonium ions with unit positive charge are already rather high energy, reactive species and isolation of stable ones requires a highly polar, yet nonnucleophilic solvent.

The first part of this thesis is concerned with evidence for the first example of a stable dipositive carbonium ion produced formally by loss of two anions from a single carbon atom. Before discussing the present work, it may be helpful to consider a few of the stereochemical features of carbonium ion reactions.

In a unimolecular nucleophilic substitution reaction, the ratedetermining step is the ionization of the reactant into a carbonium ion and an anion (or more precisely, to an ion-pair). The rate of the reaction is determined by the stability of the carbonium ion intermediate, solvation of the ions, and stability of the original molecule.

In contrast to bimolecular displacements, it has been shown that unimolecular reactions are facilitated by the introduction of bulky

groups at the reaction site (7). The following relative rate data are illustrative.

Relative Rates of Solvolysis of tert. - Alkyl Chlorides in 90%Acetone at 25° (7, 8).



As the alkyl groups become more branched, the solvolysis rate increases markedly. Two explanations have been suggested for this phenomenon. According to one, the enhanced solvolysis rates of highly branched halides are due to the strain caused by steric repulsion between the alkyl groups, or "B-strain" (9). B-strain is relieved when the central tetrahedral carbon atom (sp<sup>3</sup>) becomes trigonal (sp<sup>2</sup>) in the planar carbonium ion. Thus B-strain destabilizes the reacting halide molecule, decreases the activation energy and therefore increases the solvolysis rate.

An alternative explanation for the enhanced rates is that solvolysis is assisted by neighboring group participation. Evidence for this is that these highly branched tertiary alkyl halides react with molecular rearrangement to give branched olefins. Bartlett and Stiles (10) have presented evidence for neighboring group participation in the solvolysis of highly branched tertiary alcohol p-nitrobenzoates. For example, the solvolysis of tri-tert.-butylcarbinyl p-nitrobenzoate, which occurs

These tert-alkyl chlorides were prepared from the corresponding tertiary alcohols and hydrogen chloride. In some cases two or three products were obtained as a result of rearrangements, and the hydrolysis rates were determined on the mixture of products.

30 to 32.5 times faster than the corresponding tri-isopropyl ester, yields a rearranged olefin.



Rearrangements such as these suggest anchimeric assistance, but do not require it, since rearrangements may follow rather than accompany formation of the carbonium ion.

The above examples of enhanced rates of solvolysis of highly branched alkyl halides and esters may be due to either steric effects (B-strain) or to neighboring group participation. It would be interesting if one could study a series of compounds which would be free of this duplicity of interpretation. This may be realized in part with benzylic halides substituted with bulky groups in the ortho positions. Baddeley and Chadwick (11) have studied the solvolysis of several benzylic chlorides and found that 2, 4, 6-trimethyl-a -phenethyl chloride solvolyses approximately 2000-3500 times faster than a-phenethyl chloride. Rolih and Peters (12) prepared trichloromethylpentamethyl-

benzene



and reported that it reacts very rapidly with ethanol to form ethyl pentamethylbenzoate. Since pentamethylbenzoic acid is very resistant to Fischer esterification (13), this result is remarkable and suggests that esterification of I is due to an ionization step (rather than attack by ethanol).

Preliminary kinetic studies on the solvolysis of trichloromethylpentamethylbenzene show that it solvolyses many times more rapidly than benzotrichloride ( $t_1$  approximately 30 minutes at  $30^\circ$  in 90%aqueous acetone), and suggest that steric acceleration of ionization may be important.

Because of its facile solvolysis and because of the structural relationship to highly hindered polymethylbenzoic acids and the unusual behavior of the latter in 100% sulfuric acid (14, 15), a sample of trichloromethylpentamethylbenzene was added to concentrated sulfuric acid. Whereas neither benzotrichloride nor pentamethylbenzene were separately very soluble in cold concentrated sulfuric acid, trichloromethylpentamethylbenzene dissolved readily to form an intense deepred solution.

Reaction intermediates, such as carbonium ions, which are ordinarily unstable, are sometimes quite stable in sulfuric acid. It was with this in mind, that the investigation of this intensely red solution was undertaken.

The nature of solutions of organic compounds in sulfuric acid has been extensively studied, and was reviewed a few years ago by Gillespie and Leisten (16). Interest in sulfuric acid as a solvent stems from the development of a relatively simple, yet accurate technique for cryoscopic measurements (17). This, supplemented by spectrophotometric measurements, electrical conductivity measurements, and product recovery, provides an excellent means for a study of interesting reaction intermediates and an insight into the mechanism of certain organic reactions.

#### **RESULTS AND DISCUSSION**

#### Cryoscopic Measurements

The initial part of this study began with cryoscopic measurements in order to determine the number of particles produced when trichloromethylpentamethylbenzene dissolves in 100% sulfuric acid. Throughout this thesis Gillespie's terminology (18) will be used; vis the number of moles of particles (molecules or ions) produced in solution by one mole of solute, i is the observed multiple of the molal freezing point depression, and  $\gamma$  is the number of moles of HSO<sub>4</sub> ions (or  $H_3SO_4^+$  ions) produced by one mole of any solute. The results from cryoscopic measurements are given in Table I. Any conclusion as to structure of the intermediate or mechanism of the reaction depends on accurate  $\nu$  values. The experimental technique used in the cryoscopic measurements was therefore checked with several compounds with known v values. These data are included in Table I for comparison. Chlorosulfonic acid, benzoic acid, o-phenylenediamine and pentamethylbenzoic acid give v = 1, 2, 3 and 4 respectively and produce 0, 1, 2 and 2 bisulfate ions ( $\gamma$  values). Measurements were made using both maximum freezing point acid (10.36 - 10.41°) and slightly aqueous acid freezing at about 10.0°. The latter measurements were made in order to suppress the solvent dissociation, because self-dissociation in sulfuric acid may lead to erroneous v-values (18). i - Values calculated without correction for selfdissociation agreed well with literature values, and were not significantly different when determined in 100% or in aqueous sulfuric acid. Measurements were initially made in 100% sulfuric acid because it was thought that the water present in  $10.0^{\circ}$ -sulfuric acid might react with the carbonium ion intermediate.

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FREEZING POINT DATA

Compound	Wt., g.	g. H <sub>2</sub> SO4	T <sub>1</sub> , °c.	ΔΤ, <sup>°</sup> C.	Time <sup>a</sup> Hrs.	1.b	2	۲
CISO <sub>3</sub> H	0.2818	33.6	10.390	0.420	×	0.95 <sup>c</sup>	-	
1	0.2339	33.6	9.970 <sup>d</sup>	0.351	×	0.96 <sup>c</sup>	4	
C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H	0.1984	34.3	10.403	0.600	×	2.07c	2	l
1	0.3700	34.3	10.403 <sup>d</sup>	1.121	×	2.08 <sup>c</sup>		
	0.4709	106.53	9.838 <sup>e</sup>	0.430	×	1.91		
				0.383	12	1.73		
0-C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>2</sub>	0.3792	95.60	10.363	0.620	×	2.76	ŝ	2
1				0.661	24	2.94		
	0.4751	114.97	10.060 <sup>e</sup>	0.682	×	2.91		
				0.689	12	2.95		
(CH <sub>3</sub> ),C,CO <sub>2</sub> H <sup>f</sup>	0.1946	117.56	10.361	0.194	×	3.68	4	2
				0.206	18	3.91		
	0.2021	101.91	10.100 <sup>e</sup>	0.239	×	3.79		
				0.253	16	4.01		
(CH <sub>3</sub> ),C6CCl <sub>3</sub>	0.1541 <sup>g</sup>	32.77	10.407	0.524	×	4.84 <sup>c</sup>	Ŋ	2
				0.524	4	4.84 <sup>C</sup>		
	0.1648h	34.41	10.397	0.585	<b>X</b>	5.30 <sup>c</sup>		
	0.5012 <sup>1</sup>	81.72	10.356	0.731	×	5.17		
				0.761	24	5.30		
	0.4137 <sup>1</sup>	88.60	10.003 <sup>e</sup>	0.548	×	5.09		
				0.572	12	5.32		
	0.2040 <sup>1</sup>	45.85	10.407	0.302	0.5	2.95 <sup>c</sup>	3	শ্য
	0.3577 <sup>3</sup>	45.85	10.407	0.480	12	2.68 <sup>c</sup>		
ax signifies that t	the determin	nation was m	ade immedia	atelv. the t	ime to reach e	auilibrium	being 10	to 30

added to the solution from the previous experiment.  $^{e}98\%$  sulfuric acid was purposely added to 100% sul-furic acid, to bring it to the water side. <sup>1</sup>Pentamethylbenzoic acid. <sup>g</sup>The sum of two smaller additions which, separately, gave i = 4.86, 4.98. <sup>h</sup>The sum of three smaller additions which, separately, gave i = 4.81, 5.16, minutes.  $\dot{b}_{i}$  is calculated from the equation  $\Delta T/6$ . 12 m<sub>s</sub>, when  $m_{a}$  is the molality of the solute. <sup>c</sup>Apparatus with magnetic stirrer; all others in apparatus with mechanical stirring (see Experimental). <sup>d</sup>Solute was 4.95. <sup>1</sup>Solute added in CCl<sub>4</sub> solution. <sup>j</sup>Determinations made after the solutions were swept with anhydrous nitrogen for the time shown, to remove the hydrogen chloride (vide infra)

Because hydrogen chloride was produced in the reaction of trichloromethylpentamethylbenzene with sulfuric acid, it was necessary to make freezing point measurements at such concentrations that the solubility of hydrogen chloride in sulfuric acid would not be exceeded at the temperature of the measurement. Cupr (19) determined the solubility of hydrogen chloride in 100% sulfuric acid at 25°, and found it to be soluble to the extent of 0.11 molal. He also showed that the solubility increases with decreasing temperature (20) as expected. The maximum molality of trichloromethylpentamethylbenzene in the freezing point determinations was 0.0231; even at these concentrations, depressions were large and accurately measurable because of the high  $\nu$  values.

The data in Table I indicate clearly that trichloromethylpentamethylbenzene produces five particles when it dissolves in 100% sulfuric acid. The stability of the particles produced is indicated by no appreciable alteration of  $\underline{v}$  value over a 24-hour period. Further evidence for the stability of the intermediate produced is shown by no change in the ultraviolet-visible absorption spectrum over a 24-hour period (see Table X).

#### Stoichiometry

The stoichiometry with respect to hydrogen chloride was investigated because it was one of the most obvious products (odor, litmus) of the reaction. The amount of hydrogen chloride produced was determined quantitatively by passing a stream of dry nitrogen through the red solution at 10-15°; hydrogen chloride was trapped in a 2% sodium hydroxide solution, the latter acidified and titrated for chloride ion (Fajans' method). The results are summarized in Table II. Control experiments with the Fajans' method in the presence of varying amounts of sulfate ion (some sulfur trioxide would be carried over from the 100% sulfuric acid) gave excellent results.

#### TABLE II

Compound	Wt.(g) <sup>a</sup>	Time	Ml. of	Moles Cl <sup>-</sup> /mole of trichloro-
		(min.) <sup>b</sup>	AgNO3	methyl compound
Trichloromethyl-	0.2040	30	14.29 <sup>c</sup>	2.006
pentamethyl-	0.3577	60 <sup>f</sup>	25.12 <sup>c</sup>	2.010
benzene	0.2501	60	18.81 <sup>d</sup>	2.051
	0.2320	60	17.07 <sup>d</sup>	2.008
	0.5163	180	36.97	2.110
Trichloromethyl-	0.2540	30	23.76 <sup>e</sup>	2.088
prehnitene	0.1300	15 <sup>f</sup>	11.93 <sup>e</sup>	2.048
Trichloromethyl	0.3854	15h	9.83 <sup>c</sup>	0.654
mesitylene	0.3652	30	29.75 <sup>c</sup>	1.910
•	0.4054	120	30.24 <sup>c</sup>	2.026
	0.3917	1200 <sup>i</sup>	44.59 <sup>c</sup>	2.931

#### STOICHIOMETRY WITH RESPECT TO HYDROGEN CHLORIDE

<sup>a</sup>In 25 ml. of 100% sulfuric acid.

Length of time that nitrogen swept through the solution; the rates of flow varied. <sup>c</sup>0.1078 N

<sup>d</sup>0.1027 N

<sup>e</sup>0.0888 N

<sup>f</sup>l2 more hours of sweeping at this rate gave no detectible  $Cl^-$ .

h Sulfuric acid solution froze.

<sup>1</sup>Ultraviolet-visible spectra samples were taken at various time intervals; the solution probably inadvertently absorbed water, since the spectrum changed to that of the mesitoyl cation.

Each mole of trichloromethylpentamethylbenzene dissolved in 100% sulfuric acid produced two moles of hydrogen chloride. This quantity of hydrogen chloride was rapidly flushed from the solution, and prolonged sweeping (10-12 hours) gave negligible additional hydrogen chloride.

The nitrogen used in these experiments was pre-dried and saturated with sulfur trioxide by passage through two scrubbers containing 100% sulfuric acid; in this way sulfur trioxide swept from the red solution was continuously replaced, enabling freezing point (Table I) and conductance (Table IV) measurements to be made on the hydrogen chloride-free solutions. Consistent with the hydrogen chloride stoichiometry, the swept solutions had  $\underline{\nu} = 3$ . The ultraviolet-visible spectrum was also unchanged.

When the hydrogen chloride-free solution was poured on cracked ice, there was obtained 93.3 - 96.3% yield of pentamethylbenzoic acid. The filtrate from these hydrolyses was neutralized and titrated for chloride ion (Fajans' method), yielding 0.76 to 1.05 moles per mole of trichloromethylpentamethylbenzene (see Table III).

It was quite apparent at this point that two of the five particles produced when trichloromethylpentamethylbenzene is dissolved in 100% sulfuric acid are hydrogen chloride. One might conclude also that these would be accompanied by the formation of two bisulfate ions, because the methyl groups were unaffected; they were recovered upon hydrolysis as pentamethylbenzoic acid. The only other source of hydrogen for the hydrogen chloride was the solvent, and sulfate ions are basic to 100% sulfuric acid. Conductance measurements were made to verify the conclusion that two bisulfate ions are produced.

#### TABLE III

## DETERMINATION OF THE THIRD CHLORIDE ION AFTER HYDROLYZING THE HYDROGEN CHLORIDE-FREE TRICHLOROMETHYL COMPOUND-100% SULFURIC ACID SOLUTIONS

Compound	Sample Wt. g.	Moles Cl <sup>-</sup> /mole of trichloromethyl compound
Trichloromethyl-	0.2412	1.050 <sup>a</sup>
pentamethylbenzene	0.5163	0.760 <sup>b</sup>
Trichloromethyl-	0.4621	0.95 <sup>c</sup>
prehnitene	0.3159	0.815 <sup>b</sup>

<sup>a</sup>Chloride ion titrated by Fajans' method in the presence of sulfate ion after neutralization of the filtrate to pH 8.

<sup>b</sup>Sulfate ion precipitated with barium hydroxide, solution filtered, adjusted to pH 8 and chloride ion titrated by Fajans' method.

<sup>C</sup>Sulfate ion precipitated with barium hydroxide, solution filtered, adjusted to pH 3 and chloride ion determined gravimetrically.

#### Conductance Measurements

Hammett and Lowenheim (21) demonstrated that in solutions of barium and strontium hydrogen sulfates in sulfuric acid, greater than 99% of the current was carried by the bisulfate ion. This anomaly was explained in terms of the Grothuss chain mechanism in which protons are transferred from sulfuric acid molecules to bisulfate ions. One step in this process may be represented as follows



Thus by a succession of proton transfer the charge is transported through the solution without the actual movement of bisulfate ion.

In addition to extending the work of Hammett and Lowenheim, Gillespie and Wasif (22) have made a comprehensive investigation of the conductivities of electrolyte solutions in sulfuric acid. They pointed out the useful fact that since the conductance of any basic solute in sulfuric acid is due almost exclusively to bisulfate ions one can determine from molar conductivities the number of bisulfate ions ( $\gamma$ ) produced by the ionization of one mole of solute. Thus these data, along with cryoscopic measurements, should enable one to determine the mode of ionization of the solute. This appeared to be an ideal tool for the problem at hand.

Molar conductance measurements were carried out on compounds of known molar conductivities in order to check our experimental procedures. The molar conductances of potassium bisulfate, <u>o</u>-phenylenediamine, and trichloromethylpentamethylbenzene in 100% sulfuric acid were determined at approximately 0.05, 0.10 and 0.20 molar concentrations. The results, rounded off with regard to concentration, are given in Table IV. The data for the first two compounds are compared with those of Gillespie and Wasif (22). The results TABLE IV

MOLAR CONDUCTIVITIES<sup>(a)</sup> IN 100% SULFURIC ACID AT 25<sup>o</sup>

W	KHSO4	0-C6H4(CH2)2	(CH <sub>3</sub> ) <sub>5</sub> C <sub>6</sub> CCl <sub>3</sub>	(CH <sub>3</sub> )4C <sub>6</sub> HCCl <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CCl <sub>3</sub>
0.05		314 (306)	307	308	303
0.10	157 (156) <sup>b</sup>	227 (236)	212	212	198
0.20	121 (116)	164 (187)	156	152	162

(a) Rounded off with regard to molarity. Actual data, measured at at least four frequencies, are given in Table XIII.

(b) Values in parentheses from Gillespie and Wasif, ref. 22.

are consistent only with the formation of two moles of bisulfate ion per mole of trichloromethylpentamethylbenzene in sulfuric acid. Conductance measurements on the hydrogen chloride-free solutions also verified the production of two bisulfates (see Table XIII).

#### Interpretation

Four of the five particles have been accounted for, (two bisulfate ions and two hydrogen chloride molecules) and quite stringent requirements have been placed on the fifth particle. It must (1) produce pentamethylbenzoic acid on hydrolysis; (2) contain one chlorine atom; (3) be intensely red; (4) bear two positive charges in order to preserve neutrality. To account for these requirements the following equation is written



This equation, which involves the loss of two chloride ions from a single carbon, resulting in the dipositive carbonium ion (II), constitutes the most satisfactory explanation of all the data.

Even though equation (1) is believed to provide the most satisfactory explanation, several alternative explanations which were subsequently rejected because they did not meet all the requirements, will be discussed.



\*Bonds are used to represent methyl groups.

This equation fulfills the requirements for the formation of five particles and is consistent with the conductance measurements. However, the requirement for two molecules of hydrogen chloride is not met. Cryoscopic measurements on chlorosulfonic acid in 100% sulfuric acid gave  $\underline{\nu}$  values of one (see Table I). One might conclude that chlorosulfonic acid does not dissociate in 100% sulfuric acid. Gillespie's work (23) indicates that chlorosulfonic acid does in fact dissociate in sulfuric acid, probably as follows: ClSO<sub>3</sub>H + H<sub>3</sub>O<sup>+</sup> + HSO<sub>4</sub>  $\longrightarrow$  2H<sub>2</sub>SO<sub>4</sub> + HCl. This equilibrium upsets the series of equilibria in 100% sulfuric acid (18), so that the over-all result is the depression of the freezing point by one  $\nu$  value.

When solutions of chlorosulfonic acid in 10.0° (99.95%) sulfuric acid were swept with dry nitrogen, there was a gradual loss of hydrogen chloride from solution (see Table V). After twelve hours only 74% of the hydrogen chloride had been swept out of the chlorosulfonicsulfuric acid solution. This experiment disproved the argument that hydrogen chloride from trichloromethylpentamethylbenzene-sulfuric acid solutions reacts reversibly with sulfuric acid to form chlorosulfonic acid, which then loses hydrogen chloride when swept with dry nitrogen. Hydrogen chloride was rapidly and completely swept from the sulfuric acid solution of trichloromethyl pentamethylbenzene.



This equation also satisfies the cryoscopic measurement requirements. It would appear that the recovery of two molecules of hydrogen chloride is also satisfied. However, as pointed out in the preceding paragraph, chlorosulfonic acid is converted in part to hydrogen chloride in sulfuric acid. The equilibrium which is set up

### TABLE V

Wt., g. chlorosul- fonic acid	Wt., g. sulfuric acid <sup>a</sup>	Time, <sup>b</sup> hr.	Ml. of AgNO <sub>3</sub>	Moles Cl <sup>-</sup> /mole of chlorosulfonic acid
1.00	58.3	0.5	18,45 <sup>C</sup>	0,248
		1	10.78	0.128
		2	8.09	0.096
		4	9.73	0.131 <sup>d</sup>
1.06	60.1	0.5	12.84 <sup>e</sup>	0.172
		1	12.01	0.160
		3	17.53	0.234
		5	11.29	0.151
		12	9.66	0.129 <sup>f</sup>

## RECOVERY OF HYDROGEN CHLORIDE FROM CHLOROSULFONIC-SULFURIC ACID SOLUTIONS

<sup>a</sup>10.0<sup>°</sup> (99.95%) - sulfuric acid.

<sup>b</sup>Chloride ion titrated by the Fajans' method after time intervals shown.

<sup>C</sup>0.1067 N AgNO<sub>3</sub>.

<sup>d</sup>58.2% chloride recovered in four hours.

<sup>e</sup>0.1062N AgNO<sub>3</sub>

 $^{\rm f}74\%$  chloride recovered in twelve hours.

can be shifted by sweeping the solution with dry nitrogen; therefore more than two molecules of hydrogen chloride should be obtained.

Furthermore the spectrum shows that the pentamethylbenzoyl cation is not a product of this reaction (Figures 5 and 6). Figure 5 is a comparison of the ultraviolet and visible spectrum of the pentamethylbenzoyl cation [produced by the reaction of pentamethylbenzoic acid with 100% sulfuric acid (23)] and the product from the reaction of trichloromethylpentamethylbenzene with 100% sulfuric acid (dipositive carbonium ion). Dilute solutions of the pentamethylbenzoyl cation are colorless whereas dilute solutions of the dipositive ion are intensely red. Figure 6 shows the effect on the ultraviolet-visible spectrum, of adding small known amounts of pentamethylbenzoic acid to the trichloromethylpentamethylbenzene-100% sulfuric acid solution. From this experiment one can conclude that greater than ninety-eight per cent of the intermediate is the dipositive carbonium ion.

(4) 
$$CCl_3 + 2H_2SO_4 \longrightarrow CCl_3 + 2HCl + HSO_4$$
  $+ 2HCl + HSO_4$ 

This equation shows the production of but four particles, but if an equilibrium is established between the hydrogen chloride and the sulfuric acid,

(5) 
$$HC1 + 2H_2SO_4 \longrightarrow H_3O^+ + HSO_4^- + C1SO_3H$$

and if this is considered to proceed to 50% completion in the forward direction, five particles could be obtained. The over-all reaction would be:

(6) 
$$-CCl_3 + 2H_2SO_4 \longrightarrow -CCl_3 + 1\frac{1}{2}HCl + 1\frac{1}{2}HCl + 1\frac{1}{2}HSO_4^- + \frac{1}{2}ClSO_3H + \frac{1}{2}H_3O^+$$
Neither the stoichiometry with respect to hydrogen chloride, nor the conductance results are precisely met, but one might argue (not convincingly) that they are within the limits of experimental accuracy. But sweeping with nitrogen should reverse equilibrium (5) and alter the molar conductance from that expected for a single bisulfate ion. When conductance measurements were made on the hydrogen chloride-free solutions, the equivalent conductance was almost the same as that obtained on the original solution (see Table XIII). It appears that equations (2), (3) and (6) are not as satisfactory in explaining the experimental data as is equation (1).

# Driving Forces for the Formation of Dipositive Ions

Before discussing the possible reasons for dication formation, it might be profitable to examine some compounds with similar structures. Hine and Lee (24) and Olivier and Weber (25) have studied the solvolysis of various benzyl, benzal and benzohalides. Their work showed that there was a marked increase in solvolysis rates with accumulation of halogen atoms on the benzyl carbon (Table VI).

Initial apprasial of Table VI might lead one to suggest that B-strain could account for the increase in solvolysis rates. An indication that B-strain is not a predominant factor, however is shown by the greater effect of chlorine in accelerating solvolysis as compared with bromine. Therefore the increase must be largely due to resonance stabilization of the carbonium ion intermediate.

$$=\overset{+}{c}$$
  $-\overset{+}{x}:$   $\longleftrightarrow$   $=$   $c$   $=$   $\overset{+}{x}:$ 

**Resonance stabilization occurs to a greater extent with chlorine, due to the greater ease of double bond formation.** 

## TABLE VI

	Compound	Relative Rate	
· • • •	PhCH <sub>2</sub> Cl	1.0	
	PhCHCl <sub>2</sub>	9.60	
	PhCCl <sub>3</sub>	496.0	
	PhCH <sub>2</sub> Br	25.0	
	PhCHBr <sub>2</sub>	30.8	
	PhCBr <sub>3</sub>	5090	
	<b>PhCHClBr</b>	140	
	PhCClBr <sub>2</sub>	8160	
	PhCCl <sub>2</sub> Br	9510	
_	PhCF <sub>2</sub> Cl	0.188	

# RELATIVE RATES OF SOLVOLYSIS OF BENZYL HALIDES IN 50% AQUEOUS ACETONE AT 30<sup>0</sup> (24)

Despite the fact that fluorine has a greater tendency to form double bonds compared with chlorine, Table VI shows that the fluorine atom has less effect in accelerating the  $S_N^1$  reaction. This may be due to the greater inductive electron withdrawal and possibly the smaller size (if B-strain is important) of the fluorine atom.

If resonance stabilization of the carbon is more important than B-strain in the solvolysis of benzohalides, then if one were to introduce bulky substituents in the ortho positions, B-strain might become the predominant factor in determining the solvolysis rates. Unfortunately, there have been no studies on ortho-substituted benzohalides, but Charlton and Hughes (26) have made an extensive solvolysis study of substituted benzyl chloride derivatives.

#### TABLE VII

# SOLVOLYSIS OF SUBSTITUTED BENZYLIC CHLORIDES IN 50% ETHANOL AT 35° (26)



These results suggest that B-strain might operate to a certain extent, since  $k_{rel}(expt'l)$  for the 2, 6-dimethyl derivative is 1.06 times greater than  $k_{rel}(expected)$  and that for the mesityl derivative is five times the calculated value. However, models show that steric compression between a-hydrogens and ortho-methyl groups is scarcely appreciable. Before discussing the results of Table VII further, it would be advantageous to examine the effects of a-methyl substitution (26, 27).

#### TABLE VIII

SOLVOLYSIS OF SUBSTITUTED a-PHENETHYL CHLORIDES IN ABSOLUTE ETHANOL AT 35° (26)



Similar results were obtained by Baddeley and Chadwick (27).

To explain these results one must consider the mechanism for unimolecular substitution reactions for substituted benzylic and a-phenethyl chlorides.



The dotted line represents the plane of the benzene ring, R and R' represent ortho hydrogen or methyl groups.

In a benzyl-type halide, the bonding in the side-chain is tetrahedral  $(sp^3)$ ; in general neither of the two a-groups will be in the plane of the benzene ring and its ortho substituents. In the carbonium ion, the side-chain bonding is trigonal  $(sp^2)$  and because of conjugation, it is coplanar with the aromatic ring, so that both a-groups and both ortho-groups necessarily come into the same plane. The transition state of the rate-controlling ionization is in an intermediate stereochemical situation; the side-chain will not be fully coplanar with the benzene ring, but the bonds holding the a-groups will have moved in that direction. If, therefore, steric compression were incipient in the original molecule, it would become appreciable in the transition state. This would lead to an increased energy of activation, and thus to a steric retardation of the reaction.

From a comparison of the data in Tables VII and VIII, one sees that o- and p-methyl substituents exert comparable accelerating effects and that the second ortho group introduces a factor of acceleration which is of the same order of magnitude as that given by the first. The accelerations are too uniform to be regarded as steric accelerations. Therefore the increase in rate of solvolysis must be due to the polar (inductive and hyperconjugative) effect of the methyl groups. In Table VIII, the polar effects of the nuclear methyl groups are slightly larger than in the benzyl series. This is a logical result of greater  $S_N$ l character in the transition state. However, introduction of a second ortho-methyl group does not follow the additive principle, as it did in the benzyl series. Evidently the retarding effect of steric inhibition of resonance cancels or almost outweighs the polar effect of the second ortho-methyl group.

The above discussion on the rates of solvolysis of benzyl, benzal and benzohalides and methyl substituted benzylic halides is of interest because it points out the number of factors which must be considered in a mechanism study of such systems. Trichloromethylpentamethylbenzene cannot be exclusively compared with any one of these compounds because its structure should embrace the properties of both benzohalides and methyl substituted benzylic halides.

A Fisher-Hirschfelder model of trichloromethylpentamethylbenzene shows that steric strain in the ground state should be an important factor in dication formation. The large trichloromethyl group cannot rotate with respect to the neighboring ortho methyl groups. Every methyl group is fitted closely to its neighbor. The steric repulsion between the trichloromethyl group and the ortho methyl groups should provide a driving force for the loss of two chlorine atoms. The loss of one chlorine atom by the ionization does not help the situation markedly, because the resulting carbonium ion, pentamethylphenyldichlorocarbonium ion



cannot be stabilized unless the remaining two chlorine atoms lie

co-planar with the aromatic ring. This situation is sterically unfavorable because of the interaction of the chlorine atoms with the ortho methyl groups. However a second ionization would eliminate the steric repulsion because the structure would now be linear,  $=\overset{+}{C}-Cl$ or  $=C=\overset{+}{Cl}$ . Thus from the steric viewpoint, the most stable structure is obtained if two chloride ions are lost. The charge can be distributed in many ways, some of which are shown below.



The problem now becomes one of establishing the detailed mechanism, and in particular to determine whether the loss of two chloride ions is a simultaneous or step-wise process. At present, no definitive information is available on this point.

The ionization of trichloromethylpentamethylbenzene in sulfuric acid may be compared with the behavior of pentamethylbenzoic acid, mesitoic acid and their esters in sulfuric acid. Hammett discovered in connection with his cryoscopic studies (14), that if a highly hindered methyl benzoate is dissolved in concentrated sulfuric acid and then poured into cold water, an immediate hydrolysis takes place and the acid is produced. Methyl benzoate itself is unchanged under the same conditions. Newman followed up the corollary of this work (15), and found that a solution of a mesitoic or pentamethylbenzoic acid in 100% sulfuric acid, when poured into absolute methanol yields the ester immediately. Benzoic acid is not esterified when so treated. The explanation for this is based primarily on stereochemical considerations. When methyl benzoate or benzoic acid is dissolved in sulfuric acid, a proton attacks the carbonyl oxygen of the ester or acid (28) as follows:



When pentamethylbenzoic or mesitoic acid and their esters dissolve in sulfuric acid, the first step may also be protonation of the carbonyl oxygen. However, resonance stabilization of this ion requires coplanarity of the system, which is prohibited in the hindered structure VIII; this difference is enough to shift the equilibrium toward the unhindered acyl cation IX.



These reactions are substantiated by cryoscopic and conductance measurements.

The unusual behavior of polymethylbenzoic acids is perhaps more complex than first appearances would indicate. Other substituted benzoic acids which are just as sterically hindered, 2, 4, 6-tribromobenzoic acid and 3, 5-dibromo-2, 4, 6-trimethylbenzoic acid, do not form the acyl cation (14, 15) but behave more like benzoic acid. They are only partially in the acyl form in sulfuric acid. It appears that the inductive and resonance effects of the methyl groups help stabilize the acylium ion obtained from mesitoic and pentamethylbenzoic acids.

Steric strain may be only one factor in dication formation also. In this case, as with the polymethylbenzoic acids, it appears that electron-releasing groups substituted on the benzene ring may be required to stabilize the positive charges on the ions formed. Perchlorotoluene is reported by Ballester (29) to hydrolyze quantitatively but slowly (48 hours) in hot  $(100^{\circ})$  concentrated sulfuric acid to pentachlorobenzoic acid. a, a, a, a', a'-Pentachloro-o-xylene, another fairly strained trichloromethyl compound, was found to be insoluble in 100% sulfuric acid.

## Other Trichloromethylpolymethylbenzenes

In order to examine the scope of dicarbonium ion formation, trichloromethyltetramethylbenzene and trichloromethyltrimethylbenzene were prepared by a Friedel-Crafts reaction of carbon tetrachloride with 1, 2, 4, 5-tetramethylbenzene (durene) and 1, 3, 5-trimethylbenzene (mesitylene), respectively. The procedure was similar to that used in the preparation of trichloromethylpentamethylbenzene. In contrast to the trichloromethylpentamethylbenzene preparation, the Friedel-Crafts reaction of carbon tetrachloride with durene and mesitylene gave mixtures. The main products were shown to be trichloromethyl-2, 3, 4, 5-tetramethylbenzene (m. p. 90-91.5°) from durene and trichloromethyl-2, 4, 6-trimethylbenzene (a liquid) from mesitylene. In one experiment, trichloromethyl-2, 3, 4, 5-tetramethylbenzene was obtained in 75.4% yield. The yield depends on the reaction conditions and work-up procedure.

The proof of structure of these compounds involved hydrolysis of the trichloromethyl compound by two procedures; (1) refluxing with aqueous acetone and (2) addition of the trichloromethyl compound to 100% sulfuric acid and addition of the resulting dark red solution to cracked ice, followed by quantitative recovery of the carboxylic acid. The carboxylic acids from hydrolysis of trichloromethyl-2, 4, 6trimethylbenzene in aqueous acetone and 100% sulfuric acid-ice, were identical; the neutralization equivalent and melting point checked the literature value (15) for 2, 4, 6-trimethylbenzoic acid. The carboxylic acids from hydrolysis of trichloromethyltetramethylbenzene in aqueous acetone and 100% sulfuric acid-ice were also identical; the neutralization equivalent checked for tetramethylbenzoic acid, but the melting point (168-169°) did not agree with the literature value (30) for 2, 3, 5, 6 tetramethylbenzoic acid  $(176-179^{\circ})$ , the acid expected from a trichloromethylated durene. The melting point did agree with the literature value (31) for 2, 3, 4, 5-tetramethylbenzoic acid. The acid was decarboxylated with copper and quinoline, and the resulting hydrocarbon was purified by vapor-phase chromatography. The elution peak was rather broad, so two fractions were collected. The first of these had an infrared spectrum identical to that reported by Launer and McCauley (32) for 1, 2, 3, 4-tetramethylbenzene (prehnitene). It was also identical to an authentic sample of prehnitene prepared from durene by the Jacobsen rearrangement (33). The second fraction had the characteristic prehnitene bands, but also contained unidentified impurities (see Figure 43).

Further proof of the structure was obtained by the preparation of the corresponding methyl ester by three different procedures, methanolysis of trichloromethyltetramethylbenzene and methylation of 2, 3, 4, 5-tetramethylbenzoic acid with diazomethane and by the Newman (15) procedure. The same methyl ester, m.p.  $35-36^{\circ}$  (31), was obtained in all three experiments.

2, 3, 5, 6-Tetramethylbenzoic acid was prepared by carbonation of the Grignard reagent from bromodurene. The melting point of this acid, 178-179<sup>°</sup>, agreed with that reported by Newman and Lloyd (34); the methyl ester, prepared with diazomethane, melted at 58<sup>°</sup> (34).

Rearrangement during the trichloromethylation of durene is interesting, because it is contrary to what would be expected. A survey of the literature on the preparation of polyalkylbenzenes by the Friedel-Crafts reaction shows that the main products are often the most symmetrical isomers (33). Smith and co-workers (33, 36) reported that the methylation of technical xylene yielded a mixture of polymethylbenzenes, but no 1, 2, 3, 4-tetramethylbenzene was isolated. Isomerization of hexamethylbenzene, pentamethylbenzene, mesitylene and pseudocumene with aluminum chloride yielded some tetramethylbenzene, but no 1, 2, 3, 4-tetramethylbenzene was reported (33).

Baddeley and Pendleton (38) reported that acetophenones with ortho alkyl groups are unstable at temperatures of  $80-150^{\circ}$  in the presence of hydrogen halide and excess aluminum chloride and undergo a variety of irreversible changes. The reaction between acetyldurene and excess aluminum chloride at  $100^{\circ}$  yields a mixture of <u>80% acetylprehnitene</u>; 10% diacetyldurene and 10% of aromatic hydrocarbon. There is no reaction between acetylprehnitene and excess aluminum chloride when refluxed at  $150^{\circ}$  for three hours. Therefore acetylprehnitene is presumed to be the most thermodynamically stable isomer. Using Baddeley's work as an example, one can easily rationalize the isomerization of trichloromethyldurene to trichloromethylprehnitene, Durene is first alkylated with carbon tetrachloride to give trichloromethyldurene, which is not thermodynamically stable under the conditions of the reaction (37-42°). A Fisher-Hirschfelder model of trichloromethyldurene shows steric strain which can be relieved by migration of one ortho methyl group to the open meta position.

The Friedel-Crafts reaction of carbon tetrachloride with polymethylbenzenes is quite a unique reaction. It has been known for many years (39) that the Friedel-Crafts reaction of benzene with carbon tetrachloride gives dichlorodiphenylmethane and triphenylmethyl chloride or diphenylmethane and triphenylmethane, depending on the work-up procedure. If toluene and the xylenes are used in place of benzene, one obtains the corresponding dichlorodiphenylmethanes and triarylmethyl chloride (40, 41). It was not until recently that the mechanism of such reactions was investigated. Tsukervanik and Belinson (42) postulated that benzotrichloride is an intermediate in such reactions. To prove this, they condensed benzotrichloride with benzene using various amounts of aluminum chloride. They found that the amount of aluminum chloride is the principal factor which determines the product. With 0.1 mole of aluminum chloride per mole of benzotrichloride, dichlorodiphenylmethane was obtained in 70% yield. With one mole of aluminum chloride per mole of benzotrichloride, triphenylmethyl chloride was obtained in 80-85% yield. Further increase in the amount of aluminum chloride (2 moles) caused accumulation of tars and the yield of triphenylmethyl chloride decreased. The yields were independent of the temperature  $(15-90^{\circ})$ .

The reason that mesitylene, durene, and pentamethylbenzene yield trichloromethyl compounds, rather than condensation products may be stereochemical in nature.

Experiments to determine the ability of trichloromethylmesitylene and trichloromethylprehnitene to form dications were performed in the

same manner as those used for trichloromethylpentamethylbenzene. Both trichloromethylmesitylene and trichloromethylprehnitene dissolved readily and formed dark red solutions in 100% sulfuric acid. The intensity of the red color of the solutions increased with increasing number of methyl groups in the trichloromethyl compounds (see Figure 4 for a comparison of ultraviolet-visible spectra).

The results of cryoscopic measurements are given in Table IX. Trichloromethylmesitylene produces five particles when it dissolves in 100% sulfuric acid. The  $\underline{v}$  value increases with time, indicating that sulfonation must be taking place. Trichloromethylprehnitene also produces five particles. It appears to be more stable than trichloromethylmesitylene, but less stable than trichloromethylpentamethylbenzene, stability being indicated by no appreciable alteration of  $\underline{v}$ value over a 6-hour period, and no change in the ultraviolet-visible spectrum during this time. Cryoscopic measurements on the deep red solutions, after two moles of hydrogen chloride were removed, indicate that three particles remain in solution.

Quantitative recovery of hydrogen chloride from trichloromethylprehnitene—100% sulfuric acid solutions show that two moles of hydrogen chloride are swept out within thirty minutes; additional sweeping yields essentially no more hydrogen chloride. The ultraviolet-visible spectrum was the same before and after removal of hydrogen chloride.

Several experiments were carried out to recover hydrogen chloride from trichloromethylmesitylene. In one experiment slightly greater than two moles of hydrogen chloride were recovered in one hour. In another experiment, ultraviolet-visible spectra were taken after sweeping the system with dry nitrogen for various time intervals. There was a gradual change of the spectrum over a fourteen hour period, from a spectrum of XI to that of the mesitoyl cation. Three moles of hydrogen chloride were removed in this experiment (either the sulfuric

29

TABLE IX

FREEZING POINT DATA

Compound	Wt., g.	g. H <sub>2</sub> SO4	T <sub>1</sub> , <sup>o</sup> C.	ΔΤ, <sup>o</sup> C.	Time <sup>a</sup> Hrs.	q.1	2	۲
(CH <sub>3</sub> ),C,HCCl <sub>3</sub>	0.2718	114.26	10.098	0.300	×	5.18 <sup>c</sup>		
Trichloromethyl-	0.2868	114.00	10.098	0.315	×	5.15 <sup>c</sup>	Ŋ	2
2, 3, 4, 5-tetra-	0.2776	113.71	10.098	0.343	×	5.78 <sup>c</sup>		
methylbenzene	0.3095	94.34	9.904	0.402	×	5.04 <sup>c</sup>		
	0.3100	94.10	9.904	0.396	×	<b>4.</b> 96c		
	0.2540 <sup>f</sup>	45.85	10.421	0.394	×	2.93 <sup>d</sup>	°	2
	0.1300 <sup>f</sup>	45.85	10.418	0.190	×	2.76 <sup>d</sup>		
(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CCl <sub>3</sub>	0.1250	46.50	10.360	0.356	×	5.14 <sup>d</sup>	5	2
Trichloromethyl-	0.2471	51.30	10.315	0.631	×	5.09 <sup>d</sup>		
2, 4, 6-trimethyl-				0.789	6	6.42d		
benzene				1.189	18	9.57 <sup>d</sup>		
	0.1974	52.20	10.402	0.328	×	5.20		
				0.532	l	5.46		
				0.579	γ	5.94		
C <sub>6</sub> H <sub>5</sub> CC1 <sub>3</sub>	0.1794	35.51	10.369	0.949	×	6.00 <sup>d</sup>	9	
	0.1581	36.10	10.369	0.842	×	6.14 <sup>d</sup>		ı
	0.2892	36.10	10.369	1.530	н	6.09 <sup>d</sup>		
[(CH <sub>3</sub> ) <sub>5</sub> C <sub>6</sub> CO] <sub>2</sub> O	0.2048	107.80	10.361	0.179	×	5.64	6	ŝ
				0.193	12	6.08		
	0.2157	87.62	10.065 <sup>e</sup>	0.240	×	5.83		
				0.245	12	5.96		
ax signifies that the minutes. i is cale obtained by R. Rafo	e determina culated fron s. <sup>d</sup> Appare	tion was made n the equation atus with mag	e immediat ΔT/6.12 r netic stirre	ely, the time n <sub>s</sub> , when m <sub>i</sub> er; all other	e to reach equ s is the molal: s in apparatus	ilibrium bo ity of the s with mecl	eing 10 to olute. <sup>C</sup> Dâ hanical sti	30 ita rring
(see Experimental).	e98% sulfu	rric acid was	purposely;	added to 100	% sulfuric aci	d, to bring	g it to the	water

side. <sup>f</sup>Determinations made after the solutions were swept with anhydrous nitrogen for the time shown, to remove the hydrogen chloride (vide infra). acid was not 100% or water was absorbed by the solution when the samples were taken for spectra).

When the hydrogen chloride-free solution from trichloromethylmesitylene-100% sulfuric acid was poured on cracked ice, there was obtained 97.0% yield of mesitoic acid. The filtrate from the first experiment (the one which yielded slightly more than two moles of hydrogen chloride in the first hour and negligible amount by additional sweeping) was found to contain hydrochloric acid; the amount was not determined quantitatively.

The hydrogen chloride-free solution from trichloromethylprehnitene-100% sulfuric acid yielded 88.7% 2, 3, 4, 5-tetramethylbenzoic acid when poured on cracked ice. The filtrate was neutralized and titrated for chloride ion (Fajans' method) yielding 0.82-0.95 moles per mole of trichloromethylprehnitene.

Conductance measurements on sulfuric acid solutions of trichloromethylmesitylene and trichloromethylprehnitene show that two bisulfate ions are produced. Conductance data are given in Table IV.

The above results can be summarized in the following equations.





XI and XIII represent only one of the many resonance forms for such dipositive carbonium ion systems.

Even though trichloromethylprehnitene possesses only one ortho methyl group, it is able to form a dipositive ion. The number of

methyl groups necessary for di-ion formation has not been determined, but trichloromethylmesitylene shows that three methyl groups are sufficient.

Several attempts were made to prepare trichloromethyldurene; low temperature (10 to 15<sup>°</sup>) trichloromethylation of durene gave poor yields of trichloromethylprehnitene (no trichloromethyldurene was isolated). Other Lewis acid catalysts such as ferric chloride, zinc chloride, antimony pentachloride and stannic chloride do not catalyze the trichloromethylation reaction.

### Ultraviolet and Visible Spectra

It appears that trichloromethylmesitylene and trichloromethylprehnitene meet the requirements necessary for dication formation. Therefore 100% sulfuric acid solutions of all three trichloromethyl compounds should have similar absorption spectra in the ultraviolet and visible regions.

Before discussing the similarity in absorption spectra, it may be helpful to consider the effect of alkyl and chloroalkyl groups on the ultraviolet spectrum of benzene.

Benzene absorbs mainly in two regions, one of high intensity near 198 mµ ( $\epsilon$  ca. 8000 - K-bands) and the other of lower intensity between 230 mµ and 270 mµ ( $\epsilon$  ca. 230), a region characteristic of all benzene derivatives. These transitions are assumed to be between molecular orbitals formed from the six pi electrons. Alkyl substitution distorts the benzene ring by resonance and inductive effects and intensifies the benzene absorption at 260 mµ and shifts it to longer wavelength.

The series of substituents,  $CH_3$ ,  $CH_2CH_3$ ,  $CH_2Cl$ ,  $CHCl_2$  and  $CCl_3$ , presents a gradual transition from donation of electrons to the ring to withdrawal of electrons from the ring (43). The methyl group is considered to carry a virtual orbital on the carbon atom which is

coupled to the pi orbitals in the benzene ring. There are originally two electrons in this orbital and the net result of the interaction is that a portion of these migrate into the ring. The trichloromethyl group is thought to possess a similar virtual orbital on the carbon atom which contains considerably less than two electrons because of the electronegativity of the chlorines, so that the net result is migration out of the ring. The effect of the trichloromethyl group could be considered "negative hyperconjugation." Migration of electrons into or out of the ring distorts the hexagonal electron symmetry of the benzene ring and causes intensification of the spectrum.

A comparison of the ultraviolet absorption spectra of hexamethylbenzene, chloromethylpentamethylbenzene, dichloromethylpentamethylbenzene and trichloromethylpentamethylbenzene in cyclohexane is shown in Figure 1. The benzenoid absorption band shifts to longer wavelength and the intensity increases as the number of chlorine atoms increases. The benzenoid fine-structure bands are smoothed out with increasing numbers of chlorines. The shift of the spectrum to longer wavelengths implies a decrease in the energy level differences between the ground and activated states; this may result either from a lowering of the levels of the activated states, an increase in the ground state level or a combination of the two. A comparison of Fisher -Hirschfelder models of these compounds suggests that the ground state energy increases with increasing number of chlorine atoms, due to steric interaction of the bulky chloroalkyl group with the ortho methyl groups.

The 200 mµ band in para-disubstituted benzenes, in which one of the substituents is meta directing and the other ortho-para directing is quite unique, the shift being proportional to the product of the shifts (in mµ) of the corresponding monosubstituted benzenes. Doub and Vandenbelt have illustrated this phenomenon with aniline, nitrobenzene and p-nitroaniline (44). The large shift which accompanies the para substitution of ortho-para and meta directors may be thought of as arising from a quinoid structure  $A = A = B^+$ .

This effect could account for the shift in the second absorption band in Figure 1. This band shifts from approximately 225 mµ for hexamethylbenzene, to approximately 230 mµ for chloromethyl-, to 239 mµ for dichloromethyl-, to 250 mµ for trichloromethylpentamethylbenzene. This is also the order for increasing meta directing power of these substituents. The increase in intensity and shift in wavelength is related to the increasing electron-attracting power of the chloroalkyl substituent.

Figure 2 shows a comparison of the ultraviolet spectrum of benzotrichloride, trichloromethylmesitylene, trichloromethylprehnitene and trichloromethylpentamethylbenzene in cyclohexane. The general trend is to smooth out the benzenoid fine structure and shift the absorption peaks to longer wavelengths with increasing numbers of methyl groups. The shift is largest for trichloromethylpentamethylbenzene, indicating that steric interaction in the ground state is greater for it than for the other trichloromethyl compounds, as expected. The absence of one ortho methyl group in trichloromethylprehnitene shows up as a decrease in intensity in the 290 m $\mu$  absorption peak. One would think that the absence of one ortho methyl group would decrease the wavelength shift rather than the intensity.

A comparison of the ultraviolet spectra of trichloromethylpentamethylbenzene, pentamethylbenzene and benzotrichloride in cyclohexane is shown in Figure 3. One might expect that the superposed spectrum of benzotrichloride on the spectrum of pentamethylbenzene should be identical to the spectrum of trichloromethylpentamethylbenzene. Figure 3 shows that this is not true. This can be explained by considering the effect of a large bulky group sandwiched between two ortho methyl groups on the ground state of the molecule. The steric







interaction between these groups would increase the energy of the ground state and decrease the energy of activation so that absorption occurs at longer wavelengths. The difference in the rest of the spectrum can be explained by the quinoid structure of the activated state which results from the para substitution of ortho-para (methyl) and meta (trichloromethyl) directing groups.

In contrast to the parent trichloromethyl compounds in cyclohexane, the ultraviolet-visible spectra of trichloromethylmesitylene, trichloromethylprehnitene and trichloromethylpentamethylbenzene in 100% sulfuric acid (dipositive carbonium ions XIII, XI and II) are quite similar (Figure 4). The shift in wavelength and intensity of the B-band is slightly greater for the pentamethylbenzene and prehnitene ions than for the mesitylene ion, which would be expected, because there are more resonance forms possible. The increase in color of the sulfuric acid solutions of these trichloromethyl compounds is shown by the shift in wavelength in the visible portion of the spectrum;  $\lambda_{max}$  XIII, 485 mµ; XI, 515 mµ; II, 545 mµ. These spectra are called charge-resonance spectra (45) because the conjugated ions contain loosely bound pi electrons which, since they are spread over a number of carbon atoms, are relatively easily excited and therefore produce intense, long-wavelength absorption bands.

Figure 5 shows a comparison of the ultraviolet and visible absorption spectra of II, pentamethylbenzoyl cation (IX) and the 1, 1, 2, 3, 4, 5, 6heptamethylbenzenonium ion (XV) prepared by Doering et al. (46). Although there is some similarity in general shape, the positions of the maxima in the spectrum of IX are very different from those of II and whereas one can write plausible mechanisms for the formation of the acyl cation (see equation 3, page 15) it does not seem to be a product of the reaction of trichloromethylpentamethylbenzene with 100% sulfuric acid (see Figure 6 for the effect of small amounts of the pentamethylbenzoyl cation on the ultraviolet and visible spectrum of II). The gross features







of the spectra of II and XV also show some similarity, which is not surprising in view of certain structural features which the two ions have in common.



The long wavelength absorption of II is presumably associated with transitions made possible by the second positive charge and unavailable to IX and XV.

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

#### Proton Magnetic Resonance Spectra

A comparison of the proton magnetic resonance spectrum of II in 100% sulfuric acid with that of the parent trichloromethylpentamethylbenzene in carbon tetrachloride is shown in Figure 7. The proton magnetic resonance spectra of pentamethylbenzoic acid (XIV) in chloroform and the pentamethylbenzoyl cation (IX) are shown in Figure 8. All peaks are in cps relative to benzene as an external standard, determined at 60 Mc. The parent molecules and their derived ions have very similar spectra. Both I and XIV show two bands with relative areas 2:3; the first band presumably corresponds to the six protons on the two methyl groups ortho to the electron-withdrawing trichloromethyl or carboxyl group. The protons on the meta and para methyls appear at higher field and are not resolved. The separation between peaks is appreciably greater in I (20 cps) than in IX (5 cps). One would expect this because the chemical shifts result from differences in structural environment; the trichloromethyl group has a larger shielding effect

## TABLE X

Compound	Wavelength (mµ)	Molar Absorb ancy Index ( $\epsilon$ )
Trichloromethyl-	302 (max.)	1560
pentamethyl-	283 (min.)	920
benzene	250 (max.)	7680
	239 (min.)	6440
Trichloromethyl-	289 (max.)	1040
prehnitene	287 (min.)	1034
	281 (max.)	1085
	270 (min.)	825
	239 (max.)	8175
	232 (min.)	7820
Trichloromethyl	282 (max.)	2160
mesitylene	280 (min.)	1325
	277 (max.)	1620
	275 (min.)	1525
	272 (max.)	1825
	255 (min.)	985
	230 (max.)	4510
Chloromethylpenta-	288 (max.)	780
methylbenzene	285 (min.)	765
	283 (max.)	775
	268 (min.)	430
	238 (inflection)	8450
Dichloromethyl-	292 (max.)	1210
pentamethylbenzene	287 (min.)	1155
	285 (max.)	1170
	266 (min.)	545
	239 (max.)	8910
	235 (min.)	8525

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# ULTRAVIOLET ABSORPTION OF POLYMETHYL COMPOUNDS IN CYCLOHEXANE

## TABLE XI

Compound	Wavelength	Molar Absorb-
	(mµ <u>)</u>	ancy Index ( $\epsilon$ )
Trichloromethyl-	710 (min.)	260
pentamethyl-	545 (max.)	2370
benzene	485 (min.)	1550
	393 (max.)	34,600(34,500)*
	387 (min.)	32,200
	385 (max.)	32,600
	327 (min.)	1000
	265 (max.)	7300
	250 (min.)	5820
	235 (max.)	9160
Trichloromethyl-	705 (min.)	40
prehnitene	515 (max.)	1340
-	465 (min.)	1100
	398 (inflection	n) 21,380
	387 (max.)	22,050(21,870)
	318 (min.)	910
	285 (max.)	7300
	261 (min.)	3110
	239 (max.)	9040
Trichloromethyl-	700 (min.)	115
mesitylene	485 (max.)	2110
-	472 (min.)	2090
	372 (max.)	20,650
	304 (min.)	1315
	281 (max.)	5670
	258 (min.)	2420
	239 (max.)	7860
Pentamethyl-	362 (max.)	4820
benzoic Ácid	319 (min.)	6900
	293 (max.)	57,900
	244 (min.)	2400

## VISIBLE AND ULTRAVIOLET ABSORPTION OF POLYMETHYL COMPOUNDS IN 100% SULFURIC ACID

\* Molar absorbancy index of solution stored in a glass-stoppered flask for 24 hours.

Continued

## TABLE XI - Continued

Compound	Wavelength Molar Absorb-		
	(mµ)	ancy Index ( $\epsilon$ )	
Chloromethyl-	710 (min.)	115	
pentamethyl -	480 (max.)	1535	
benzene	465 (min.)	1500	
	398 (max.)	2500	
	372 (min.)	1850	
	332 (max.)	11,600	
	290 (min.)	3060	
	265 (inflection	) 4510	
	238 (max.)	8375	
	230 (min.)	7930	

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Figure 7. Proton magnetic resonance spectra,  $v_0 = 60$  Mc., reference: external-benzene.

- (a) Trichloromethylpentamethylbenzene in CCl<sub>4</sub> (2M)
  - (b) Pentamethylphenylchlorodicarbonium ion (100% sulfuric acid - 2M)





(a) Pentamethylbenzoic acid in CHCl<sub>3</sub> (slightly less than 2M).

(b) Pentamethylbenzoyl cation in 100% sulfuric acid (2M).

than the carboxyl group, so the protons on the two ortho methyl groups of I would appear at a lower field.

The spectra of the two ions (II and IX) are consistent with their structures. The spectra are virtually identical with three distinct bands having relative areas 2:1:2. These presumably correspond to the ortho, para, and meta methyls respectively. The ortho methyl protons would be expected to appear at the lowest field because of the shielding effect of C = O group or C = C group. If IIa and IX a are important resonance structures, the para methyl protons would be expected to appear next. (The relative areas also indicate this.) The spectrum of IX may be shifted 5 cps toward higher field than that of II, but this difference is possibly within the experimental error; the separations (o-p = 8 cps and o-m = 20 cps) are identical for both ions. It is gratifying that both ions have nearly identical n-m-r spectra, because of the similarity of important contributing structures as IIa with IXa, IIb with IXb, etc.



The virtual identity of the magnetic environment of the methyl protons in both species is expected.

It is interesting to compare these results with the assignment given by Doering, <u>et al</u>. (46) to the bands in the proton magnetic resonance spectrum of XV. The chemical shifts of II, IX and XV are given in Table XII (the chemical shifts of XV were converted to 60 Mc. by multiplication of the reported values (41) by 3/2). In each case the <u>meta</u> methyl hydrogens appear at highest field, but in II and IX the <u>ortho</u> methyl hydrogens are at lower field than the para methyl hydrogens, whereas the reverse is true for XV. This is consistent with the presence of strongly electron-withdrawing groups (Z in Table XII) adjacent to the ortho methyls in II and IX, but of insulating and indeed electron-releasing gem-dimethyl as Z in XV. Thus similarities (to IX) and differences (from XV) in the proton magnetic resonance spectrum of II when compared with ions of known structure provide confirmatory evidence for its structure.

#### TABLE XII

			1	
·····	· · · · · · · · · · · · · · · · · · ·			
Ion	2	ortho	para	meta
п <sub>р</sub>	=c=č1 (=č-C1)	223	231	243
IXp	<b>≠</b> C <b>=</b> 0	228	236	248
xv <sup>c</sup>	< <sup>сн</sup> ,	218	206	234

CHEMICAL SHIFTS OF SOME CARBONIUM IONS<sup>(a)</sup>

(a) Shifts in cps relative to benzene, 60 Mc.

(b) in 100% sulfuric acid

(c) in concentrated hydrochloric acid, data from reference 46.

Extensive proton magnetic resonance studies on trichloromethylmesitylene and trichloromethylprehnitene have not been made. Preliminary work indicates that the ring hydrogens complicate the spectrum of trichloromethylmesitylene.

# EXPERIMENTAL

#### Miscellaneous Experiments

Many other solvent systems have been examined to determine their ability to initiate dication formation with the trichloromethyl compounds. Sulfuric acid appears to be the only mineral acid which is useful, but mixed acids might be interesting solvent systems.

The dipositive ions (II. XI, XIII) can be prepared by adding excess aluminum chloride to a solution of the trichloromethyl compound in nitromethane or nitrobenzene (excess aluminum chloride is necessary because some of it is complexed with nitromethane or nitrobenzene). Other organic solvents and aluminum chloride have been tried, but they suffer from lack of solubility of the dication (carbon tetrachloride, carbon disulfide, chloroform, aromatic and aliphatic hydrocarbons), or form such a tight complex with aluminum chloride (ethers, dimethyl sulfoxide, dimethyl formamide and ethylene dichloride) that there is very little reaction with the trichloromethyl compound.

Another very interesting solvent system is trifluoroacetic acid saturated with boron trifluoride. The trichloromethyl compounds are not very soluble in trifluoroacetic acid, but when boron trifluoride is passed through the suspension the trichloromethyl compound dissolves rapidly giving a deep red solution of the dication. Evaporation of the solvent in an inert atmosphere furnishes a red crystalline residue insoluble in hexane, slightly soluble in chloroform, very soluble in ether giving an intense red solution, and stable for long periods in trifluoroacetic acid containing a little trifluoroacetic anhydride.

The reaction of trichloromethylpentamethylbenzene with trifluoroacetic acid-boron trifluoride has been extensively studied. The spectra (visible, nmr--Figures 29 and 30) of the red crystalline material in trifluoroacetic acid are similar to those of II, except for solvent effects. Attempts to convert the red crystalline residue to a stable crystalline

salt of definite composition by recrystallization from various solvents such as hexane, benzene, carbon tetrachloride and chloroform were not successful.

To remove the last traces of solvent from the red solid, it was sometimes heated, which caused a white solid to sublime onto the sides of the flask. Heating under reduced pressure after the solvent had been removed caused a colorless liquid to distill (b.p.  $130-142^{\circ}/$ 5mm). It solidified immediately. The white solid, which had an odor of trifluoroacetic acid, was recrystallized from anhydrous ether, yielding nice white crystals,  $C_{24}H_{30}O_3$ , m.p.  $212-214^{\circ}$ . The ether filtrate had a strong odor of trifluoroacetic acid. An infrared spectrum of the white crystals showed two carbonyl bands; a strong band at 5.56  $\mu$  and a weaker band at 5.75  $\mu$ , suggesting that it might be an anhydride (Figure 17).

The white solid, before recrystallization from ether, reacted readily with dilute sodium hydroxide, consuming two equivalents of base. This material also gave a positive Beilstein test for fluorine. The recrystallized product, m.p.  $212-214^{\circ}$ , was very inert; it did not hydrolyze when an acetone-ether solution of it was refluxed with aqueous sodium hydroxide. It did not react with lithium aluminum hydride and ether, but when it was refluxed twenty-four hours with lithium aluminum hydride-tetrahydrofuran, pentamethylbenzyl alcohol, m.p.  $160^{\circ}$ , (54) was obtained.

An identical anhydride was obtained when trichloromethylpentamethylbenzene was refluxed with trifluoroacetic acid containing a small amount (about 3%) trifluoroacetic anhydride, solvent removed, brown solid material distilled under reduced pressure and the white

<sup>\*</sup>While this thesis was being written; Buckles et al. (67) reported the preparation of crystalline dark, blue-green trihalide salts of tetraanisylethylenedicarbonium ion from the reaction of tetraanisylethylene with bromine or iodine monochloride in carbon disulfide. Spectra of the tetraanisylethylenedicarbonium ion have been reported by H. M. Buck, W. Bloemhoff and L. J. Oosterhoff, Tetrahedron Letters, No. 9, (1960) pp. 5-11.
solid recrystallized from anhydrous ether. The following equation and structure XVII was assigned on the basis of the above results, elementary analysis, and Rast molecular weight (camphor--found, 350-360; calc'd, 366.5).



 $+ (CF_3CO)_2O$ 

The only evidence for the existence of the unsymmetrical anhydride XVII is that the colorless liquid which solidifies has a trifluoroacetic acid odor, contains fluorine and hydrolyzes readily with dilute sodium hydroxide to give pentamethylbenzoic acid. The only other way that these results could be attained is that trifluoroacetic acid or trifluoroacetic anhydride azeotropes with the pentamethylbenzoic anhydride, which does not seem reasonable.

The conversion of the salt, II, to XVII may proceed via the intermediate XVI, if II is considered analogous to a ketene.



A common method for preparing unsymmetrical anhydrides is to add an acid to a ketene (47, 48). Addition of water to ketene yields the corresponding carboxylic acid; similarly, addition of water to II yields pentamethylbenzoic acid.

It has been known for some time that unsymmetrical anhydrides readily disproportionate into the two symmetrical anhydrides (49). Tedder discusses this reaction quite thoroughly in his review article on the use of trifluoroacetic anhydride in organic synthesis (50). Thus it seems reasonable that XVII disproportionates readily to give pentamethylbenzoic anhydride.

Pentamethylbenzoic anhydride is very resistant to alkaline hydrolysis, but reacts instantly with sulfuric acid. Because of its unusual behavior in sulfuric acid, cryoscopic measurements were run. The results are given in Table IX. The six particles which are formed can be accounted for by the following equation.



Addition of the anhydride-sulfuric acid solution to ice gave a quantitative yield of pentamethylbenzoic acid.

In the study of the trichloromethyl compounds, it was desirable to find a new method of introducing a trichloromethyl group into a polymethylbenzene nucleus, because the Friedel-Crafts reaction caused methyl migration (page 25). A literature search for potential methods was not informative.

In an attempt to prepare benzotrichloride, benzoyl chloride was refluxed twelve hours with excess phosphorus pentachloride, but no benzotrichloride was formed. A 15-20% yield of benzotrichloride was obtained when a 1:2 ratio of benzoyl chloride-phosphorus pentachloride in a sealed tube was heated at 200-225° in a tube furnace for twentyfour hours. Because these conditions were quite drastic, an experiment to determine the thermal stability of polymethylbenzotrichlorides was run. This involved heating trichloromethylpentamethylbenzene slightly above its melting point,  $(110-125^{\circ})$  for three hours. The white platelets of trichloromethylpentamethylbenzene melted to give a clear colorless liquid, which gradually darkened and gave off small bubbles of a gas (a later experiment showed that one mole of hydrogen chloride was evolved). The cooled reaction mixture was a brown crystalline residue which, when recrystallized from n-pentane, gave a white crystalline dichloro compound, C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>, m.p. 73-74<sup>°</sup>, in 89% yield. This dichloro compound was shown to be a. a-dichlorotetramethylbenzocyclobutene. The interesting cyclization reaction which produced this compound will be discussed in the second part of this thesis.

Methyl groups have a stabilizing effect on the dipositive carbonium ion by their inductive effect and hyperconjugative effect of distributing the positive charges over a larger number of carbon atoms. The ion is also stabilized by the ease with which the chlorine atom can form double bonds by overlap of its "p" orbital with that of the adjacent carbon. If the chlorine was replaced by a phenyl group or anisyl group the dipositive carbonium should be even more stable. Fisher-Hirschfelder models of the parent 2, 3, 4, 5, 6-pentamethylbenzophenone dichloride show that the molecule is very congested with no free rotation between the two phenyl groups.

2, 3, 4, 5, 6-Pentamethylbenzophenone was readily prepared by the Friedel-Crafts acylation of pentamethylbenzene with benzoyl chloride. Attempts to convert this ketone to the corresponding dichloro compound with phosphorus pentachloride were futile. If carbon tetrachloride or benzene were used as solvents, the reaction did not go; the use of tetrachloroethane caused decomposition.

Friedel-Crafts alkylation of pentamethylbenzene with benzotrichloride using aluminum chloride and low temperatures gave only tars. When stannic chloride was used as the catalyst, the reaction went very smoothly. Difficulty was encountered in separating the excess benzotrichloride from the dichloro compound. This problem may be eliminated by using carbon tetrachloride as the solvent and an equimolar amount of benzotrichloride and pentamethylbenzene. Carbon tetrachloride does not react with pentamethylbenzene in the presence of stannic chloride at room temperature.

Whether the dipositive carbonium ion of pentamethylbenzophenone dichloride is more stable than the dipositive carbonium ion from trichloromethylpentamethylbenzene has not been determined.

An interesting phenomenon related to the above work was discovered when it was found that neither benzotrichloride nor pentamethylbenzene were very soluble in cold concentrated sulfuric acid, but separate colorless suspensions of these, on mixing, gave a deep red solution, with evolution of hydrogen chloride. When this deep red solution was poured on ice only two products were isolated, benzaldehyde and benzoic acid. The filtrate from the hydrolysis had a phenolic odor. The same phenomenon occurs with other aromatic hydrocarbons; durene, mesitylene, xylenes and fluorene. To account for the benzaldehyde, a hydride transfer must take place. This might be presumed to take place by loss of chloride ion from benzotrichloride and abstraction of a hydride ion from the aromatic hydrocarbon by the carbonium ion. This explanation was refuted when it was found that triphenyl- and diphenylmethane, good hydride donors, do not initiate the reaction.

Another explanation for this phenomenon is that the aromatic hydrocarbon is alkylated with benzotrichloride under the acidic conditions of the reaction, and in the hydrolysis step the alkylated product is cleaved, yielding benzaldehyde and possibly pentamethylphenol, which has not been isolated.

The ultraviolet-visible spectra of an equimolar amount of benzotrichloride and pentamethylbenzene in 100% sulfuric acid is variable, depending on the length of time the reaction mixture stands. Therefore a good explanation for this phenomenon has not yet been found, and the reaction requires further study.

Another interesting compound, dichloromethylpentamethylbenzene, was prepared from pentamethylbenzaldehyde and phosphorus pentachloride. Unlike trichloromethyl- and chloromethylpentamethylbenzene, it is very unstable, decomposing to a brick-red solid on standing in a desiccator. Recrystallization of the decomposition product from npentane yields pentamethylbenzaldehyde. A comparison of the ultraviolet absorption spectrum (Figure 1) suggests that there is more B-strain in trichloromethylpentamethylbenzene than in dichloromethylpentamethylbenzene. Therefore one would not expect the dichloromethyl compound to be less stable than the trichloromethyl compound, unless it decomposes in air, by a different mechanism. The dichloromethyl compound may decompose by a free radical or carbene mechanism.

Dichloromethylpentamethylbenzene gives a red color in sulfuric acid, but an extensive study of its reaction in sulfuric acid has not been made. If it forms a dipositive carbonium ion in sulfuric acid,

one would not expect it to be as stable as II, because hydrogen cannot stabilize the charge as well as a chlorine atom. Also the loss of one chloride ion would give the pentamethylphenylchlorocarbonium ion. VII, which should be stable because it can be stabilized by resonance, through the double bond formation of the chloro group and the ability of the methyl groups to further distribute the positive charge.



Chloromethylpentamethylbenzene is a stable white crystalline compound, m.p.  $80-81^{\circ}$ , prepared by chloromethylation of pentamethylbenzene. This compound dissolves in 100% sulfuric acid, forming a dark red solution. An extensive study of this compound has not been made. The ultraviolet-visible spectrum of the dark red-sulfuric acid solution has the following absorption peaks: 238 mµ,  $\epsilon = 8,375;332$  mµ,  $\epsilon = 11,600;398$  mµ,  $\epsilon = 2500;$  and 480 mµ,  $\epsilon = 1535$ . One might predict that chloromethylpentamethylbenzene and pentamethylbenzyl alcohol in sulfuric acid would have similar absorption spectra. Deno et al. (51) studied pentamethylbenzyl alcohol in 80-100% sulfuric acid. They found that its behavior is complicated; at least two spectroscopically distinguishable species are present, one absorbing at 470 mµ and the other at 520 mµ. The latter is more stable at higher concentrations of sulfuric acid. They suggest that one of the species is



and the other the protonated specie.

The visible spectrum of chloromethylpentamethylbenzene in 100% sulfuric acid suggests that only one specie is present, since there is a single absorption peak at 480 m $\mu$ .

# EXPERIMENTAL

## A. Syntheses

### **Trichloromethylpentamethylbenzene**

Trichloromethylpentamethylbenzene was prepared by the Friedel-Crafts reaction of pentamethylbenzene with carbon tetrachloride (12).

In a dry one-liter three-necked round-bottomed flask equipped with a Tru-bore stirrer, thermometer, reflux condenser and addition funnel was placed 80.0 g. (0.6 mole) of anhydrous, powdered aluminum chloride and 100 ml. of carbon tetrachloride. To this stirred suspension, there was slowly added (2 hours) a solution of 45.0 g. (0.3 mole) of pentamethylbenzene in 100 ml. of carbon tetrachloride. The slurry became deep purple and hydrogen chloride evolved immediately. The stirred reaction mixture was maintained at 37-42°, by occasional heating. After all the pentamethylbenzene was added, stirring was continued for four hours, after which hydrogen chloride evolution had essentially ceased. (Better yields were obtained if the reaction mixture was stirred overnight.) The purple aluminum chloride complex was poured slowly into a vigorously stirred mixture of 100 ml. of carbon tetrachloride, 300 g. of ice, 200 ml. of water and 50 ml. of concentrated hydrochloric acid. The orangecolored organic layer was washed with three 50-ml. portions of warm (40) water and dried over anhydrous calcium chloride. The solvent was removed, either by distillation under reduced pressure or on a Rinco rotary evaporator, (in either case the temperature was kept below  $60^{\circ}$ ) leaving a tan residue of crude product in nearly quantitative yield. Several treatments with Norite and recrystallizations from n-pentane

<sup>\*</sup>All analyses by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Melting points are uncorrected.

(dried over sodium wire) gave 55.5 g. (91% of cream-colored platelets, m.p. 92-94°. Early work on physical properties of sulfuric acid solutions was done on this material, but it was not quite analytically pure (C about 1% high, Cl about 1% low, H in agreement with theory). Later, analytically pure white crystals of I, m.p. 95.5-96.0°, were obtained by repeated Norite treatment of a dilute solution of I in pentane, followed by concentration and recrystallization.

Anal. Calc'd for  $C_{12}H_{15}Cl_3$ : C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.33; H, 5.72; Cl, 39.97.

The infrared absorption spectrum of trichloromethylpentamethylbenzene is shown in Figure 9.

Trichloromethylpentamethylbenzene and the other trichloromethyl compounds are quite sensitive to sunlight. The white platelets become yellow, lose hydrogen chloride to form pentamethylbenzoic acid when exposed to sunlight in a desiccator. They do not lose hydrogen chloride when stored in a dark desiccator.

### Trichloromethyl-2, 3, 4, 5-tetramethylbenzene

A mixture of trichloromethyltetramethylbenzenes was obtained from the Friedel-Crafts reaction of 1, 2, 4, 5-tetramethylbenzene (durene) with carbon tetrachloride. Using the procedure described in the preparation of trichloromethylpentamethylbenzene, 40.0 g. (0.3 mole) of durene (Shell Chemical Corp.) dissolved in 100 ml. of carbon tetrachloride was slowly added (2 hours) to a stirred suspension of 80.0 g. (0.6 mole) of anhydrous, powdered aluminum chloride in 100 ml. of carbon tetrachloride, maintained at  $37-42^{\circ}$ . The color of the reaction mixture was not as intense as with pentamethylbenzene. The hydrolysis procedure was the same as that described previously.

Several purification procedures were tried; fractional crystallization, similar to the method used in the purification of trichloromethylpentamethylbenzene was only moderately successful because the reaction mixture was



Per Cent Transmission

often an oil and crystallization occurred only on standing. The creamcolored platelets which were obtained had a melting point range,  $86-88^{\circ}$ ; treatment with Norite and several recrystallizations from dry n-pentane gave white platelets of trichloromethyl-2, 3, 4, 5-tetramethylbenzene, m.p. 90-91.5°. The yield was 35.9 g. (48.0%).

Anal. Calc'd for C<sub>11</sub>H<sub>13</sub>Cl<sub>3</sub>: C, 52.51; H, 5.21; Cl, 42.28.

Found: C, 52.39; H, 5.13; Cl, 42.34.

The infrared spectrum of this compound is shown in Figure 10.

Purification of the crude product by vacuum distillation was carried out using a dry-ice trap and a large ascarite tower to protect the vacuum pump. The usual procedure was to carry out a fast vacuum distillation to separate the product from the crude reaction mixture, with no attempt to fractionate the material. Then the product was carefully fractionated. In one experiment, using the conditions stated above, the first distillation gave a pale yellow liquid with a boiling point range  $120-139^{\circ}/4$  mm. This material was then fractionated giving the following results.

Fraction .	Boiling Point	Weight,
. 110.	at 5.5 mm.	8.
1	117-120	1.2
2	120-125	2.8
3	125-130	7.9
4	130-135	22.7
5	135-138	32.6
6	138-141	3.4

Fractions 1, 2 and 3 were pale yellow liquids containing chlorine; no attempt was made to identify this material. Fractions 4, 5 and 6 solidified on cooling; this white solid was recrystallized from dry n-pentane, yielding 56.6 g. (75.4%) of white platelets, m.p. 86-89°. Additional recrystallizations gave white platelets, m.p. 90-91.5° of trichloromethyl-2, 3, 4, 5-tetramethylbenzene. Proof of structure of this material was



Per Cent Transmission

carried out by hydrolysis to the 2, 3, 4, 5-tetramethylbenzoic acid, which was decarboxylated, giving the hydrocarbon 1, 2, 3, 4-tetramethylbenzene (prehnitene).

# Trichloromethyl-2, 4, 6-trimethylbenzene

Trichloromethyl-2, 4, 6-trimethylbenzene was prepared by the Friedel-Crafts reaction of mesitylene with carbon tetrachloride, using a procedure similar to that used to prepare trichloromethylpentamethylbenzene.

To a 500-ml. three-necked round-bottomed flask equipped with a Tru-bore stirrer, thermometer, dropping funnel and reflux condenser was added 67 g. (0.5 mole) of anhydrous powdered aluminum chloride and 100 ml. of carbon tetrachloride. To this stirred suspension, there was slowly added (1.5 hours) 30 g. (0.25 mole) of freshly distilled mesitylene in 50 ml. of carbon tetrachloride. The slurry became dark red and hydrogen chloride evolved immediately. The stirred reaction mixture was maintained at  $37-42^{\circ}$  by occasional heating for three hours, after which hydrogen chloride evolution had essentially ceased. The dark red reaction mixture was poured into an ice-5% hydrochloric acid solution which was stirred vigorously. The orange-brown organic layer was washed with three 50-ml. portions of warm ( $50^{\circ}$ ) water and dried over anhydrous calcium chloride. The solvent was removed by distillation under reduced pressure and the product was separated from the crude reaction mixture by a rapid distillation under reduced pressure. The colorless liquid was then fractionated.

Fraction	Boiling Point		Weight
No.	at 5 mm.	n <sup>25</sup> D	(g.)
1	120-124 <sup>0</sup>	1.5603	2.3
2	124-126 <sup>0</sup>	1.5637	12.6
3	126-126.5 <sup>0</sup>	1.5640	33.4

The infrared spectra of the three fractions differed only in the intensity of some of the absorption peaks (See Figure 11). The yield was 48.3 g. (81.7%).

In another experiment, using the same procedure as described above, the product from the rapid distillation solidified in the receiver. The white solid was recrystallized from dry n-hexane yielding white crystals, m.p.  $52-54^{\circ}$ . Several more recrystallizations increased the melting point to  $55-57^{\circ}$ .

Anal. Calc'd for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>: C, 59.72; H, 5.01; Cl, 35.26. mol. wt. 201.09 Found: C, 59.90; H, 5.10; Cl, 35.27. Rast mol. wt. (camphor) 209.

This substance was presumably 1, 1-dichloro-4, 6-dimethylbenzocyclobutene, rather than the desired trichloromethylmesitylene (see Figure 42). Attempts to repeat this experiment were not successful.

### Bromodurene

Bromodurene was prepared according to the procedure of Newman and Lloyd (34). In a 500-ml. three-necked round-bottomed flask equipped with a Tru-bore stirrer, short reflux condenser, addition funnel and a thermometer was placed a solution of 68 g. (0.5 mole) of durene in 100 ml. of chloroform. Several crystals of iodine were added and the flask was placed in a salt-ice bath. (The reaction was carried out in the absence of light.) After the contents of the flask had cooled to about  $0^{\circ}$ , a solution of 88 g. (0.55 mole) of bromine in 100 ml. of chloroform was added to a well-stirred solution of durene. The bromination proceeded readily, the evolved hydrogen bromide being absorbed in water. The addition of bromine required about two hours, during which time the temperature was maintained at  $0^{\circ}$ .

After the addition of bromine was complete, the reaction mixture was allowed to stand at room temperature for one hour. The solution was red in color and yellow crystals began forming on the sides of the flask. The solution was washed first with water, then with three 25-ml. portions of 20% sodium hydroxide (to remove dissolved hydrogen bromide). The



Per Cent Transmission

yellow solution was dried over anhydrous calcium chloride and the chloroform distilled through a packed column.

The residue was added to a solution of 5 g. of sodium in 100 ml. of 95% ethanol. The mixture was refluxed for two hours and allowed to stand overnight, then diluted with 500 ml. of water and the layers separated. The aqueous layer was extracted with three 30-ml. portions of chloroform. The organic solutions were combined, washed three times with water and dried over anhydrous calcium chloride. The chloroform was removed under reduced pressure with the aid of the Rinco rotary evaporator. The residue was fractionated under reduced pressure.

Fraction	Boiling Point	Weight
No.	at 16 mm.	g.
1	120-134 <sup>0</sup>	2.4
2	134-138 <sup>0</sup>	89.2
3	138-160 <sup>0</sup>	9.7

Fraction 2 solidified as soon as it was distilled. The white solid was recrystallized from n-hexane, yielding 87.0 g. (80.7%) of long white needles of bromodurene, m.p.  $59-60.5^{\circ}$  (34).

#### Durenecarboxylic Acid

Durenecarboxylic acid was prepared by the Grignard reaction of bromodurene by a modified procedure of Newman and Lloyd (34).

In a dry one-liter three-necked flask, equipped with a Tru-bore stirrer, a condenser protected by a drying tube, and a dropping funnel, were placed 12 g. (0.5 mole) of magnesium turnings, 50 ml. of dry tetrahydrofuran (freshly distilled from lithium aluminum hydride) and 3 g. of ethyl bromide. Stirring was commenced and the reaction began almost at once. Vigorous refluxing was maintained by the slow addition (1.5 hours) of a solution of 40.6 g. (0.2 mole) of bromodurene and 18.8 g. (0.2 mole) of ethyl bromide in 150 ml. of dry tetrahydrofuran. After addition was complete, the

mixture was refluxed for two more hours. The reaction mixture was cooled and then poured rapidly into a two-liter beaker containing 250 g. of pulverized Dry Ice. When the bulk of the Dry Ice had evaporated, 250 ml. of 20% hydrochloric acid and enough ice to keep the mixture cold was added with stirring. The acid precipitated out of solution and was extracted with five 100-ml. portions of ether. The ether layer was washed several times with water and the product was extracted with 100 ml. of ice-cold 10% sodium hydroxide. The basic aqueous layer was separated and acidified by the slow addition of 75 ml. of 20% hydrochloric acid. The suspension was cooled, and the white granular product was collected and washed several times with water. The crude acid, amounting to 22.8 g. (67.3%) was recrystallized from a 50% methanol solution yielding white crystals m.p. 176-177°C. Newman and Lloyd (34) reported a melting point of  $179^{\circ}$ . The infrared spectrum of durenecarboxylic acid is given in Figure 12.

### Prehnitene (1, 2, 3, 4-tetramethylbenzene)

(a) Decarboxylation of the carboxylic acid obtained from hydrolysis of trichloromethyltetramethylbenzene, m.p. 90-91.5°.

To a 50-ml. Claisen distillation flask equipped with a side-arm condenser, was added 5.0 g, of tetramethylbenzoic acid (m. p.  $168-169^{\circ}$ , obtained from aqueous hydrolysis of trichloromethyltetramethylbenzene, m. p.  $90-91.5^{\circ}$ ), 20 g. of quinoline and 0.5 g. of cupric sulfate. The reaction mixture was heated slowly for the first hour; during this time a gas was evolved (presumably carbon dioxide). The temperature was gradually increased; the first material which came over was quinoline. The fraction with the boiling point range of  $190^{\circ}$  to  $210^{\circ}$  was acidified with 10% hydrochloric acid (to remove the quinoline) and the hydrocarbon was extracted with two 20-ml. portions of ether. After the ether layer was washed with two 10-ml. portions of 10% sodium hydroxide (to remove



Per Cent Transmission

traces of the tetramethylbenzoic acid which might not have been decarboxylated), it was washed three times with water and dried over anhydrous calcium chloride. Evaporation of the ether gave 2.1 g. of hydrocarbon. In order to purify the hydrocarbon fraction, one ml. of it was passed through the Perkin-Elmer vapor-phase chromatograph using the silicome prep-column, temperature of 145° and 5 pounds of nitrogen. The elution peak was rather broad, so two fractions were collected. An infrared spectrum of the first fraction was identical to that of 1, 2, 3, 4tetramethylbenzene (prehnitene) reported by Launer and McCaulay (32). It was also identical to the 1, 2, 3, 4-tetramethylbenzene prepared by the Jacobsen rearrangement of durene ( below ). The infrared spectrum of the second fraction was almost the same as the first except for several extraneous absorption peaks (Figure 13).

(b) Preparation of prehnitene from durene by the Jacobsen rearrangement. [The procedure was similar to that developed by Smith and Cass (33).]

To a 250-ml. round-bottomed flask equipped with a reflux condenser was added 100 g. of durene and 50 ml. of 98% sulfuric acid and 50 ml. of 30% fuming sulfuric acid. The mixture was shaken until most of the durene had reacted. The temperature of the reaction mixture was about  $80^{\circ}$ ; this temperature was maintained for eight hours in a electrically heated oil bath. Cooling of the reaction mixture caused solidification. The black solid mass was broken up and poured into a two-liter beaker containing 500 g. of ice. A brown insoluble layer was collected on a filter and the black filtrate was cooled to  $10^{\circ}$ . To this cold, black filtrate, 250 ml. of cold concentrated sulfuric acid was carefully added and a brown crystalline precipitate formed. This material was collected in a sinteredglass Büchner funnel and pressed as dry as possible with a rubber dam. Yield of crude tetramethylbenzenesulfonic acid was 57.4 g., m.p.  $96-100^{\circ}$ .

The brown crystalline sulfonic acid was neutralized with a slight excess of aqueous sodium hydroxide. The sodium salt of the sulfonic acid was hydrolyzed by a flash hydrolysis procedure.

A one-liter three-necked round-bottomed flask equipped with a thermometer, a dropping funnel and a set up for steam distillation, was charged with 100 ml. of water and immersed in a 200° oil bath. Concentrated sulfuric acid was added from the dropping funnel until the temperature of the diluted acid in the flask reached  $150^{\circ}$ . The flask was attached to a super-heated steam line (steam from the line was passed through a copper coil which was heated to about  $150^{\circ}$ ) and the aqueous solution of sodium prehnitenesulfonate was added at such a rate that the temperature of the reaction remained between 140-150°. After the sodium prehnitenesulfonate solution was added, steam distillation was continued until no more oily liquid came over. The oil was extracted from the distillate with two 50-ml. portions of ether. The ether layer was dried over anhydrous calcium chloride, then distilled. The brown hydrocarbon oil was distilled under reduced pressure. All of the product came over as a colorless liquid at 75-82 $^{\circ}/10$  mm. (6.3 g.). One ml. of this hydrocarbon was passed through the Beckman Megachrom vapor phase chromotagraph using the Apiezon prep-column; column temperature,  $150^{\circ}$ ; detector temperature, 195<sup>0</sup> and 8 pounds of helium. The retention time was about one hour. The elution peak was quite broad, however there were no shoulders. An infrared spectrum (Figure 13) of this hydrocarbon was identical to that of the 1, 2, 3, 4-tetramethylbenzene (prehnitene) obtained from the decarboxylation of 2, 3, 4, 5-tetramethylbenzoic acid and that of prehnitene reported by Launer and McCaulay (32). Refractive index,  $n_D^{16}$  1.5205 (Literature value,  $n_D^{20}$  1.52031 (32).

# Methyl 2, 3, 5, 6-tetramethylbenzoate

Methyl 2, 3, 5, 6-tetramethylbenzoate was prepared by the esterification of the corresponding acid using the procedure developed by Arndt (52).



Figure 13. Infrared spectrum of 1, 2, 3, 4-tetramethylbenzene (prehnitene) ( $CS_2$  solution).

To a 500-ml. two-necked round-bottomed flask equipped with a dropping funnel and a condenser set for distillation, was added 60 ml. of 50% aqueous potassium hydroxide and 200 ml. of ether. The mixture was cooled to  $5^{\circ}$ , and 20.6 g. (0.2 mole) of nitrosomethylurea was added with shaking. The lower end of the condenser carried an adapter which passed through a two-holed rubber stopper and dipped below the surface of 50 ml. of ether containing 18 g. (0.1 mole) of durenecarboxylic acid, all in a 500-ml. Erlenmeyer flask cooled in an ice-salt bath mixture. The exit gases were passed through a second 50-ml. portion of ether, similarly cooled below  $0^{\circ}$ . The reaction flask was placed in a  $50^{\circ}$  water bath and brought to the boiling point of the ether. The ether was distilled until it came over colorless. The diazomethane reacted immediately with the carboxylic acid to form the methyl ester. The ether solution was washed with two 25-ml. portions of 10% sodium hydroxide to remove any unesterfied acid and finally washed twice with water. After evaporating the solvent, the whitish-yellow crystals were recrystallized from aqueous methanol yielding 14.0 g. (72.5%) of white platelets of methyl 2, 3, 5, 6 tetramethylbenzoate, melted at 56-57°, (literature value,  $58^{\circ}$  (30)). The infrared spectrum of this ester is shown in Figure 14.

# Methyl 2, 3, 4, 5-tetramethylbenzoate

Methyl 2, 3, 4, 5-tetramethylbenzoate was prepared by the methylation of 2, 3, 4, 5-tetramethylbenzoic acid with diazomethane.

To a 250-ml. Erlenmeyer flask was added 1.8 g. (0.01 mole) of 2, 3, 4, 5-tetramethylbenzoic acid (m.p.  $168-169^{\circ}$ ) and 50 ml. of anhydrous ether. After the acid had dissolved, 20 ml. of a standard solution of diazomethane in ether (0.032 g./ml.) was added and the flask swirled to ensure complete mixing of the reactants. The flask was stoppered and allowed to stand two hours. The ether solution was washed with 25 ml. of 10% sodium carbonate, twice with 25 ml. of water and dried over



Per Cent Transmission

anhydrous calcium chloride. After evaporating the ether, the white residue was recrystallized from aqueous methanol yielding 1.59 g. (81.7%) of white platelets of methyl 2, 3, 4, 5-tetramethylbenzoate, m.p. 35-36<sup>°</sup> (31). The infrared spectrum of this ester had no shoulders on the carbonyl band (see Figure 15).

### Methyl 2, 4, 6-trimethylbenzoate

Methyl 2, 4, 6-trimethylbenzoate was prepared by the methylation of 2, 4, 6-trimethylbenzoic acid, analogous to the procedure of Arndt (52). Using the procedure described in the preparation of methyl 2, 3, 5, 6-tetramethylbenzoate (page 71), 10.3 g. (0.1 mole) of nitrosomethylurea was added to a cold ( $5^{\circ}$ ) solution of 30 ml. of aqueous potassium hydroxide and 100 ml. of ether. The solution was warmed to  $50^{\circ}$  and the diazomethane evolved was collected in a 500-ml. Erlenmeyer flask containing 8.6 g. (0.05 mole) of 2, 4, 6-trimethylbenzoic acid dissolved in 50 ml. of ether. The ether solution was dried over anhydrous calcium chloride, evaporated and the ester distilled under reduced pressure, b. p.  $80-81^{\circ}/2$  mm.  $n_D^{25}$  1.5058 (53). An infrared spectrum of the ester showed only one carbonyl peak (5.78  $\mu$ ). See Figure 16.

# Pentamethylbenzoic Anhydride

Into a solution of 25 ml. of trifluoroacetic acid and 2 ml. of trifluoroacetic anhydride in a 50-ml. two-necked round-bottomed flask equipped with a gas-inlet and drying tube, a stream of dry boron trifluoride (bubbled through a sulfuric acid scrubbing tower) was passed until the solution became saturated. This solution was poured into a 100-ml. roundbottomed flask containing 5.0 g. of trichloromethylpentamethylbenzene. Boron trifluoride was bubbled into this solution until all the trichloromethylpentamethylbenzene had dissolved (solution was deep red). The excess boron trifluoride and trifluoroacetic acid were removed under reduced



Per Cent Transmission





pressure. The reaction flask was then heated with a  $60^{\circ}$  water bath to remove most of the solvent. The dark red residue remaining was heated slowly under reduced pressure (5 mm.-vacuum pump protected via a dry-ice trap and a large ascarite tower). An almost colorless liquid distilled over  $(130-142^{\circ}/5 \text{ mm.})$  and solidified in the receiver as a white solid, m.p.  $180-185^{\circ}$ , yield-3.28 g. Recrystallization of this material from anhydrous ether gave 1.97 g. (57.1%) of nice white crytals of pentamethylbenzoic anhydride, m.p.  $212-214^{\circ}$ . The ether filtrate had a strong odor of trifluoroacetic acid. An infrared spectrum of this anhydride had two carbonyl bands; 5.56  $\mu$  and 5.75  $\mu$  (see Figure 17).

Anal. Calc'd for C<sub>24</sub>H<sub>30</sub>O<sub>3</sub>: C, 78.65; H, 8.25

mol. wt. 366.48

Found: C. 78.75; H, 8.40

Rast mol. wt. (camphor) 350-360.

Pentamethylbenzoic anhydride was also prepared by refluxing 0.015 mole of trichloromethylpentamethylbenzene with 25 ml. (0.33 mole) of trifluoroacetic acid-3% trifluoroacetic anhydride for three hours, followed by distillation of the solvent and dark brown residue (under reduced pressure) and recrystallization of the white solid which formed, with ether.

(a) Evidence for a mixed anhydride intermediate.

The white solid, m.p. 180-185°, which resulted from the solidification of the distillate had a strong trifluoracetic acid odor and was easily hydrolyzed. One gram of the white solid, dissolved in 25 ml. of acetone and 50 ml. of 0.2159 N sodium hydroxide, was heated on the steam bath for fifteen minutes. After cooling the solution, the excess sodium hydroxide was titrated with standard hydrochloric acid (24.37 ml. of 0.1953 N hydrochloric acid required for neutralization to phenolphthalein end-point). The solution consumed 6.04 milliequivalents of sodium hydroxide. If the white solid had been the mixed anhydride of trifluoracetic acid and pentamethylbenzoic acid, 6.4 milliequivalents would have been consumed. The results are probably within experimental error.

Pentamethylbenzoic anhydride is very resistant to alkaline hydrolysis; only 0.2 milliequivalents of base was consumed when an acetone-ether solution of it was refluxed with aqueous sodium hydroxide for three hours.

(b) Reduction of pentamethylbenzoic anhydride

To a 300-ml. three-necked flask equipped with a reflux condenser (fitted with a drying tube), an addition funnel and a Tru-bore stirrer was added 2.0 g. (0.05 mole) of lithium aluminum hydride and 50 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride). One gram (0.003 mole) of pentamethylbenzoic anhydride in 100 ml. of tetrahydrofuran (the anhydride was not very soluble) was added slowly to the stirred lithium aluminum hydride-tetrahydrofuran slurry. The reactants were stirred at a gentle reflux for five hours, after which the reaction mixture was cooled with an ice bath and the excess hydride was decomposed by the dropwise addition of 10% sulfuric acid. The organic layer was extracted with three 25-ml. portions of ether. The ether solution was washed with 25 ml. of water, twice with 25 ml. of 10% sodium carbonate (to remove the pentamethylbenzoic acid formed by the hydrolysis of the anhydride) and twice with 25 ml. of water. The organic layer was dried over anhydrous calcium chloride. Evaporation of the ether gave 0.2 g. (20.7%) (0.6 g. of pentamethylbenzoic acid was isolated) of a white solid. Recrystallization from ether gave nice white crystals, m.p. 159-160° (54). The melting point and infrared spectrum (Figure 18) were identical to that of the pentamethylbenzyl alcohol obtained from hydrolysis of chloromethylpentamethylbenzene and lithium aluminum hydride reduction of pentamethylbenzoic acid.

# 2, 3, 4, 5, 6-Pentamethylbenzophenone

2, 3, 4, 5, 6-Pentamethylbenzophenone was prepared by Friedel-Crafts acylation of pentamethylbenzene with benzoyl chloride.



Per Cent Transmission



Per Cent Transmission

Figure 18. Infrared spectrum of pentamethylbenzyl alcohol (mineral oil mull).

In a 300-ml. three-necked round-bottomed flask equipped with a Tru-bore stirrer, thermometer and reflux condenser was placed 30 g. (0.2 mole) of pentamethylbenzene, 28.1 g. (0.2 mole) of benzoyl chloride and 100 ml. of carbon disulfide. Over a two-hour period, 6.5 g. (0.05 mole) of anhydrous powdered aluminum chloride was added in small portions to the stirred reaction mixture. After stirring for three more hours, the mixture was slowly poured into a liter beaker containing 300 g. of ice and 100 ml. of concentrated hydrochloric acid. The layers were separated and the carbon disulfide was evaporated on a steam bath. The organic residue was washed with two 50-ml. portions of 10% sodium carbonate and then steam distilled to remove any unhydrolyzed benzoyl chloride and unreacted hydrocarbon. The residue was extracted with three 100-ml. portions of ether and the ether extract was washed with three 25-ml. portions of 10% sodium hydroxide, followed by two 25-ml. portions of water. The ether was evaporated and the yellow residue recrystallized from absolute ethanol yielding white needle-like crystals of pentamethylbenzophenone, m.p.  $133-134.5^{\circ}$ . (Literature value:  $135-136^{\circ}$  (55)). Pentamethylbenzophenone has a very strong carbonyl band at 5.98  $\mu$ (see Figure 19).

#### Pentamethylbenzophenone dichloride

Several attempts were made to prepare pentamethylbenzophenone dichloride from pentamethylbenzophenone, phosphorus pentachloride and various solvents. Solvent systems tried were tetrachloroethane, carbon tetrachloride and benzene, all of which were unsatisfactory. Tars resulted from tetrachloroethane and there was no reaction when benzene or carbon tetrachloride were used.

In a typical experiment, there was placed 10 g. (0.028 mole) of pentamethylbenzophenone, 50 ml. of carbon tetrachloride and 10 g. (0.5 mole) of phosphorus pentachloride in a 100 ml. round-bottomed flask equipped with



Per Cent Transmission

a reflux condenser. The yellow reaction mixture was refluxed for twentyfour hours. The solvent was distilled under reduced pressure, leaving a yellow-white residue. The organic material was extracted from this residue with n-hexane. A white crystalline product (9.5 g.) was obtained which had a melting point of  $130-132^{\circ}$ . An infrared spectrum of this material was identical to that of pentamethylbenzophenone.

An attempt to prepare pentamethylbenzophenone dichloride by alkylation of pentamethylbenzene with benzotrichloride and aluminum chloride was unsuccessful; only tars were obtained.

Pentamethylbenzene can be alkylated with benzotrichloride if stannic chloride is used as the catalyst. The procedure used was similar to the Friedel-Crafts alkylation of pentamethylbenzene with carbon tetrachloride.

To a cold  $(10-15^{\circ})$ , stirred solution of 65 g. (0.25 mole) of stannic chloride and 30 ml. of benzotrichloride was slowly added (3 hours) a solution of 20 g. (0.13 mole) of pentamethylbenzene in 30 ml. of benzotrichloride. The solution became deep purple and hydrogen chloride evolved immediately. The stirred reaction mixture was maintained at  $10-15^{\circ}$  for six hours, after which hydrogen chloride evolution had essentially ceased. The purple reaction mixture was poured slowly into a vigorously stirred mixture of 200 g. of ice, 25 ml. of concentrated hydrochloric acid and 100 ml. of carbon tetrachloride. The orange-brown organic layer was washed with three 50-ml. portions of warm  $(40^{\circ})$  water and dried over anhydrous calcium chloride. The carbon tetrachloride was removed with a Rinco rotary evaporator, leaving an orange-brown solution. Difficulties were encountered in removing the excess benzotrichloride (b.p. 214<sup>0</sup>). Even at a reduced pressure of 2 mm. the pentamethylbenzophenone dichloride decomposed. A small amount of pentamethylbenzophenone was obtained from the decomposed product.

Carbon tetrachloride does not react with pentamethylbenzene in the presence of stannic chloride at room temperature. Therefore one should

be able to use an equimolar amount of pentamethylbenzene and benzotrichloride, excess stannic chloride and carbon tetrachloride as solvent to get good yields of pentamethylbenzophenone dichloride.

A series of Lewis acids (aluminum chloride, zinc chloride, ferric chloride, antimony pentachloride and stannic chloride) were tried as catalysts for alkylation of polymethylbenzenes with benzotrichloride. Stannic chloride was the most satisfactory catalyst.

#### Pentamethylbenzaldehyde

Pentamethylbenzaldehyde was prepared according to the procedure of Fuson (56). In a three-necked 500-ml. round-bottomed flask, fitted with a Tru-bore stirrer, a reflux condenser, a gas inlet tube and a thermometer, was placed 25.4 g. (0.21 mole) of pentamethylbenzene, 36.7 g. (0.31 mole) of zinc cyanide and 200 ml. of dry tetrachloroethane. The gas inlet tube was connected to a cylinder of dry hydrogen chloride gas and the mixture was stirred at room temperature, while a rapid stream of dry hydrogen chloride gas was passed into the solution. This was continued until the zinc cyanide had decomposed--approximately one and onehalf hours. (The reaction mixture became white and viscous at first, then it became pink and finally light red in color.) The flask was immersed in an ice bath, the gas inlet tube removed and 73.3 g. (0.55 mole) of powdered anhydrous aluminum chloride was slowly added to the vigorously stirred reaction mixture. After addition of the aluminum chloride, the ice bath was removed and dry hydrogen chloride gas was passed into the reaction mixture for four hours, while the mixture was heated to  $50^{\circ}$  on the steam bath. The reaction mixture was cooled and hydrolyzed by pouring it with stirring into a one-liter beaker containing crushed ice and 100 ml. of hydrochloric acid. The mixture was allowed to stand overnight, transferred to a two-liter round-bottomed flask equipped with a reflux condenser, and refluxed for three hours. The organic layer was separated and the

aqueous layer extracted with two 50-ml. portions of tetrachloroethane. The tetrachloroethane solutions were washed with 10% sodium carbonate, then steam distilled to remove the tetrachloroethane and unreacted pentamethylbenzene. The residue was extracted with benzene, washed three times with water, and dried overnight with anhydrous potassium carbonate. The benzene was removed under reduced pressure with the aid of a Rinco rotatory evaporator. The cream-colored residue was treated with Norite and recrystallized from aqueous ethanol, to yield 18.4 g. (61%) of white flaky platelets of pentamethylbenzaldehyde, m.p. 147-148° Literature value: 130.5°(57).

The infrared spectrum of pentamethylbenzaldehyde shows a strong carbonyl band at 5.93  $\mu$  (see Figure 20).

# a, a-Dichloromethylpentamethylbenzene

a, a-Dichloromethylpentamethylbenzene was prepared from pentamethylbenzaldehyde by modifying a procedure used by A. H. Blatt (58) to prepare benzophenone dichloride.

To a 250-ml. round-bottomed flask equipped with a reflux condenser (fitted with a calcium chloride drying tube) was added 10.0 g. (0.056 mole) of pentamethylbenzaldehydæ dissolved in 100 ml. of carbon tetrachloride. Fifteen grams (0.07 mole) of phosphorus pentachloride was added and the light yellow solution was refluxed for twelve hours. The carbon tetrachloride and phosphorus oxychloride were removed by distillation under reduced pressure, leaving light yellow crystals. These were dissolved in 100 ml. of n-pentane (dried over sodium wire) and the insoluble, excess phosphorus pentachloride was removed by filtration. Several Norite treatments and recrystallizations from n-pentane gave white platelets, m.p. 75-76<sup>°</sup>. An infrared spectrum showed a small carbonyl band (see Figure 21). No analytical data was obtained because of the instability of the dichloromethyl compound.



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Several work-up procedures were tried, but the one described above gave the most satisfactory results. To remove the excess phosphorus pentachloride in one case, the pentane solution was washed several times with small amounts of water and then dried over anhydrous calcium chloride. However, the pentane solution turned red from decomposition of the dichloromethylpentamethylbenzene.

a.a-Dichloromethylpentamethylbenzene appeared quite unstable; even in a desiccator hydrogen chloride was evolved, yielding a brick-red decomposition product. Recrystallization of this material from pentane gave pentamethylbenzaldehyde.

## Chloromethylpentamethylbenzene

Chloromethylpentamethylbenzene was prepared from pentamethylbenzene using a modified procedure of Aitken et al. (59).

To a 300-ml. three-necked flask equipped with a Tru-bore stirrer and a reflux condenser, was added 15.0 g. (0.1 mole) of pentamethylbenzene, 15 g. (approx. 0.5 mole) of 37% formaldehyde, 30 ml. of glacial acetic acid and 50 ml. of concentrated hydrochloric acid. The reaction mixture was refluxed on the steam bath for six hours with stirring, cooled and the organic layer was extracted with two 50-ml. portions of benzene. The benzene solution was washed with water, twice with 10% sodium carbonate and then three times with water. The benzene layer was dried overnight with anhydrous potassium carbonate. The benzene was removed under reduced pressure with the aid of a Rinco rotary evaporator. The white residue was recrystallized several times with n-pentane to give white platelets, m.p. 80-81°. The melting point of chloromethylpentamethylbenzene according to Jacobsen (54) is 99°. The earlier preparation involved treatment of hexamethylbenzene with phosphorus pentachloride. Because a variety of products was obtained, the literature value is questionable. Therefore the compound was submitted for microanalysis.

Note: See F. Benington, R.D. Morin + L.C. Clark, Jr., J. Org. Chem. 23, 2034 (1958).

<u>Anal.</u> Calc'd for C<sub>12</sub>H<sub>17</sub>Cl: C, 73.26%; H, 8.71%; Cl, 18.03% Found: C, 73.06%; H, 8.64%; Cl, 18.10%. The infrared spectrum of chloromethylpentamethylbenzene is given in Figure 22.

B. Structure Proof of the Trichloromethyl Compounds

# Reactions of solutions of trichloromethylpentamethylbenzene in 100% sulfuric acid.

(a) With water.

Five grams of trichloromethylpentamethylbenzene was dissolved in 25 ml. of cold 100% sulfuric acid. The intensely red solution was slowly poured onto crushed ice giving a flocculent white precipitate which was collected on a filter, and the filtrate was extracted twice with ether. After evaporation of the ether, the combined solids were recrystallized from aqueous ethanol. The total yield of pentamethylbenzoic acid was 3.48 g. (96.2%), m.p.  $208-210^{\circ}$  (30). The infrared spectrum is given in Figure 23.

(b) With methanol (analogous to the Newman procedure (15)).

In a similar experiment, the intensely red solution was stirred until most of the hydrogen chloride had been removed. This solution was poured carefully into 50 ml. of absolute methanol, kept at 0°. The colorless liquid was transferred to a 200-ml. round-bottomed flask equipped with a Claisen distillation head. The excess methanol was distilled under reduced pressure (without heating). After most of the methanol had been removed, 50 ml. of water was added, and more of the methanol was distilled under reduced pressure (external heat-50° water bath). The white platelets which precipitated were extracted with two 50-ml. portions of ether; the ether layer was washed twice with a 10% sodium carbonate solution and finally with water. After the ether layer was dried over anhydrous calcium chloride, the ether was evaporated, leaving a cream colored



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Figure 23. Infrared spectrum of pentamethylbenzoic acid (CCl4 solution).

residue. The residue was treated with Norite and recrystallized from methanol giving white platelets of methyl pentamethylbenzoate, m.p. 67-67.5° (30), in nearly quantitative yield. The infrared spectrum of methyl pentamethylbenzoate has a carbonyl absorption at  $5.80 \mu$  (see Figure 24).

# Solvolysis of trichloromethylpentamethylbenzene

(a) With aqueous acetone.

One gram of trichloromethylpentamethylbenzene was dissolved in 25 ml. of 50% aqueous acetone. The resulting solution was refluxed on a steam bath for one hour, then poured into 100 ml. of ice-water; the white precipitate which formed was collected on a filter. The filtrate was distilled under reduced pressure to remove most of the acetone, and the solution was extracted with two 25-ml. portions of ether. The ether layer was washed several times with water and the ether evaporated. The combined precipitates were recrystallized from aqueous ethanol to give 0.69 g. (95.6%) of white platelets of pentamethylbenzoic acid, m.p.  $208-210^{\circ}$  (30).

(b) With absolute methanol containing sodium methoxide.

To a 50-ml. round-bottomed flask equipped with a reflux condenser was added 1.007 g. (.004 mole) of trichloromethylpentamethylbenzene, 0.707 g. (.013 mole) of sodium methoxide and 15 ml. of absolute methanol. After the initial exothermic reaction, the mixture was refluxed for three hours. The excess methanol was distilled under reduced pressure; 25 ml. of water was added and the residual methanol removed by distillation. On cooling, the remaining solution gave 0.711 g. of crystals. A second crop, obtained by further evaporation and extraction with ether amounted to 0.048 g. The total yield of methyl pentamethylbenzoate before recrystallization was 0.759 g. (97.1%), m.p. (crude) 64-65.5°. Recrystallization of the ester from aqueous methanol gave white platelets, m.p.  $67-68^{\circ}$  (30).



Figure 24. Infrared spectrum of methyl pentamethylbenzoate (CCl<sub>4</sub> solution).

# Reaction of trichloromethyl-2, 3, 4, 5-tetramethylbenzene-100% sulfuric acid

(a) With water.

One gram of trichloromethyl-2, 3, 4, 5-tetramethylbenzene, m. p.  $90-91.5^{\circ}$ , was dissolved in 10 ml. of 100% sulfuric acid. The dark red solution was slowly poured onto crushed ice giving a flocculent white suspension. The product was collected on a filter and the filtrate extracted several times with ether. The ether extract was washed with water and dried over calcium chloride. After removal of the ether, the combined solids were recrystallized from aqueous methanol. The total yield of tetramethylbenzoic acid was 0.63 g. (88.7%), m.p. 168-169°. This melting point agrees with that given by Jacobsen (30) for 2, 3, 4, 5-tetramethyl-benzoic acid. The infrared spectrum is given in Figure 25.

(b) With absolute methanol, (analogous to the Newman procedure (15)).

Two grams of trichloromethyl-2, 3, 4, 5-tetramethylbenzene was added to 10 ml. of 100% sulfuric acid. After allowing the dark red solution to stand several minutes it was poured slowly into 25 ml. of cold  $(0^{\circ})$  absolute methanol. The slightly cloudy solution was transferred to a 100-ml. round-bottomed flask equipped with a Claisen distillation head. The excess methanol was distilled under reduced pressure (without heating). After most of the methanol had been distilled, 50 ml. of water was added and more of the solvent was removed by heating the flask with a  $50^{\circ}$  water bath, under reduced pressure. The organic product was extracted with two 25-ml. portions of ether; the ether layer was washed twice with 10% sodium carbonate solution (to remove any unesterified acid) and finally with water. After drying the ether layer with anhydrous calcium chloride, the solvent was evaporated leaving an oil, which was transferred to a 10 ml. distillation flask and fractionated. The product, which solidified on cooling, had a melting point of 33-35°. Recrystallization from aqueous methanol gave white platelets, m.p. 35-36°. This melting point agrees



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with the literature value (3) for methyl 2, 3, 4, 5-tetramethylbenzoate. The infrared spectrum is given in Figure 15. The carbonyl absorption is the same for both methyl 2, 3, 4, 5-tetramethylbenzoate and methyl 2, 3, 5, 6tetramethylbenzoate. The 10 to 14 micron region of the infrared spectra of the two esters differ, (see Figure 26 for an infrared spectrum of an equimolar mixture of the two esters).

# Solvolysis of trichloromethyltetramethylbenzene (m. p. 90-91.5°).

(a) With water.

Two grams of trichloromethyltetramethylbenzene (m. p.  $90-91.5^{\circ}$ ) and 50 ml. of 50% aqueous acetone were added to a 100-ml. round-bottomed flask equipped with a reflux condenser. The solution was refluxed on a steam bath for ten hours. After most of the acetone was removed under reduced pressure, 50 ml. of water was added and the acid which precipitated was collected on a filter. The filtrate was extracted with ether and the ether evaporated. The combined solids were recrystallized twice from aqueous methanol. Total yield of 2, 3, 4, 5-tetramethylbenzoic acid was 1.31 g. (91.8%), m.p. 169-170° (31). The infrared spectrum of this acid was identical to that of the prehnitenecarboxylic acid obtained from hydrolysis of trichloromethyl-2, 3, 4, 5-tetramethylbenzene-100% sulfuric acid solution (see Figure 25).

(b) With methanol.

Five grams of trichloromethyltetramethylbenzene (m. p.  $90-91.5^{\circ}$ ) and 25 ml. of purified absolute methanol (distilled from magnesium metal) were added to a 50-ml. round-bottomed flask equipped with a reflux condenser. After refluxing the solution ten hours, the excess methanol was distilled under reduced pressure with a Rinco rotary evaporator, leaving a yellow-white residue. Recrystallization from aqueous methanol gave 3.41 g. (89.3%) of methyl 2, 3, 4, 5-tetramethylbenzoate, m. p.  $34-36^{\circ}$ .



Recrystallization from ether gave white platelets, m.p.  $35-36^{\circ}$  (30). An infrared spectrum was the same as the methyl ester obtained by the reaction of trichloromethyl-2, 3, 4, 5-tetramethylbenzene-100% sulfuric acid solution with methanol and the ester from methylation of 2, 3, 4, 5-tetramethylbenzoic acid (see Figure 15).

# <u>Reaction of trichloromethyl-2, 4, 6-trimethylbenzene-100% sulfuric</u> acid solution.

(a) With water.

Trichloromethylmesitylene (1.462 g. b.p.  $126-126.5^{\circ}/5$  mm.  $n_D^{25}$  1.5640) was dissolved in 10 ml. of cold 100% sulfuric acid. The dark red solution was carefully poured onto crushed ice giving a gelatinous white precipitate which could not be collected on a filter quantitatively. The organic material was extracted with three 25-ml. portions of ether, the ether layer washed several times with water and dried with anhydrous calcium chloride. After evaporation of the ether, the white solid was recrystallized from aqueous methanol. The total yield of 2, 4, 6-trimethylbenzoic acid was 0.98 g. (97.0%), m.p. 153-154° (53). The infrared spectrum of this acid is given in Figure 27.

(b) With methanol, [analogous to the Newman procedure (15)].

Ten grams of trichloromethylmesitylene (b. p.  $124-126^{\circ}/5$  mm.  $n_D^{25}$  1.5637) was dissolved in 25 ml. of cold 100% sulfuric acid. The dark red solution was carefully poured into 100 ml. of cold (0°) absolute methanol (light purple-colored solution). The ester was isolated by a procedure analogous to that described on page 92, for methyl pentamethylbenzoate. The ester isolated was a yellow oil, which was distilled under reduced pressure, b.p. range 80-86°/2mm,  $n_D^{25}$  1.5081, yield 6.91 g. (91.2%) (literature value: 130-131°/23 mm.,  $n_D^{20}$  1.5083 (53)).

An infrared spectrum of the colorless ester showed a strong carbonyl band at  $5.79 \mu$  with two small shoulders. The ester was fractionated and



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Figure 27. Infrared spectrum of 2, 4, 6-trimethylbenzoic acid (CS<sub>2</sub> solution)

all fractions gave the same infrared spectrum with two small shoulders (5.62  $\mu$  and 5.68  $\mu$ ) on the carbonyl peak (5.78  $\mu$ ).

## Solvolysis of trichloromethyl-2, 4, 6-trimethylbenzene

(a) With aqueous acetone.

To a 100-ml. round-bottomed flask equipped with a reflux condenser was added 5.0 g. of trichloromethylmesitylene and 50 ml. of 50% aqueous acetone. The resulting solution was refluxed on a steam bath for twelve hours. The reaction mixture was poured into 100 ml. of ice water; the white suspension was collected on a filter. The filtrate was distilled under reduced pressure to remove most of the acetone. This solution was extracted with three 25-ml. portions of ether. The ether layer was washed several times with water and the ether evaporated. The combined precipitates were recrystallized from aqueous methanol to give 3.28 g. (95.0%) of white crystalline mesitoic acid, m.p.  $153-154^{\circ}$  (53).

(b) With sodium methoxide-methanol.

To a 100-ml. round-bottomed flask equipped with a reflux condenser, was added 50 ml. of purified absolute methanol and 5.0 g. of sodium metal. After cooling this solution in an ice-bath, 15.0 g. of trichloromethylmesitylene ( $n_D^{25}$  1.5639) was added (mild exothermic reaction) and the mixture was refluxed for twelve hours. The solution was filtered to remove the insoluble sodium chloride and the excess methanol was removed under reduced pressure. The ester was transferred to a 25-ml. Claisen flask, and distilled under reduced pressure. Product boiling from 100-101<sup>°</sup>/6 mm.,  $n_D^{25}$  1.5184 (literature values: 130-131/23mm.  $n_D^{20}$  1.5083 (53)), weighing 8.8 g. (86.1%) was collected as methyl mesitoate. An infrared spectrum showed three carbonyl peaks, 5.62  $\mu$  (weak), 5.68  $\mu$  (medium) and 5.78  $\mu$ (strong) - see Figure 28. A careful fractionation of this material did not separate the three components present.



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C. Reaction of trichloromethylpentamethylbenzene with trifluoroacetic acid saturated with boron trifluoride.

A stream of dry boron trifluoride (bubbled through a sulfuric acid scrubbing tower) was passed into a solution of 20 ml. of trifluoroacetic acid and 2 ml. of trifluoroacetic anhydride in a 50-ml. two-necked flask, equipped with a gas-inlet and a drying tube, until the solution became saturated. Trichloromethylpentamethylbenzene, 2.65 g. (0.01 mole), was added and boron trifluoride was bubbled into the mixture until all of the trichloromethyl compound had dissolved. (Trichloromethylpentamethylbenzene is not very soluble in trifluoroacetic acid). The excess boron trifluoride and trifluoroacetic acid were removed with a water aspirator (solution protected from water by a calcium chloride drying tower). The last traces of solvent were removed by heating the flask with a 60° water bath. The dark red residue remaining after removal of the solvent was almost crystalline. It had an odor of trifluoroacetic acid; and was insoluble in aromatic and aliphatic hydrocarbons and carbon tetrachloride. It was slightly soluble in chloroform and dissolved readily in ether giving an intense red solution. Attempts to isolate a definite crystalline salt were futile. The red solid turned white when exposed to the air and pentamethylbenzoic acid was isolated. A 90 to 95% yield of pentamethylbenzoic acid was isolated when the dark red solution was poured on ice and when the dark red residue was hydrolyzed with water.

The red residue gave a positive Beilstein test and an insoluble white silver salt formed when it was dissolved in ethanolic silver nitrate.

The proton magnetic resonance and visible spectra of the dark red solution (after the excess boron trifluoride had been removed) and that of the red residue dissolved in trifluoroacetic acid-3% trifluoroacetic anhydride were identical. These spectra were similar to the spectra of pentamethylphenylchlorodicarbonium ion in 100% sulfuric acid, except for solvent effects (see Figures 29 and 30).



Figure 29. Visible spectrum of trichloromethylpentamethylbenzene in trifluoroacetic acid saturated with boron trifluoride.



Figure 30. Proton magnetic resonance spectrum of trichloromethylpentamethylbenzene in trifluoroacetic acid-boron trifluoride solvent.  $v_0$  60 Mc, reference:

Trichloromethylmesitylene and trichloromethylprehnitene also dissolve readily and form dark red solutions in trifluoroacetic acid saturated with boron trifluoride. No solvent was necessary for trichloromethylmesitylene; it formed an intense red solution when boron trifluoride was bubbled into it.

Intense red solutions are formed when boron trifluoride is bubbled into nitromethane solutions of the trichloromethyl compounds.

D. Reaction of benzoyl chloride with phosphorus pentachloride.

The reaction of ketones or aldehydes with phosphorus pentachloride usually gives the corresponding dichlorocompound (60). The reaction of phosphorus pentachloride with benzoyl chloride might be a new method for preparing trichloromethyl compounds. Several attempts were made to prepare benzotrichloride by this method.

To a 100-ml. round-bottomed flask equipped with a reflux condenser (fitted with a drying tube) was added 52 g. (0.25 mole) of phosphorus pentachloride and 28 g. (0.2 mole) of benzoyl chloride. The yellow solution was refluxed for twelve hours and then distilled under reduced pressure. No benzotrichloride was found in any of the fractions (shown by infrared spectra and refractive indices).

In another attempt, 42 g. (0.3 mole) of benzoyl chloride and 120 g. (0.6 mole) of phosphorus pentachloride were added to a combustion tube. The sealed combustion tube was heated at  $200-225^{\circ}$  in a tube furnace for twenty-four hours. Two fractional distillations of the reaction mixture gave 14.6 g. (20% yield) of benzotrichloride, b.p.  $82-84^{\circ}/8$  mm.,  $n_{D}^{20}$ 1.5575. Literature value, b.p.  $214^{\circ}$ ,  $n_{D}^{20}$  1.5578 (6). An infrared spectrum was identical to that of an authentic sample of benzotrichloride.

This method can not be applied to the preparation of trichloromethylpolymethylbenzenes because they are not stable when heated above their melting points (see page 54).

# E. Reaction of benzotrichloride with 100% sulfuric acid in the presence of several aromatic hydrocarbons.

Benzotrichloride is not very soluble in 100% sulfuric acid; a light yellow solution forms after standing several hours. The addition of a small amount of certain aromatic hydrocarbons such as pentamethylbenzene, durene, mesitylene, xylenes and fluorene gives a deep red-colored solution with immediate evolution of hydrogen chloride. The reverse reaction was similar; the aromatic hydrocarbons mentioned above are not very soluble in 100% sulfuric acid, but the addition of a small amount of benzotrichloride produced a deep red-colored solution with immediate evolution of hydrogen chloride. The addition of diphenyl- and triphenylmethane to a mixture of benzotrichloride-100% sulfuric acid did not initiate the reaction. Several attempts were made to determine the reason for this phenomenon, but an adequate explanation has not yet been found.

A study of the ultraviolet-visible spectrum of an equimolar solution of pentamethylbenzene-benzotrichloride in 100% sulfuric acid was quite complex. Absorption maxima appear at 262 m $\mu$ , 298 m $\mu$ , 344 m $\mu$ , 467 m $\mu$ and 665 m $\mu$ . The intensity of these absorption peaks changed with time, even if the solutions were kept cold.

When the deep red solution, from an equimolar solution of pentamethylbenzene-benzotrichloride in 100% sulfuric acid was poured on ice the color disappeared and a white precipitate formed. Collection of this material on a filter and recrystallization from hot water gave white crystals of benzoic acid, m.p. 121°. The cloudy filtrate was extracted with carbon tetrachloride. The organic layer was washed with 10% sodium carbonate, several times with water and dried over anhydrous calcium chloride. Evaporation of the carbon tetrachloride left a yellow oil which had an almond odor. The oil was purified by passing it through the Perkin-Elmer vapor-phase chromatograph, using the silicone preparative column at 140° and 5 pounds of nitrogen pressure. An infrared spectrum of this colorless liquid was identical to that of authentic benzaldehyde. The ratio of benzoic acid to benzaldehyde depends on the reaction time.

The aqueous solution from the carbon tetrachloride extraction had a phenolic odor, but no derivative of pentamethylbenzene was isolated.

#### F. Cryoscopic Measurements

### Apparatus:

The apparatus was similar to that described by Gillespie, Hughes and Ingold (62) except that a thermistor was used in place of a Beckmann thermometer.

The thermistor consisted of a bead of metallic oxides, with lead wires sealed in a glass envelope, designed by Fenwal Electronics Inc. The glass envelope was sealed to a piece of lead glass tubing extending from the cap of the freezing point cell to within a half inch of the bottom of the cell. The thermistor was calibrated from  $-5^{\circ}$  to  $20^{\circ}$  against a U. S. Bureau of Standards platinum resistance thermometer (No. 1016073). A Leeds and Northrup 5-decade Wheatstone bridge and a Rubicon lamp-scale galvanometer with a sensitivity of 0.0015  $\mu$ a/mm. were used to measure resistance. Measurements were precise to  $0.002^{\circ}$  but accurate perhaps only to  $0.01^{\circ}$ .

The freezing point cell was equipped with ground-glass joints which were lubricated with silicone grease to prevent incursion of water vapor during measurements. The cell cap was equipped with three standard ground joints, one accommodating the stirrer, one for the thermistor and the third was fitted with a stopper and used to add solutes.

The freezing point cell was surrounded by a Styrofoam insulated airjacket provided with an upward sloping side arm through which a piece of Dry Ice could be inserted to touch the cell wall and induce crystallization. Early measurements were made with magnetic stirring. A magnet, sealed in glass, was placed in the body of the apparatus, the whole of which, including cooling bath, was mounted above a magnetic stirrer. Because the magnet stopped after freezing commenced, later experiments were stirred with a mercury-sealed motor-driven stirrer of special design to permit scraping of the cell walls without touching the sensitive thermistor (see Figure 31).

## Procedure:

The techniques used in the freezing point determinations were similar to those described by Newman and co-workers (53).

The apparatus was always cleaned, dried in the oven and cooled in a dry nitrogen atmosphere before each determination. The freezing point cell was assembled, weighed and approximately 50 ml. of stock sulfuric acid was added. After placing the cell in the insulated air jacket, the entire apparatus was surrounded by a cooling bath filled with crushed ice and the solution was stirred. The temperature of the sulfuric acid was reduced to approximately two degrees below the freezing point of the acid, and crystallization was induced by touching the side of the cell with Dry Ice. The steady maximum of temperature, obtained by one-minute temperaturereading intervals, reached after crystallization was the freezing point. Because the stock acid solution was kept on the sulfur trioxide side, a calculated amount of concentrated sulfuric acid was added and the freezing point redetermined, as described above. This procedure was repeated until sulfuric acid with a maximum freezing point (10.37 $^{\circ}$ (63) was obtained. After the acid remained in the apparatus for at least twelve hours, the freezing point was redetermined; if it remained the same over the twelvehour period, the cell was reweighed. (Difference in the two weighings was the weight of the sulfuric acid.) Sufficient solute was then added to lower the freezing point of the solution 0.2 to  $0.5^{\circ}$ . After all the solute had dissolved, the freezing point apparatus was returned to the ice bath and the new freezing point was determined. The freezing point was rechecked after various time intervals; if the "i" value did not change markedly



Figure 31. Diagram of freezing point apparatus.

- a. Mercury sealed stirrer.
- b. Thermistor sealed to lead glass tubing.
- c. Styrofoam insulation.
- d. Air-jacket.
- e. Stirrer arm which scrapes the cell wall.
- f. Side arm for introducing a piece of Dry Ice to induce crystallization.
- a Ground glass joint and stonne- for adding solutor

with time, then three to five weighed portions of solute were added and the freezing point determined after each addition.

Several techniques were used to introduce the solute into the cell. When the magnetic stirrer was used, the solute was weighed out in a small glass capsule and the capsule was placed in the cell. However, this technique did not work with the mercury-sealed stirrer because the capsule usually became lodged between the stirrer and thermistor and broke the thermistor. Liquid solutes were added with the aid of weight burette or pipette. Some solids were weighed on glazed paper and poured into the cell by means of a long funnel made of glazed paper, long enough to reach almost to the surface of the sulfuric acid. Some solid solutes were dissolved in carbon tetrachloride and added by a pipette or long funnel in this form.

In some experiments the solvent was sulfuric acid having the maximal freezing point. In others it was sulfuric acid to which sufficient water had been added to suppress the self-ionization of the pure acid.

### Stock sulfuric acid

Stock sulfuric acid is slightly greater than 100% sulfuric acid. It was prepared by two procedures: Dilution of J. T. Baker's reagent grade fuming (20-30% sulfur trioxide) sulfuric acid with reagent grade concentrated (96-98%) sulfuric acid, or distillation of sulfur trioxide from oleum through an all glass apparatus into reagent grade concentrated (96-98%) sulfuric acid. The first method was simpler and equally satisfactory.

G. Conductance Measurements.

### Apparatus:

The conductance bridged used for these measurements is described in detail by Thompson and Rogers (64). Measurements were made at frequencies of 400, 600, 1000 and 2000 cps. The conductance cell was a

30-ml. Leeds-Northrup-Jones Type B cell with bright platinum electrodes (cell constant 29.9). The conductance cell was thermostated at 25.000  $\pm$  0.003°, in a fifteen gallon transformer oil constant-temperature bath.

# Procedure:

Before each series of measurements, the cell was rinsed 12 times with distilled water, 12 times with conductivity water, dried for several hours at 110<sup>°</sup> and while still warm, attached to a vacuum pump, protected by a drierite tower, to remove any traces of water vapor. It was then dried for two more hours in the oven and allowed to cool in a dry nitrogen atmosphere. After rinsing the cell several times with 100% sulfuric acid. the cell was filled under a blanket of dry nitrogen and thermostatted for 30 to 45 minutes, before the electrodes were attached to the bridge and measurements taken. Measurements were taken until the resistance values were constant, then resistances were measured at frequencies of 400, 600, 1000 and 2000 cps. Variation with frequency was less than 0.1%. For this reason, only a single conductance value is given for each molarity in Table XIII. Then the cell was emptied and a calculated amount of 98% sulfuric acid was added to the 100% sulfuric acid. All transfers were carried out under a blanket of dry nitrogen. The above procedure was repeated until minimum conductance sulfuric acid was obtained. The equivalent conductance was  $0.01046 \pm 0.0003$  ohm<sup>-1</sup> cm<sup>-1</sup>, literature value (65) was 0.010432 ohm<sup>-1</sup> cm<sup>-1</sup>. The values for the equivalent conductance of 100% sulfuric acid at  $25^{\circ}$  for a one year period is given in Table XIV. Solutions of solutes corresponding to 0.05, 0.1 and 0.2 M were made up with this minimum conductance sulfuric acid and conductance measurements were taken using the technique described above.

# H. Quantitative Determination of Hydrogen Chloride from the Dissolution of Trichloromethyl Compounds in Sulfuric Acid

### Apparatus:

The apparatus for the quantitative determination of hydrogen chloride consisted of a series of four traps. Each trap was equipped

TABLE XIII

Solute	М	۸	λ
KHSO4	0.1006	156.7	1
	0.1987	121.6	
$0 - C_{\ell} H_{\ell} (NH_{2})$	0.0550	301.2	2
0 - 061 4 (1112/2	0.0531	307.0	5
	0.1052	207.8	
	0.1128	215.1	
	0.2046	166.5	
	0.2044	161.7	
(CH <sub>3</sub> ) <sub>5</sub> C <sub>6</sub> CCl <sub>3</sub>	0.0513	304.3	2
( = = -3/9 = 0 = =	0.0538	292.8, 297	.3 <sup>a</sup>
	0.1001	210.5 <sup>b</sup>	
	0.1005	213.4	
	0.2008	155.3	
(CH <sub>3</sub> ) <sub>4</sub> C <sub>6</sub> HCCl <sub>3</sub>	0.0522	308.0	2
	0.0520	306.9	
	C.0988	203.7	
	0.0991	212.3	
	0.1920	149.2	
	0.1933	151.8	
(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CCl <sub>3</sub>	0.0491	308.4	2
	0.0992	197.5	
	0.1118	200.1	
	0.2017	162.2	

CONDUCTANCE DATA IN 100% SULFURIC ACID, 25.060°

<sup>a</sup>The second value was obtained after flushing the solution free of hydrogen chloride with dry nitrogen; the first value was obtained before removing the hydrogen chloride.

b Measured on a hydrogen chloride-free solution.

# TABLE XIV

# EQUIVALENT CONDUCTANCE VALUES<sup>a</sup> FOR 100% SULFURIC ACID FOR A ONE YEAR PERIOD

Experiment Number	Equivalent Conductance at 25.000 $\pm$ 0.003 <sup>o</sup> (ohm <sup>-1</sup> cm <sup>-1</sup> )	
1	0.01047	
2	0.01043	
3	0.01046	
4	0.01042	
5	0.01046	
6	0.01045	
7	0.01044	
8	0.01049	

<sup>a</sup>Equivalent conductance value for minimum conductance sulfuric acid accepted is 0.010432 ohm<sup>-1</sup>cm<sup>-1</sup> (65).

with ground glass joints, an inlet tube with a fritted glass tip protruding below the surface of the solution, and an outlet tube connecting it to the next trap. The first two traps contained 100% sulfuric acid for drying the nitrogen and saturating it with  $SO_3$ . The third trap contained a solution of the trichloromethylcompound in 100% sulfuric acid maintained at  $10-15^{\circ}$  in a cold water bath. The fourth trap contained a 2 to 5% sodium hydroxide solution for collecting the hydrogen chloride swept from the third trap.

#### Procedure:

The train was assembled as described above. A sample of the trichloromethyl compound, weighed out in a small glass capsule, was dropped into the third trap containing 100% sulfuric acid. After making sure that there were no leaks, a stream of oil-pumped nitrogen was passed through the system. After various time intervals, the aqueous sodium hydroxide trap was changed, the solution acidified with dilute nitric acid to a pH 8, (pH was determined with a Beckman pH meter) and the chloride ion determined by the Fajans' method (66), using dichloro-fluorescein indicator and dextrin as the protective colloid. Results are given in Table II. The results of control experiments with Fajans' method in the presence of varying amounts of sulfate ion are given in Table XIV.

The third chloride ion from the dipositive carbonium ion, was found in the filtrate, after removing the carboxylic acid obtained from pouring the hydrogen chloride-free, deep red-sulfuric acid solution on ice. Several procedures were tried to determine the third chloride ion quantitatively. One method involved neutralization of the cold sulfuric acid filtrate with concentrated sodium hydroxide until a pH 8 was attained (pH was determined with a Beckman pH meter). Then the chloride was determined by Fajans' method using the above procedure. Because of the large volume of solution, this method was not very accurate.

# TABLE XV

Wt., g. NaCl	Conditions	Per Cent Cl (Theory-60.66)
0.1321	50 ml. of water	60.84
0.2976	50 ml. of water	60.89
0.2479	50 ml. of water	60.65
0.1706	50 ml. of water and 0 ml. of 0.2 N sulfuric	.5 60.75 acid <sup>*</sup>
0.2003	50 ml. of water and 0 ml. of 0.2 N sulfuric	.5 60.74 acid <sup>*</sup>
0.4208	50 ml. of water and l of 2 N sulfuric acid <sup>*</sup>	ml. 60.85

# DETERMINATION OF CHLORIDE ION IN THE PRESENCE OF SULFATE ION BY FAJANS' METHOD AT $_{\rm PH}$ 8

\*Solution neutralized to pH 8 with dilute sodium hydroxide.

In another experiment, solid barium hydroxide was added to the cold sulfuric acid filtrate, this neutralized the solution and precipitated the sulfate as insoluble barium sulfate which was filtered off, washed and discarded. The filtrate was acidified with dilute nitric acid to a pH 8. The chloride was titrated by Fajans' method. In one experiment the filtrate from the barium sulfate precipitation was acidified with dilute nitric acid, filtered and the chloride determined gravimetrically by weighing the silver chloride. The last two experiments gave low results for chloride, probably because of coprecipitation of barium chloride with the barium sulfate (see Table III).

I. Spectra

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

The proton magnetic resonance spectra were obtained with a highresolution nuclear-induction type NMR spectrometer, Varian Associates (VA) Model V-4300-2.

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

#### SUMMARY

1. The aluminum chloride catalyzed reaction of carbon tetrachloride with pentamethylbenzene, developed by Rolih and Peters (12), was modified to increase the yield of trichloromethylpentamethylbenzene and extended to the preparation of trichloromethyl-2, 3, 4, 5-tetramethylbenzene and trichloromethyl-2, 4, 6-trimethylbenzene.

2. Trichloromethylpentamethylbenzene was found to give an intense red color in 100% sulfuric acid. This solution was studied to determine the structure of the specie responsible for the red color. Cryoscopic measurements showed that five particles were produced when trichloromethylpentamethylbenzene was added to 100% sulfuric acid. Two of these, swept from the solution with dry nitrogen, were hydrogen chloride. Conductance measurements on the original solution and the hydrogen chloride-free solution showed that two bisulfate ions were produced. Hydrolysis of the trichloromethylpentamethylbenzene-100% sulfuric acid gave 93-96% yield of pentamethylbenzoic acid. Hydrolysis of the hydrogen chloride-free solutions gave 93% pentamethylbenzoic acid and 0.76 to 1.05 moles of chloride ion per mole of trichloromethylpentamethylbenzene. Thus four of the particles are two hydrogen chloride molecules and two bisulfate ions; the fifth must therefore give pentamethylbenzoic acid and chloride ion on hydrolysis, must be red and must be dipositively charged.



3. The structure of the dipositive carbonium ion was investigated by ultraviolet, visible and proton magnetic resonance spectroscopy. The exact position of the positive charges was not established, but comparison of the proton magnetic resonance spectrum of II with that of the

pentamethylbenzoyl cation indicated that



are important resonance forms. These structures also provide an explanation for the intense red color of the dipositive carbonium ion.

4. Other solvent systems which produce the dication are: nitromethane with excess aluminum chloride, nitrobenzene with excess aluminum chloride, nitromethane saturated with boron trifluoride and trifluoroacetic acid saturated with boron trifluoride.

5. A dark red, almost crystalline salt of the dication was formed when the excess solvent was removed from a solution of trichloromethylpentamethylbenzene in trifluoroacetic acid which had been saturated with boron trifluoride. Attempts to convert this red residue to a crystalline salt of definite composition were not successful, but it was converted to a colorless liquid when heated under reduced pressure. Distillation of this liquid, followed by cooling of the distillate, gave a white fluorine-containing solid which was converted to pentamethylbenzoic anhydride by recrystallization from dry ether. The mechanism and structure proof are discussed.

6. Trichloromethylation of durene (1, 2, 4, 5-tetramethylbenzene) with carbon tetrachloride and aluminum chloride gave a 75% yield of trichloromethyl-2, 3, 4, 5-tetramethylbenzene. This structure was established by hydrolysis to 2, 3, 4, 5-tetramethylbenzoic acid, followed by decarboxylation of this acid to 1, 2, 3, 4-tetramethylbenzene.

7. Trichloromethyl-2, 3, 4, 5-tetramethylbenzene and trichloromethyl-2, 4, 6-trimethylbenzene also form dipositive carbonium ions in 100% sulfuric acid and in trifluoroacetic acid saturated with boron trifluoride.

# SYNTHESIS AND REACTIONS OF TETRAMETHYLBENZOCYCLOBUTENE DERIVATIVES

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PART II

### INTRODUCTION

This part of the thesis is concerned with a new synthesis of benzocyclobutene derivatives. To place the present work in perspective, it will be instructive to consider earlier methods of synthesis of benzocyclobutene and related compounds.

In 1888 Perkin suggested the benzocyclobutene structure in his classical study of cyclic systems (68). But he dismissed the possibility of preparing this ring system on the basis of excessive strain. Even the synthesis of dibenzocyclobutadiene (diphenylene) by Lothrop (69) scarcely suggested that benzocyclobutene should be a readily prepared and stable compound, because diphenylene was thought to be a special case.

Finkelstein was the first to prepare benzocyclobutene derivatives (70, 71). Unfortunately his work was not published and it was not until recently that Cava and Napier reinvestigated and extended the work of Finkelstein (72).

Finkelstein obtained 1, 2-dibromobenzocyclobutene (II) in 60% yield when a, a, a', a'-tetrabromo-o-xylene (I) was refluxed in an ethanolic solution of sodium iodide for two days.



These results were confirmed by Gava and Napier (72).

Kirmse, Horner and Muth (73) developed a different entry into the benzocyclobutene series. 2-Oximinoindan-1-one (III) was converted by chloramine into 2-diazoindan-1-one (IV); irradiation of the diazoketone in aqueous tetrahydrofuran gave a 20-25% yield of benzocyclobuten-1carboxylic acid (V).



Cava, Litle and Napier (74) simultaneously found similar results with substituted and unsubstituted indanones.

Sulfur dioxide can add to butadiene to give 2, 5-dihydrothiophene-1, 1-dioxide (VI); the reaction can be reversed by heat.



Cava and Deana (75) investigated the feasibility of extending the reverse reaction to the cyclic aromatic analog of VI and found a new route to benzocyclobutene. A pyrolysis study of 1, 3-dihydroisothianapthene-2, 2-dioxide (VIII) showed that the number of products and the yield of benzocyclobutene (IX) vary considerably with the solvent and temperature. Benzocyclobutene was obtained in 59-63% yield by vapor phase pyrolysis over Nichrome wire at 460-670°, in a low pressure nitrogen atmosphere.



Jensen and Coleman (76) prepared 1, 2-diphenylbenzocyclobutene (X) by the reaction of sodium iodide with a, a'-dibromo-a, a'-diphenyl-oxylene (XI) and by the reaction of bases with a-bromo-a, a'-diphenyl-oxylene (XII).



Baker, McOmie and Pope (77) reported that they could not cyclize XI to X with sodium iodide in acetone, but obtained 9-phenyl-anthracene (XIII) and the related 10, 10<sup>\*</sup>-dianthranyl. In their hands the reaction of XI with potassium tert. -butoxide gave 9-bromo-10-phenylanthracene (XIV).



A novel synthesis of benzocyclobutene was developed by ter Borg and Bickel (78). In an investigation of the reaction of dichlorocarbene with cycloheptatriene, an addition product 1, 1-dichloro-[5, 1, 0]-bicycloocta-3, 5-diene (XV) was isolated in a 20% yield. When XV was refluxed with ethylbenzene (140<sup>°</sup>), a 50% yield of 1-chlorobenzocyclobutene (XVI) was obtained.



In spite of the apparent instability of this ring system, benzocyclobutene and its derivatives have been synthesized by a variety of methods.

### **RESULTS AND DISCUSSION**

The novel rearrangement, with loss of one mole of hydrogen chloride, which trichloromethylpentamethylbenzene undergoes when heated above its melting point  $(95^{\circ})$ , was mentioned in Part I of this thesis.



The structure of the crystalline dichloro compound,  $C_{12}H_{14}Cl_2$  (XIX), m.p. 73-74<sup>°</sup>, which was isolated in 89% yield, was established by elementary analysis, molecular weight determinations [calc'd-229, found - 201, (camphor)] and results of solvolysis studies. The dichloro compound is quite stable; in contrast to trichloromethylpentamethylbenzene, it does not liberate hydrogen chloride on standing, and can be distilled under reduced pressure (140<sup>°</sup> at 5 mm.). Figure 32 shows a comparison of the ultraviolet spectrum of XIX with that of trichloromethylpentamethylbenzene.

The chlorine atoms were found to be quite reactive to ethanolic silver nitrate and aqueous acetone hydrolysis, yielding two moles of silver chloride per mole of dichloro compound. Evaporation of the solvent from these experiments gave long white needles,  $C_{12}H_{14}O$ , m.p. 153-154<sup>°°</sup>. This compound formed an oxime and a red 2, 4-dinitrophenylhydrazone, suggesting a conjugated aldehyde or ketone. It gave a negative Fuchsin-aldehyde test. The ultraviolet absorption spectrum (in ethanol), Figure 33, had bands at 306 mµ (log  $\epsilon = 3.47$ ) and 265 mµ (log  $\epsilon = 4.18$ ). The 306 mµ band is characteristic of a,  $\beta$ -unsaturated or aromatic ketones (79). The infrared spectrum, Figure 38, has a




strong carbonyl band; in carbon disulfide, a doublet<sup>\*</sup> 5.64  $\mu$  and 5.68  $\mu$ ; in carbon tetrachloride, a single peak at 5.68  $\mu$ . Strained cyclic ketones have carbonyl absorptions in this region.



It would be difficult to account for a cyclic ketone with more than four carbons, unless dimerization took place, or the aromatic ring was destroyed. Dimerization was rejected by molecular weight determinations calc'd. 174, found 169 (camphor).

The following equation and structures XIX and XX were assigned on the basis of the above ultraviolet and infrared data and elementary analysis of the dichloro compound, ketone, oxime and 2, 4-dinitrophenylhydrazone.



XVIII

XIX



The proton magnetic resonance spectra of XIX (Figure 34) and XX (Figure 35) are consistent with the assigned structures. XIX has four

<sup>&</sup>lt;sup>\*</sup>Yates et al. (80) reported that substituted  $\alpha$ ,  $\beta$ -unsaturated cyclopentanones show a split carbonyl in certain solvent. This phenomenon was interpreted in terms of intermolecular hydrogen bonding.



 $v_0 = 60 \text{ Mc.}$ , reference; benzene-external.



peaks with relative areas 2:3:6:3. The low-field peak, 165 cps., corresponds to the methylene hydrogens. The peaks at 259, 270 and 274 cps. correspond to the methyl hydrogens on the ring. The peak at 259 cps. presumably corresponds to the hydrogens of the methyl group on carbon six; because of the proximity the electronegative chlorine atoms should have a greater shielding effect on these hydrogens than the other methyl hydrogens. It is difficult to determine which methyl hydrogens correspond to the 270 and 274 cps. peaks. XX has three peaks with relative areas 2:9:3. The low-field peak, 180 cps., again correspond to the methyl hydrogens, but again it is difficult to determine which of the methyl hydrogens, but again it is difficult to determine which of the methyl hydrogens correspond to the high-field peak. The hydrogens of the methyl group on carbon five are the only ones which cannot participate in hyper-conjugative resonance with the carbonyl group, and may correspond to the peak at 268 cps.

A comparison of the proton magnetic resonance spectra of XIX and XX shows that the methylene hydrogens of XIX are shifted to a lower field than those of XX. This would be expected, because the two electronegative chlorine atoms should have a larger shielding effect than the carbonyl group. The methyl hydrogens of XX appear at a lower field than the methyl hydrogens of XIX. This may be due to the greater ability of the carbonyl group to participate in resonance with these methyl hydrogens.

Only a tentative assignment can be made at this time. A study of the proton magnetic resonance spectra of a series of substituted derivitives, such as 4-halo-3, 5, 6-trimethylbenzocyclobutenones may provide a definitive assignment.

To determine whether the cis-diene, structure XVIII, is an intermediate in this rearrangement, an equimolar amount of maleic anhydride and trichloromethylpentamethylbenzene was heated to 110-120<sup>0</sup> in a nitrogen atmosphere for three hours. Three products were isolated from this reaction: a 63.1% yield of  $a_{,a}a$ -dichlorotetramethylbenzocyclobutene; 0.26 g. of maleic acid; and 0.2 g. of a brown amorphous solid, decomposition range 245-250°. This material gave a positive Beilstein test for chlorine. Attempts to recrystallize it from chloroform and benzene caused it to oil.

The conversion of trichloromethylpentamethylbenzene to a, a-dichlorotetramethylbenzocyclobutene in the absence of maleic anhydride gave an 89% yield of the dichlorocompound. The reduction in yield (from 89%, to 63%) may be due to the Diels-Alder addition of maleic anhydride to the cis-diene intermediate (XVIII). The brown amorphous solid may be a Diels-Alder adduct. Characterization of the high melting amorphous material would be conclusive, but time has not permitted this to be accomplished.

The intramolecular cyclization reaction (conversion of trichloromethylpentamethylbenzene to a, a-dichlorotetramethylbenzocyclobutene) is unusual in that a strained four-membered ring is formed under relatively mild conditions (110-125°). Presumably, despite the ring strain, XIX is thermodynamically more stable than trichloromethylpentamethylbenzene. This is another manifestation of the large steric strain in the latter compound.

Having in hand a relatively simple synthesis of benzocyclobutene derivatives, several reactions of this series were studied.

Many attempts have been made to prepare and isolate benzocyclobutadiene. Cava and Stucker (83) investigated the golden yellow product, m.p. 121<sup>o</sup>, which Finkelstein had obtained by heating 1, 2-dibromobenzocyclobutene (II) with methanolic potassium hydroxide. This was proven to be identical with 3-bromo-1, 2-benzodiphenylene (XXIII), which probably arises by loss of hydrogen bromide from II to give 1-bromobenzocyclobutadiene (XXI) which immediately undergoes dimerization to give dibromodihydrobenzodiphenylene (XXII).



Cava and Napier (84) reported a similar dimerization when II was treated with zinc dust.

Nenitzescu and co-workers (85) trapped the benzocyclobutadiene intermediate by the reaction of an ether solution of 1, 2-dibromobenzocyclobutene with lithium amalgam in the presence of cyclopentadiene.



Roberts, Streitweiser and Regan (86) calculated the resonance energy of benzocyclobutadiene and found it to be approximately 40.5 Kcal/mole. The strain energy is probably of the order of 50-70 Kcal/mole. Therefore, it is not surprising that benzocyclobutadiene is unstable and that if it does form, it immediately dimerizes.

Even though calculations show that the strain is greater than the resonance energy for benzocyclobutadiene, certain substituted derivatives may be stable enough to isolate. The four methyl groups on tetramethylbenzocyclobutenone, XX, might be bulky enough to prevent dimerization of tetramethylbenzocyclobutadiene. There are a number of ways in which tetramethylbenzocyclobutenone might be converted to tetramethylbenzocyclobutadiene. A number of preliminary experiments were tried. The first experiment to show the transient existence of tetramethylbenzocyclobutadiene was a deuterium exchange study. Isolation of a deuterated ketone should establish the existence of a tetramethylbenzocyclobutadiene intermediate, because the hydrogens on the carbon alpha to the carbonyl carbon can exchange with the deuterated solvent only if the ketone enolizes.



Tetramethylbenzocyclobutenone was refluxed with a 3:2 volume ratio of ethanol-deuterium oxide for one hour. The reaction was quenched with ice-water and the product extracted with pentane. Evaporation of the solvent gave little white needles, m.p.  $152-153^{\circ}$ . An infrared spectrum of this material was almost identical to that of tetramethylbenzocyclobutenone, except for a sharp band at  $4.5\mu$  (see Figure 41), indicating a carbon-deuterium band.

In a similar experiment, a four-ml. aliquot was withdrawn from the reaction mixture after one hour of refluxing. The aliquot was quenched with ice-water and the product extracted with pentane. Evaporation of the pentane gave white needles, m.p.  $152-153^{\circ}$ . The infrared spectrum showed a sharp band at 4.5 $\mu$ . A small piece (approx. 20 mg.) of sodium was added to the remainder of the reaction mixture and the solution refluxed for an additional hour. The reaction mixture was worked up by the same procedure; the product had an identical infrared spectrum, with the same sharp band at 4.5  $\mu$ . Figure 36 shows a proton magnetic resonance spectrum of deuterated tetramethylbenzocyclobutenone. In addition to the loss of the peak for the methylene hydrogens at 180 cps in the proton magnetic resonance spectrum of the deuterated material, there was a change in the chemical shifts of the methyl hydrogens also.

The deuterum exchange study was repeated in order to determine whether one or two of the alpha methylene hydrogens were exchanged. However, in all the other experiments tried, <u>no deuterium exchange</u> <u>occurred</u>. The base concentration was varied; in one experiment too much sodium (0.1 g.) was added and the product isolated was pentamethylbenzoic acid. A trace of p-toluenesulfonic acid did not initiate deuterium exchange either. The reason for the inability to reproduce the deuterium exchange study has not been found. Whereas the mass spectrum of tetramethylbenzocyclobutenone was entirely consistent with its structure, that of the deuterated material indicated that rather deep-seated changes had occurred.



Figure 36. Proton magnetic resonance spectrum of deuterated tetramethylbenzocyclobutenone in carbon tetrachloride (concentration-25%).  $v_0 = 60$  Mc.

Schönberg and Mustafa have carried out some very interesting photochemical reactions on non-enolizable ketones (87). The photoaddition product obtained from exposing a benzene solution of phenanthraquinone (XXIV) and stilbene to sunlight, in a carbon dioxide atmosphere, was 2, 3-diphenylphenanthro (9':10':5:6) dioxen (XXV).



If tetramethylbenzocyclobutadienoquinone (XXVI) were treated in an analogous manner, one might be able to isolate a stable benzocyclobutadiene derivative (XXVII).



Attempts to prepare tetramethylbenzocyclobutadienoquinone (XXVI) were unsuccessful. One method involved refluxing a dioxane solution of tetramethylbenzocyclobutenone and selenium dioxide for twenty-four hours; only starting material was isolated. Another method was an attempt to prepare the a-oximinoketone from the reaction of tetramethylbenzocyclobutenone with a mixture of methyl cellosolve, hydrochloric acid and n-amyl nitrite. Again, only starting material was isolated.

Cava and Napier (88) reported the preparation of benzocyclobutadienequinone (XXX), by stirring 1, 2-diiodobenzocyclobutene (XXVIII) with an acetonitrile solution of silver nitrate at 25<sup>°</sup> for eight days, and refluxing this mixture of cis- and trans-benzocyclobutene-1, 2-diol-dinitrates (XXIX) with triethylamine in methylene chloride.



Tetramethylbenzocyclobutenone is quite stable to dilute mineral acids, for when it was refluxed with an ethanolic l N hydrochloric acid solution for several hours, it was recovered unchanged. An ethanolic alkaline solution (0.1 N sodium hydroxide), destroyed the ketone by a ring opening process similar to the base-catalyzed conversion of cyclopropanone hydrate to propionic acid (89).



The methyl adjacent to the carbonyl must shield it, so that the hydroxide ion attacks only one side of the carbonyl group, because pentamethylbenzoic acid was obtained in 82% yield. Cava and Muth (90) reported the base cleavage of unsubstituted benzocyclobutenone occurred in an indiscriminate manner at either side of the carbonyl group to give a mixture of o-toluic acid and phenylacetic acid.

Refluxing tetramethylbenzocyclobutenone with 0.1 M sodium methoxide in absolute methanol for three hours caused some decomposition; but only the starting ketone was isolated. Other evidence that the carbonyl group is shielded by the adjacent methyl group is shown by the low reactivity of the ketone to reduction. Attempts to reduce tetramethylbenzocyclobutenone with lithium aluminum hydride in tetrahydrofuran (reflux temperature for 24 hours) were unsuccessful. A mixture of ketone, tetramethylbenzocyclobutenol, and an unidentified crystalline material, m.p. 196-197<sup>°</sup>, was isolated when the ketone was refluxed twenty-four hours with excess sodium borohydridealuminum chloride (3:1) in diglyme. When the ketone was refluxed for thirty-six hours with sodium borohydride in diglyme, a mixture of tetramethylbenzocyclobutenol and pentamethylbenzoic acid was isolated. Flat, colorless needles, m. p. 155.5-156<sup>°</sup>, of tetramethylbenzocyclobutene were isolated in 82.6% yield when tetramethylbenzocyclobutenone was refluxed twenty-four hours with lithium aluminum hydride in diglyme.

Low temperature  $(25^{\circ} \text{ and } 50^{\circ})$ , low pressure (50 lbs. of hydrogen), platinum oxide catalyzed hydrogenation did not effect the ketone. High pressure (1200 psi of hydrogen) catalytic hydrogenation of tetramethylbenzocyclobutenone over copper chromite at 220° gave a 97% yield of hexamethylbenzene. The same reaction conditions at 200-205° gave a mixture of tetramethylbenzocyclobutenone, tetramethylbenzocyclobutene and hexamethylbenzene. Tetramethylbenzocyclobutenone was not reduced at 150° and 180°, over copper chromite catalyst.

Isolation of tetramethylbenzocyclobutene and hexamethylbenzene as reduction products of tetramethylbenzocyclobutenone is supporting evidence for the structures assigned to XIX and XX. A comparison of the infrared spectrum of tetramethylbenzocyclobutene with that of hexamethylbenzene is shown in Figure 40. As would be expected, there is very little difference in the two spectra. The infrared spectrum of tetramethylbenzocyclobutene has all the absorption bands of hexamethylbenzene, plus small absorption bands at 7.96  $\mu$ , 8.36  $\mu$  and 13.05  $\mu$ . Only a few of the many reactions applicable to tetramethylbenzocyclobutene and compounds therefrom have been studied. Further studies on these compounds should be fruitful.

An attempt to convert trichloromethylpentamethylbenzene to a, a-dichlorotetramethylbenzene by refluxing it with a high-boiling, inert solvent (n-octane) was not successful. Trichloromethyl-2, 3, 4, 5-tetramethylbenzene could not be converted to 1, 1-dichloro-3, 4, 5-trimethylbenzocyclobutene by heating it at 100-110<sup>°</sup> for ten hours in a nitrogen atmosphere. Under more drastic conditions the intramolecular cyclization may occur.

In one experiment, the trichloromethylation of mesitylene gave a white solid when the hydrolyzed reaction mixture was distilled. Recrystallization from n-hexane gave white crystals, m.p.  $56-57^{\circ}$ , which analyzed for  $C_{10}H_{10}Cl_2$  (page 65). This substance is presumably 1, 1-dichloro-4, 6dimethylbenzocyclobutene. An infrared spectrum of this material is shown in Figure 42. Attempts to repeat this experiment were not successful. Attempts to convert trichloromethylmesitylene to 1, 1-dichloro-4, 6dimethylbenzocyclobutene by refluxing it in a nitrogen atmosphere were also unsuccessful.

Although several of the experiments that were repeated were unsuccessful, an extensive study to determine the conditions necessary for carrying out the reaction was not made. Therefore more work will be necessary to find the optimum conditions.

One should be able to apply the simple preparative procedure for tetramethylbenzocyclobutenone to para-substituted trichloromethyl-2, 3, 5, 6tetramethylbenzenes and obtain an interesting series of substituted benzocyclobutenones.

### EXPERIMENTAL

#### A. Syntheses

# a, a-Dichlorotetramethylbenzocyclobutene

To a 100-ml. round-bottomed flask equipped with a side arm for nitrogen inlet and a take-off for gaseous outlet, there was placed 5.0 g. of trichloromethylpentamethylbenzene. After filling the outlet-tube with glass wool, to prevent any solid material from subliming out of the reaction vessel, it was connected to a trap containing a standard solution of sodium hydroxide. A stream of dry nitrogen was passed through the system to sweep out any gaseous products formed. The flask was immersed in a  $110-120^{\circ}$  oil bath; the white crystals melted to form a colorless solution, which turned yellow and finally light brown. Little bubbles of gas evolved from the solution. After heating and passing nitrogen into the flask for three hours, the standard sodium hydroxide trap was removed and the excess sodium hydroxide titrated with standard hydrochloric acid, using phenolphthalein as the indicator. After one equivalent of hydrogen chloride had been collected, usually within a three-hour period, the flask was removed from the oil-bath and cooled. The light brown crystalline residue was treated with Norite and recrystallized from dry n-pentane, yielding 3.86 g. (89.4%) of white platelets, m.p. 69-71°. Several more recrystallizations from n-pentane raised the melting point to  $73-74^{\circ}$ . The infrared spectrum of this material was unlike that of trichloromethylpentamethylbenzene (see Figure 37).

<u>Anal.</u> Calc'd for C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>: C, 62.89; H, 6.16; Cl, 30.95; mol. wt. 229 Found: C, 62.93; H, 6.27; Cl, 30.88; Rast molecular weight (camphor), 201.



Figure 37. Infrared spectrum of a, a-dichlorotetramethylbenzocyclobutene (CS<sub>2</sub> solution).

### <u>Tetramethylbenzocyclobutenone</u>

Tetramethylbenzocyclobutenone was prepared by hydrolysis of a, a-dichlorotetramethylbenzene with aqueous-ethanolic silver nitrate or aqueous acetone. To a 300-ml. Erlenmeyer flask there was added 6.5 g. of silver nitrate and 100 ml. of approximately 80% aqueous ethanol. After the silver nitrate had dissolved, 3.5 g. of a, a-dichlorotetramethyl benzocyclobutene was added. There was instantaneous dissolution, followed by immediate precipitation of silver chloride. The reaction mixture was heated to reflux temperature on a steam bath and then allowed to stand overnight. After filtering off the silver chloride, the filtrate was distilled under reduced pressure with a Rinco rotary evaporator. A white residue formed on the walls of the flask after most of the ethanol had been removed. The white residue, recrystallized from aqueous ethanol, gave long white needles, m.p. 153-154°. An identical compound was obtained when a, a-dichlorotetramethylbenzocyclobutene was hydrolyzed with aqueous acetone. A ketonic carbonyl absorption peak appeared at 5.68  $\mu$  in the infrared (see Figure 38).

Anal. Calc'd for  $C_{12}H_{14}O$ ; C, 82.72; H, 8.10 Found: C, 82.57; H, 8.16

An oxime and a 2, 4-dinitrophenylhydrazone were prepared by the general procedures of Shriner and Fuson (91). Oxime-white granules, m.p.  $179-180^{\circ}$  (cyclohexane-ether)

<u>Anal.</u> Calc'd. for  $C_{12}H_{15}NO$ : C, 76.15; H, 7.99; N, 7.40. Found: C, 76.06; H, 7.91; N, 7.56.

2,4-Dinitrophenylhydrazone -- long red-orange needles, m.p. 300° (dec.; ethyl acetate-ethanol).

Anal. Calc'd. for  $C_{18}H_{18}N_4O_4$ : C, 61.06; H, 5.12; N, 15.81 Found: C, 61.08; H, 5.08; N, 15.73.



Per Cent Transmission

Figure 38. Infrared spectrum of tetramethylbenzocyclobutenone (CS<sub>2</sub> solution).

#### <u>Tetramethylbenzocyclobutenol</u>

Several attempts were made to prepare tetramethylbenzocyclobutenol by the reduction of tetramethylbenzocyclobutenone.

(1) Attempted reduction of tetramethylbenzocyclobutenone with lithium aluminum hydride.

To a 300-ml. three-necked round-bottomed flask fitted with a Tru-bore stirrer, reflux condenser and an addition funnel was added 0.5 g. (0.013 mole) of lithium aluminum hydride and 50 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride). To this well-stirred slurry, 0.5 g. (0.002 mole) of tetramethylbenzocyclobutenone in 25 ml. of freshly distilled tetrahydrofuran was slowly added. After addition, the reaction mixture was stirred and refluxed for 12 hours. The excess lithium aluminum hydride was decomposed by slow addition of 10% sulfuric acid. The organic material was extracted with two 100-ml. portions of ether. The ether layer was washed twice with 10%sodium carbonate and three times with 25 ml. of water. After drying the ether solution overnight with anhydrous calcium chloride, the solvent was removed with the Rinco rotary evaporator. The white crystalline residue was recrystallized from aqueous ethanol yielding 0.45 g. of little needle-like crystals of recovered tetramethylbenzocyclobutenone, m. p. 153-154°.

(2) Sodium borohydride-aluminum chloride reduction of tetramethylbenzocyclobutenone.

The mixed hydride reduction procedure of Brown and Rao (92) was followed. To an ice-cooled mixture of 1.2 g. (0.03 mole) of sodium borohydride in 50 ml. of diglyme (freshly distilled from lithium aluminum hydride), in a 250 ml. three-necked round-bottomed flask equipped with a Tru-bore stirrer, reflux condenser and an addition funnel, was added 1.3 g. (0.01 mole) of anhydrous powdered aluminum chloride, in small portions. To this stirred slurry, there was slowly added 2.0 g. (0.012 mole) of tetramethylbenzocyclobutenone in 25 ml. of diglyme. The reactants were stirred at a gentle reflux for twelve hours, after which the reaction mixture was cooled to room temperature and poured into a mixture of 100 g. of ice and 25 ml. of concentrated hydrochloric acid. The white precipitate which formed was extracted with four 50-ml. portions of ether. The ether layer was washed several times with water and dried overnight with anhydrous calcium chloride. The ether was evaporated leaving a white residue, which was recrystallized from aqueous ethanol, yielding 1.95 g. of white granules m.p. 180-183°. After several recrystallizations from ethyl acetate the melting point increased to 186-188°. An infrared spectrum of this material showed a hydroxyl band at 2.96  $\mu$ and a small carbonyl band at 5.69  $\mu$ . Repeated fractional crystallizations from ethyl-acetate and petroleum ether gave white platelets, m.p. 196-197°. An infrared spectrum of this material showed no hydroxyl or carbonyl band. This material has not been identified.

(3) Sodium borohydride reduction of tetramethylbenzocyclobutenone in diglyme.

To a 300-ml. three-necked round-bottomed flask equipped with a Tru-bore stirrer, reflux condenser and an addition funnel was added 2.5 g. (0.066 mole) of sodium borohydride and 50 ml. of diglyme (distilled from lithium aluminum hydride). A solution of 2 g. (0.012mole) of tetramethylbenzocyclobutenone in 50 ml. of diglyme was slowly added to the stirred sodium borohydride-diglyme slurry. The reactants were stirred at a gentle reflux temperature for thirty-six hours; after which the reaction mixture was cooled to room temperature and slowly poured into 100 g. of ice and 25 ml. of concentrated hydrochloric acid. The white solid material which precipitated was extracted with four 50-ml. portions of ether. The ether layer was washed several times with water and dried over anhydrous calcium chloride. Evaporation of the ether layer left a white residue which was recrystallized from aqueous ethanol, yielding 1.45 g. of white granules, m. p. 131-133°. An infrared spectrum of this material indicated that it was a mixture of an alcohol and a carboxylic acid. The white granules were dissolved in 100 ml. of ether. The ether solution was washed with two 25-ml. portions of 10% sodium carbonate and three 25-ml. portions of water. Evaporation of the ether layer gave a white residue which yielded 0.73 g. (36.1% yield) of small white crystals, m.p. 149.5-151°. The infrared spectrum is shown in Figure 39.

The sodium carbonate wash solution was acidified with dilute hydrochloric acid; the white solid material which precipitated was extracted with two 25-ml. portions of ether. The ether layer was washed three times with water and dried over anhydrous calcium chloride. Evaporation of the ether gave a white residue, which yielded 0.42 g. of white platelets, m.p.  $204-206^{\circ}$ , when recrystallized from aqueous ethanol. Two more recrystallizations from aqueous ethanol increased the melting point to  $208-210^{\circ}$  (pentamethylbenzoic acid).

#### Tetramethylbenzocyclobutene

To a 300-ml. three-necked flask equipped with a reflux condenser (fitted with a drying tube), an addition funnel and a Tru-bore stirrer was added 2.4 g. (0.06 mole) of lithium aluminum hydride and 50 ml. of diglyme (distilled from lithium aluminum hydride). A solution of 2 g. (0.012 mole) of tetramethylbenzocyclobutenone in 50 ml. of diglyme was slowly added to the stirred lithium aluminum hydride-diglyme slurry. The reactants were stirred at a gentle reflux for twenty-four hours, after which the reaction mixture was cooled and the excess hydride decomposed by the dropwise addition of 10% sulfuric acid. The crude white product was extracted with three 50-ml. portions of ether. The ether layer was washed with 10 ml. of 85% phosphoric acid and three times with 25 ml. of water. After drying the ether solution overnight with anhydrous



calcium chloride, the ether was evaporated. Recrystallization of the white crystalline residue from ethanol gave 1.52 g. (82.6%) of clear flat crystals of tetramethylbenzocyclobutene, m.p.  $155.5-156^{\circ}$ . Figure 40 shows a comparison of the infrared spectrum of tetramethylbenzocyclobutene with that of hexamethylbenzene. A mixed-melting point with hexamethylbenzene (m.p.  $161-162^{\circ}$ ) gave a melting point range,  $157-160^{\circ}$ .

Anal. Calc'd for  $C_{12}H_{16}$ : C, 89.94; H, 10.06.

Found: C, 89.75; H, 10.14.

Tetramethylbenzocyclobutene was also prepared by high-pressure, high-temperature hydrogenation of tetramethylbenzocyclobutenone over copper chromite (see page 154).

B. Attempt to trap the intermediate (in the transformation of trichloromethylpentamethylbenzene to a, a-dichlorotetramethylbenzocyclobutene) with maleic anhydride.

The procedure was similar to the one described in the preparation of a, a-dichlorotetramethylbenzocyclobutene (page 137).

To a 50-ml. round-bottomed flask equipped with a side arm for nitrogen inlet and a take-off (packed with glass wool) for gaseous outlet, there was placed a finely powdered mixture of 1.0 g. (0.01 mole) of maleic anhydride and 2.65 g. (0.01 mole) of trichloromethylpentamethylbenzene. After connecting the gas outlet to a trap containing a standard solution of sodium hydroxide, a stream of dry nitrogen was passed into the system to sweep out any gaseous products formed by the reaction. The reaction flask was immersed in a  $110-120^{\circ}$  oil bath; the white powdered mixture melted and turned brown immediately. Little bubbles of gas evolved from the solution. After three hours, the standard sodium hydroxide trap was disconnected and the excess sodium hydroxide was titrated with standard hydrochloric acid. Approximately one equivalent of hydrogen chloride had been collected, so the flask was removed from the





oil bath and cooled to room temperature. The dark brown solid was extracted three times with 50 ml. of warm pentane. The pentane-insoluble material was a dark brown oil. This material was soluble in hot chloroform. A flocculent brown precipitate settled out when the solution was cooled to room temperature. The brown precipitate was collected on a filter; attempts to recrystallize the brown amorphous solid (0.2 g.) caused it to form a brown oil. This material gave a positive Beilstein test for chlorine. It had a decomposition range of  $245-250^{\circ}$ .

The chloroform soluble material which was treated with Norite several times gave 0.26 g. of white crystals, m.p. 139-140°. The infrared spectrum was identical to that of maleic acid. The mixed melting point with maleic acid was 139-140°.

The pentane soluble material was treated with Norite and recrystallized from pentane giving 1.44 g. (63.1%) of white platelets of dichlorotetramethylbenzocyclobutene, m.p.  $73-74^{\circ}$ .

The conversion of trichloromethylpentamethylbenzene to a, a-dichlorotetramethylbenzocyclobutene in the absence of maleic anhydride gave an 89% yield of the dichloro compound. This reduction in yield may be due to the trapping of the cis-diene intermediate (XVIII) by the maleic anhydride.

### C. Stability of Tetramethylbenzocyclobutenone

(1) Reaction of tetramethylbenzocyclobutenone with ethanolic 1 N hydrochloric acid.

To a 50-ml. round-bottomed flask equipped with a reflux condenser was added 1.5625 g. of tetramethylbenzocyclobutenone, 20 ml. of absolute ethanol, 7 ml. of water and 2.5 ml. of concentrated hydrochloric acid. This solution was refluxed on the steam bath for three hours, after which most of the ethanol was removed under reduced pressure with a Rinco rotary evaporator. Twenty-five ml. of water was added and the organic material was extracted with three 20-ml. portions of pentane. After washing the pentane layer several times with water, the pentane was evaporated. The white needle-like crystals of tetramethylbenzocyclobutenone, m. p.  $151-152^{\circ}$  weighed 1.5571 g. (99% recovery).

(2) Reaction of tetramethylbenzocyclobutenone with ethanolic 0.1 N sodium hydroxide.

To a 50-ml. round-bottomed flask equipped with a reflux condenser was added 20 ml. of absolute ethanol and 0.1 g. of sodium metal. After cooling this solution, 2.0 g. of tetramethylbenzocyclobutenone and 5 ml. of water were added. This solution was refluxed for three hours, (the solution changed from colorless to yellow), cooled to room temperature and the alkaline solution was neutralized with dilute hydrochloric acid. The material which precipitated was collected on a filter and the excess ethanol was removed with a Rinco rotary evaporator. The solid which deposited on the walls of the flask was collected on a filter. The combined solids were recrystallized from aqueous ethanol, giving 1.83 g. (81.9%) of white platelets, m.p.  $208-210^{\circ}$ . An infrared spectrum of this material was identical to pentamethylbenzoic acid.

In one experiment the work-up procedure involved pouring the yellow reaction mixture (2.0 g. of ketone and 25 ml. of ethanolic 0.1 N sodium hydroxide) into 100 ml. of cold 0.1 N hydrochloric acid. This mixture was extracted with three 50-ml. portions of ether, washed with water and twice with 25 ml. of 10% sodium carbonate. After acidification of the sodium carbonate solution, the white solid which precipitated was extracted with two 50-ml. portions of ether. Evaporation of the ether gave a white residue which on recrystallization from aqueous ethanol gave 1.68 g. (76.0%) of white platelets of pentamethylbenzoic acid, m.p.  $207-209^{\circ}$ .

Evaporation of the ether solution from the first sodium carbonate washings gave a yellow gummy residue. Recrystallization from pentane gave 0.32 g. of a non-crystalline almost white solid, m.p.  $147-151^{\circ}$ . An infrared spectrum of this material showed two carbonyl bands, 5.68  $\mu$ and 5.80  $\mu$ . This material is presumably a mixture of tetramethylbenzocyclobutenone and ethyl pentamethylbenzoate.

(3) Reaction of tetramethylbenzocyclobutenone with 0.1 M sodium methoxide.

To a 50-ml. round-bottomed flask equipped with a reflux condenser (fitted with a drying tube) was added 1.25 g. of tetramethylbenzocyclobutenone, 25 ml. of dry methanol (distilled from magnesium turnings) and 0.14 g. of sodium methoxide. This solution was refluxed for three hours in an oil bath. (The solution changed from colorless to yellow.) Then the excess methanol was distilled under reduced pressure, with a Rinco rotary evaporator. The yellow residue in the flask was washed with 50 ml. of dilute hydrochloric acid and recrystallized with aqueous methanol. The long needle-like crystals, 1.06 g., melted at 152-153°. An infrared spectrum of this material was identical to that of tetramethylbenzocyclobutenone.

#### D. Reactions of Tetramethylbenzocyclobutenone

(1) Deuterium exchange study.

Experiment I.--In a dry 50-ml. round-bottomed flask equipped with a reflux condenser fitted with a drying tube, was placed 0.178 g. of tetramethylbenzocyclobutenone, 2.0 ml. of deuterium oxide (> 99.5% D<sub>2</sub>O, obtained from the Stuart Oxygen Co., San Francisco) and 3.0 ml. of purified absolute ethanol. The reaction mixture was refluxed in a sand bath for two hours. After quenching the reaction with 30 ml. of ice-cold distilled water, the organic material was extracted with three 10-ml. portions of n-pentane and the pentane evaporated under a stream of dry air. The white needle-like crystals, m. p. 151-152, were dried over calcium chloride in a vacuum desiccator. An infrared spectrum of this material (Figure 41) was similar to that of the starting material except for a 4.5  $\mu$  band (carbon-deuterium (81)).

Experiment II. --Using the same procedure as described in experiment I, 0.397 g. of tetramethylbenzocyclobutenone, 4.0 ml. of deuterium oxide and 6.0 ml. of purified absolute ethanol were refluxed for two hours. After removing 4,0 ml. of the reaction mixture with a hypodermic syringe, the withdrawn portion was quenched immediately with 20 ml. of cold distilled water and extracted with three 10-ml. portions of pentane.

To the remaining reaction mixture, there was added approximately 50 mg. of sodium metal and the reaction mixture refluxed an additional two hours. The reaction mixture was worked up by a procedure similar to that described in experiment I. Infrared spectra of the two portions were identical, and the carbon-deuterium band was stronger than that obtained in experiment I.

Experiments III to VI. -- These experiments were attempts to duplicate the work in experiments I and II, however no deuterium exchange occurred. The deuterium oxide was checked for purity by a density determination and was found to have a purity greater than 99%.

Experiment VII.--To a 50-ml. round-bottomed flask equipped with a reflux condenser, fitted with a drying tube, there was added 0.523 g. of tetramethylbenzocyclobutenone, 6 ml. of purified absolute ethanol, 5 ml. of deuterium oxide and 0.1 g. of sodium metal. After refluxing for two hours, the solution which had turned a pale yellow, was poured into ice water (no precipitate formed). Addition of a dilute solution of hydrochloric caused immediate precipitation of a white solid material. This solid was insoluble in pentane, so the solution was extracted with three 20-ml. portions of ether. Evaporation of the ether gave 0.54 g. of a white solid, m.p. 205-209°. Recrystallization from aqueous ethanol gave white platelets, m.p. 208-210°. An infrared spectrum of this material was identical to that of pentamethylbenzoic acid.



Per Cent Transmission

Experiment VIII. -- This experiment was designed to determine if the deuterium exchange was acid catalyzed. The same procedure was used as described in experiments I and II, except 50 mg. of p-toluenesulfonic acid was added. The work-up procedure was the same. An infrared spectrum of the product isolated showed no carbon-deuterium band at 4.5  $\mu$ .

## Attempted Oxidation of Tetramethylbenzocyclobutenone

#### 1. Selenium dioxide oxidation

Using a procedure similar to that of Riley and Gray (93), for the preparation of phenylglyoxal from acetophenone, an attempt was made to prepare tetramethylbenzocyclobutadienoquinone.

In a 300-ml. three-necked round-bottomed flask, fitted with a Tru-bore stirrer, reflux condenser and addition funnel, was placed 60 ml. of purified dioxane, 0.9 g. (0.008 mole) of selenium dioxide and 0.5 ml. of water. The mixture was heated to  $50-55^{\circ}$  and stirred until the solid had gone into solution. One gram (0.005 mole) of tetramethylbenzocyclo-butenone in 10 ml. of dioxane was added in one lot, and the resulting mixture was refluxed with continuous stirring for twelve hours. (The solution changed from yellow to red and finally to gray; black selenium formed on the stirrer blade.) The hot solution was filtered and the dioxane was removed under reduced pressure. The yellow residue was treated with Norite and recrystallized from aqueous ethanol, yielding 0.8 g. of white needles of recovered tetramethylbenzocyclobutenone, m. p.  $153-154^{\circ}$ .

# 2. Nitrous acid oxidation

Using the procedure of Cava, Litle and Napier (74) for preparation of oximinoketone of indane, an attempt was made to prepare the oximinoketone of tetramethylbenzocyclobutene.

In a 250-ml. Erlenmeyer flask was placed 2.0 g. (0.012 mole) of tetramethylbenzocyclobutenone, 50 ml. of methyl cellosolve and 10 ml. of concentrated hydrochloric acid. This mixture was swirled while 3.5 ml. (0.025 mole) of freshly distilled n-amyl nitrite was slowly added. The mixture was allowed to stand at room temperature for four hours, then poured into 500 ml. of ice-water. The yellow-white residue was collected on a filter, and recrystallized from aqueous ethanol yielding white needles, m.p.  $151-152^{\circ}$ . (Recovered starting material.) After standing six weeks, several long yellow needles formed in the filtrate. (The oximino-ketone is yellow, so the reaction will probably work.)

# <u>Catalytic hydrogenation of tetramethylbenzocyclobutenone.</u>

(1) A 300-ml. hydrogenation bottle was charged with 50 ml. of absolute ethanol, 2 g. (0.012 mole) of tetramethylbenzocyclobutenone, and 0.2 g. of platinum oxide. The apparatus was flushed with hydrogen several times, charged with 50 pounds of hydrogen, warmed to  $50^{\circ}$  and shaken for 24 hours. The apparatus was then cooled to room temperature, but there was no uptake of hydrogen. The apparatus was vented, opened, and 0.2 ml. of glacial acetic acid and 0.2 g. of PtO<sub>2</sub> were added. The apparatus was flushed with hydrogen several times, charged with 50 pounds of hydrogen, warmed to  $50^{\circ}$  and shaken for an additional 24 hours. The contents of the hydrogenation bottle was poured into a sintered glass filter funnel to remove the catalyst. The ethanol was removed on a Rinco rotary evaporator; the white residue which deposited on the sides of the flask was recrystallized from aqueous ethanol, yielding 1.9 g. of white needles m.p.  $152-153^{\circ}$ . The infrared spectrum was identical to that of tetramethylbenzocyclobutenone.

(2) A 200-ml. Hasteloy-B Magne-Dash autoclave was charged with 4 g. (0.025 mole) of tetramethylbenzocyclobutenone, 25 ml. of absolute ethanol and 0.5 g. of copper chromite. The autoclave was flushed several times with hydrogen and then charged with 1200 p.s.i. of hydrogen. The magnetic stirrer was adjusted to operate at low speed and the autoclave heated electrically to 220°. (The pressure rose to 2600 p.s.i.). After twelve hours the autoclave was cooled to room temperature, vented, and the contents of the bomb were filtered. A colorless, crystalline substance had formed, which was quite insoluble in ethanol. This material was recrystallized from hot ethanol, yielding 3.61 g. (97.5%) of colorless needles, m.p. 160-161°. The infrared spectrum (Figure 43) of this material was identical to that of pure hexamethylbenzene (m.p. 161°); mixed melting point 160-161°.

(3) The preparation of hexamethylbenzene was another structure proof for tetramethylbenzocyclobutenone, but preparation of tetramethylbenzocyclobutene or tetramethylbenzocyclobutenol were of more interest. A series of experiments were carried out using copper chromite catalyst, 1200 p.s.i. (initial hydrogen pressure), ten hour reaction times and temperatures ranging from 150 to 205<sup>o</sup>.

Using the procedure described in (2) the first two experiments were performed at temperatures of  $150-155^{\circ}$  and  $180-185^{\circ}$ . In both experiments, only the ketone was isolated, in better than 90% yield.

In the third experiment 2 g. of tetramethylbenzocyclobutenone, 0.5 g. of copper chromite, 20 ml. of absolute ethanol and 1200 p.s.i. of hydrogen were heated at 200-205° in the Magne-Dash autoclave for ten hours. (The hydrogen pressure dropped to 975 p.s.i. during the reaction.) After filtering off the catalyst, the solvent was evaporated giving a white solid material. Recrystallization from ethanol gave 1.48 g. of small white crystals, m.p. 155-160°. An infrared spectrum showed a small carbonyl band at 5.70  $\mu$ . The rest of the spectrum was similar to the infrared spectrum of tetramethylbenzocyclobutene. It is presumably a mixture of hexamethylbenzene and tetramethylbenzocyclobutene because the melting point was 156-159° after the ketone was removed.

#### E. Miscellaneous Experiments

1. Attempt to convert trichloromethylpentamethylbenzene to **a. a.**-dichlorotetramethylbenzocyclobutene using n-octane as a solvent.

To a 50-ml. round-bottomed flask equipped with a reflux condenser (fitted with a drying tube) was added 5 g. of trichloromethylpentamethylbenzene and 25 ml. of n-octane (b.p.  $126^{\circ}$ ). The solution was refluxed for twelve hours; during this time a tan residue precipitated out of solution. The solution was cooled to room temperature and the tan finely divided solid (2.78 g.) was collected on a filter. It was insoluble in pentane, benzene and carbon tetrachloride and had a decomposition range of 285- $300^{\circ}$ . It gave a positive Beilstein test for chlorine. This material has not been identified.

Evaporation of the n-octane filtrate gave a white residue. Recrystallization from n-pentane gave 1.6 g. of white platelets, m.p. 93-94<sup>o</sup>. The infrared spectrum was identical to that of trichloromethylpentamethylbenzene.

2. Attempt to convert trichloromethyl-2, 3, 4, 5-tetramethylbenzene to 1, 1-dichloro-3, 4, 5-trimethylbenzocyclobutene.

The procedure used in this experiment was similar to the one described on page 137 for the preparation of a, a-dichloromethyltetramethylbenzocyclobutene from trichloromethylpentamethylbenzene. Five grams of trichloromethyl-2, 3, 4, 5-tetramethylbenzene (m. p.  $90-91^{\circ}$ ) was heated at  $100-110^{\circ}$  in a nitrogen atmosphere for ten hours. (The white crystals melted to a colorless liquid which gradually turned light purple and finally to light brown.) There was very little hydrogen chloride evolved. Recrystallization of the cooled reaction mixture from n-hexane gave 4.9 g. of white crystals, m.p.  $91-91.5^{\circ}$ . An infrared spectrum of this material was identical to trichloromethyl-2, 3, 4, 5-tetramethylbenzene. 3. Attempt to convert trichloromethyl-2, 4, 6-trimethylbenzene to 1, 1-dichloro-4, 6-dimethylbenzocyclobutene.

In a 50-ml. two-necked flask equipped with a nitrogen inlet tube and a reflux condenser (fitted with a drying tube) was placed 10 g. of trichloromethyl-2, 4, 6-trimethylbenzene. The flask was immersed in a  $150^{\circ}$  oil bath and dry nitrogen was bubbled into the solution, to sweep out any gaseous products formed. The solution began to darken immediately and hydrogen chloride was evolved. After six hours at  $150^{\circ}$ , the dark brown solution was cooled in a Dry Ice-alcohol bath. The material solidified to a glass, but no crystals formed. The dark brown material was fractionated under reduced pressure. The fractions had a boiling point range and refractive indices approximately the same as the starting material. The infrared spectra of all fractions were identical to trichloromethyl-2, 4, 6-trimethylbenzene. Only 5.8 g. of starting material was recovered; the residue from the distillation was a viscous, black, polymeric material which was insoluble in pentane and carbon tetrachloride.

## **SUMMARY**

 Thermal decomposition of trichloromethylpentamethylbenzene at 110-125° has been found to be an excellent preparative procedure for benzocyclobutene derivatives. a, a-Dichlorotetramethylbenzocyclobutene was isolated in 89% yield when trichloromethylpentamethylbenzene was heated above its melting point, in a dry nitrogen atmosphere. Hydrolysis of the dichlorocompound with ethanolic silver nitrate or aqueous acetone gave a quantitative yield of tetramethylbenzocyclobutenone. The structures of these compounds were established by ultraviolet, infrared and proton magnetic resonance spectroscopy, solvolysis studies, molecular weight determinations and elemental analysis of the dichloro compound, ketone, oxime and 2, 4-dinitrophenylhydrazone.

2. An equimolar amount of maleic anhydride and trichloromethylpentamethylbenzene was heated to  $110-120^{\circ}$  in a nitrogen atmosphere, in an attempt to trap the intermediate from the intramolecular cyclization of trichloromethylpentamethylbenzene to a, a-dichlorotetramethylbenzocyclobutene. Three products were isolated from this reaction; a 63%yield of a, a-dichlorotetramethylbenzocyclobutene, maleic acid, and a high melting (245-250°), brown, amorphous solid. The reduction in yield of the dichlorocompound (from 89% to 63%) and isolation of the high melting solid, may be evidence that the intermediate has a cis-diene structure (XVIII) and part of it is trapped by a Diels-Alder addition with maleic anhydride.

3. Tetramethylbenzocyclobutenone was refluxed with deuteroethanol (3:2 ratio of ethanol and deuterium oxide) to determine its ability to enolize to a tetramethylbenzocyclobutadienolate anion. In two experiments, a ketone was isolated which had the same melting point as

tetramethylbenzocyclobutenone, an almost identical infrared spectrum, except for a sharp band at 4.5  $\mu$  (carbon-deuterium band), and a proton magnetic spectrum which did not have a low-field peak for the methylene hydrogens. Attempts to repeat these experiments met with failure. Also, the mass spectrum of the deuterated material was not consistent with that of a tetramethylbenzocyclobutenone.

4. Reduction of tetramethylbenzocyclobutenone with lithium aluminum hydride in diglyme gave an 82.6% yield of tetramethylbenzocyclobutene. Reduction of the ketone with sodium borohydride in diglyme gave a mixture of tetramethylbenzocyclobutenol and pentamethylbenzoic acid. A mixture of ketone, tetramethylbenzocyclobutenol and an unidentified crystalline material, m.p.  $196-197^{\circ}$ , was isolated, when the ketone was reduced with a three to one ratio of sodium borohydride-aluminum chloride in diglyme. Tetramethylbenzocyclobutenone was not reduced with lithium aluminum hydride in tetrahydrofuran.

High pressure (1200 psi of hydrogen), catalytic hydrogenation of tetramethylbenzocyclobutenone over copper chromite at  $220^{\circ}$  gave a 97% yield of hexamethylbenzene. The same reaction conditions at  $200-205^{\circ}$  gave a mixture of tetramethylbenzocyclobutenone, tetramethylbenzocyclobuteno butene and hexamethylbenzene. Tetramethylbenzocyclobutenone was not reduced at  $150^{\circ}$  and  $180^{\circ}$ , over copper chromite catalyst.

Tetramethylbenzocyclobutenone was not oxidized with selenium dioxide or with nitrous acid.

Tetramethylbenzocyclobutenone is quite stable to dilute mineral acids; it was recovered unchanged when refluxed with ethanolic 1 N hydrochloric acid. An ethanolic 0.1 N sodium hydroxide solution destroyed the ketone by a ring opening process similar to the basecatalyzed conversion of cyclopropanone hydrate to propionic acid (89), giving an 82% yield of pentamethylbenzoic acid.
5. An attempt to convert trichloromethylpentamethylbenzene to a, a-dichlorotetramethylbenzocyclobutene, by refluxing it with n-octane was unsuccessful.

In one experiment, distillation of the hydrolyzed product from the trichloromethylation of mesitylene gave a white solid material. Recrystallization from n-hexane gave white crystals,  $C_{10}H_{10}Cl_2$ , which presumably is 1, 1-dichloro-4, 6-dimethylbenzocyclobutene. Attempts to repeat this experiment were not successful.

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## APPENDIX

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Per Cent Transmission

166



Figure 43. Infrared spectrum of hexamethylbenzene ( $CS_2$  solution).



Per Cent Transmission



Per Cent Transmission



Per Cent Transmission

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