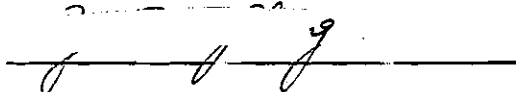


In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

A handwritten signature in cursive script, written over a horizontal line. The signature appears to be 'J. J. J.' with a flourish at the end.

3/17/65
b

REACTION OF 4-CHLORO-1,1,1-TRIPHENYLBUTANE
WITH ALKALI METALS

A THESIS

Presented to
the Faculty of the Graduate Division

by

Yao-Ming Cheng

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemistry

Georgia Institute of Technology

January, 1967

REACTION OF 4-CHLORO-1, 1, 1-TRIPHENYLBUTANE
WITH ALKALI METALS

Approved:

[Signature]
Chairman

Date approved by Chairman: 1-26-67

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. Erling Grovenstein, Jr. for his suggestion of the problem and for his advice and assistance and, above all, for his valuable criticism and encouragement during the course of this work. The author also wishes to thank Dr. Eugene C. Ashby and Dr. Charles L. Liotta for serving as members of the reading committee.

The graduate assistantships provided by the Department of Chemistry, support by the Petroleum Research Fund of The American Chemical Society, all of which were held by the author during the course of this research, are greatly appreciated.

The author is also grateful to Mr. and Mrs. Frank W. Walker for their reading in the first draft of this thesis.

The author is indebted to his family and especially to his wife for the patience and encouragement they have given throughout the entire period of study.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES.	v
SUMMARY	vii
Chapter	
I. INTRODUCTION	1
II. REAGENTS AND SOLVENTS.	5
III. INSTRUMENTAL ANALYSES.	11
IV. EXPERIMENTAL DETAILS	15
Synthesis of 4-Chloro-1,1,1-triphenylbutane.	15
Triphenylchloromethane	
4-Chloro-1,1,1-triphenylbutane	
Synthesis of 5,5,5-Triphenylpentanoic Acid	18
5,5,5-Triphenylpentanenitrile	
5,5,5-Triphenylpentanoic Acid	
Methyl 5,5,5-Triphenylpentanoate	
Synthesis of 2,2-Diphenylpentanoic Acid.	20
Attempted Synthesis of 2,2,5-Triphenylpentanoic Acid . .	22
Methyl Diphenylacetate	
2,2,5-Triphenylpentanoic Acid	
Synthesis of 2,2,5-Triphenylpentanoic Acid	25
1,1,4-Triphenylbutanol-1	
2,2,5-Triphenylpentanoic Acid	
Synthesis of Triphenylacetic Acid.	30
Synthesis of 1,1,1-Triphenylbutane	31

TABLE OF CONTENTS (Concluded)

	Page
Synthesis of 1,1,4-Triphenylbutane	32
Synthesis of 1,1-Diphenylbutane.	33
Synthesis of 1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene.	34
Synthesis of 1,1,2-Triphenylbutene-1	35
Methyl 2-Phenylbutanoate 1,1,2-Triphenylbutene-1	
Synthesis of 1-Methyl-2,3-diphenylindene	37
2,3-Dibromobutanoic Acid 2,3-Diphenylbutanoic Acid 3-Methyl-2-phenylindanone 1-Methyl-2,3-diphenylindene	
Synthesis of 9-Phenyl-9-n-propylfluorene	40
9-Phenylfluorene 9-Phenyl-9-n-propylfluorene	
Reaction of 4-Chloro-1,1,1-triphenylbutane with Lithium at -60°.	42
Reaction of 4-Chloro-1,1,1-triphenylbutane with Potassium and Sodium-Potassium Alloy	45
Reaction of 4-Chloro-1,1,1-triphenylbutane with Cesium and Cesium-Potassium Alloy.	53
V. DISCUSSION	68
Syntheses.	68
Reactions.	71
VI. RECOMMENDATIONS.	90
LITERATURE CITED.	91

LIST OF TABLES

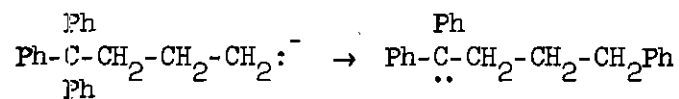
Table		Page
1.	Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Lithium in Tetrahydrofuran at 25° (Run 4)	46
2.	Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Potassium in Refluxing Tetrahydrofuran (Run 1)	48
3.	Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Sodium-Potassium Alloy in Tetrahydrofuran at 15° (Run 3).	52
4.	Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium in Tetrahydrofuran at 35° (Run 1).	54
5.	Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at -25 ± 3° (Run 2).	56
6.	Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at -26 ± 3° (Run 3).	59
7.	Vapor-Phase Chromatographic Analysis of the Methyl Esters of the Acidic Material Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at -41 ± 4° (Run 4)	61
8.	Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at -42° Followed by Addition of Methanol	63
9.	Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at -30° to -45° Followed by Addition of Methanol	66

LIST OF TABLES (Concluded)

Table		Page
10.	Nuclear Magnetic Resonance Spectroscopic Data of the Unknown Hydrocarbon [29] from the Cesium-Potassium Alloy Reactions, 1-Methyl-2,3-diphenylindene, 1,1,2-Triphenylbutene, and Unknown Methyl Ester [7].	82
11.	Ultraviolet Absorption Maxima of the Unknown Hydrocarbon [29] from the Cesium-Potassium Alloy Reactions, 9-Phenyl-9-n-propylfluorene, 1-Methyl-2,3-diphenylindene, 1,1,2-Triphenylbutene, 1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene, and Unknown Methyl Ester [7]	83
12.	Infrared Spectroscopic Data of Unknown Hydrocarbon [29].	84
13.	Infrared Spectroscopic Data of 1-Methyl-2,3-diphenylindene	85
14.	Infrared Spectroscopic Data of 1,1,2-Triphenylbutene-1	86
15.	Infrared Spectroscopic Data of Unknown Methyl Ester [7].	87
16.	The Calculated and Analytical Found C, H Contents and Molecular Weights of Hydrocarbon [29] and Methyl Ester [7]	89

SUMMARY

The purpose of this research was to study the products from the reaction of 4-chloro-1,1,1-triphenylbutane with various alkali metals to determine if rearrangements of the carbon skeleton involving 1,4-shifts of phenyl occur in the carbanion.



Many reactions of organic halides with lithium, sodium and potassium are known, but study of the reactions between the highly reactive cesium metal and organic halides has been very limited. Therefore, it was of great interest to study, in addition to the reactions of lithium, potassium, and potassium-sodium alloy, the reactions of cesium metal with selected organic halides.

For this research, the starting compound 4-chloro-1,1,1-triphenylbutane was prepared. The reaction of 4-chloro-1,1,1-triphenylbutane with lithium in tetrahydrofuran at -60° , followed by carbonation, gave only a 29 percent yield of acidic material; 75 percent of this acidic material was found to be 5,5,5-triphenylpentanoic acid. The yield of acidic material decreased with increasing temperature. At 0° , the yield of acidic material, which was mainly 5,5,5-triphenylpentanoic acid, was only 15 percent; and at 25° , the acidic material constituted only four percent of the

total product. This acidic material was shown by vapor-phase chromatography to contain 46 percent 5,5,5-triphenylpentanoic acid and 17 percent of an acid which was found to be not 2,2,5-triphenylpentanoic acid. The 96 percent yield of neutral material at 25° was found to contain 87 percent 1,1,1-triphenylbutane and 10 percent unreacted 4-chloro-1,1,1-triphenylbutane together with three percent of a hydrocarbon which had the same retention time as 1,1,4-triphenylbutane and 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene. Therefore, it was concluded that 4,4,4-triphenylbutyllithium produced from the reaction of lithium with 4-chloro-1,1,1-triphenylbutane at different temperatures does not undergo any appreciable rearrangement involving 1,4-shift of the phenyl group.

The reaction of 4-chloro-1,1,1-triphenylbutane with potassium in refluxing tetrahydrofuran, followed by carbonation, gave approximately 75 percent yield of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene. This hydrocarbon results from the intramolecular cyclization of the organopotassium compound, 4,4,4-triphenylbutylpotassium, followed by hydride elimination. This neutral material also contained an appreciable amount of 1,1,1-triphenylbutane (14 percent of the neutral material). The approximately 10 percent yield of acidic material from the potassium reaction was tentatively identified as four percent 2,2-diphenylpentanoic acid, three percent triphenylacetic acid, six percent 2,2,5-triphenylpentanoic acid, and some 47 percent and 28 percent of two unidentified acids.

When potassium and 4-chloro-1,1,1-triphenylbutane were allowed to reflux in tetrahydrofuran for 105 minutes, mostly acidic material was isolated after carbonation. The recrystallization of this reaction prod-

uct from different solvents gave several fractions of solid material with different melting ranges, but they were not further investigated because each fraction still contained many compounds according to analysis by vapor-phase chromatography.

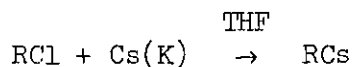
The reaction of sodium-potassium alloy with 4-chloro-1,1,1-triphenylbutane in the same solvent at ca. 15° gave, upon carbonation, 70 percent yield of acidic material which was tentatively identified as 22 percent 2,2-diphenylpentanoic acid, four percent triphenylacetic acid and six percent 2,2,5-triphenylpentanoic acid together with 39.0 percent, 16 percent and 12 percent of three unidentified acids. The neutral material contained 15 percent of unreacted 4-chloro-1,1,1-triphenylbutane, 31 percent 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (and/or 1,1,4-triphenylbutane) and 35 percent of a mixture of two unidentified hydrocarbons.

The reaction of cesium with 4-chloro-1,1,1-triphenylbutane in tetrahydrofuran at 35° gave, after carbonation, a 20 percent yield of acidic material which is tentatively identified as six percent 2,2-diphenylpentanoic acid, five percent triphenylacetic acid, six percent 2,2,5-triphenylpentanoic acid together with 26 percent, 35 percent, and 16 percent of three unidentified acids. The 80 percent yield of neutral material contained 45 percent 1,1,1-triphenylbutane, eight percent 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (and/or 1,1,4-triphenylbutane), and 35 percent 9-phenyl-9-n-propylfluorene. Reactions of cesium-potassium alloy in tetrahydrofuran at -25° gave, after carbonation, an 82 percent yield of acidic material, which contained 28 ± 5 percent of an acid with the same retention time as 2,2-diphenylpentanoic acid, 7 ± 3 percent triphenylacetic acid and 17 ± 2 percent of an acid with the same retention time as

2,2,5-triphenylpentanoic acid. The acid which had the same retention time as 2,2-diphenylpentanoic acid was isolated as its methyl ester and purified to give a colorless crystalline solid. The structure of this methyl ester was investigated by nuclear magnetic resonance spectroscopy, ultraviolet spectroscopy, and infrared spectroscopy together with C,H analysis and molecular weight determination, but the material has not been positively identified.

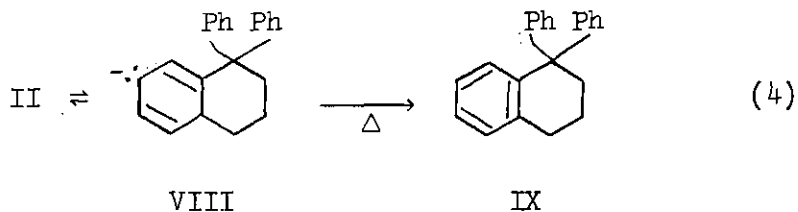
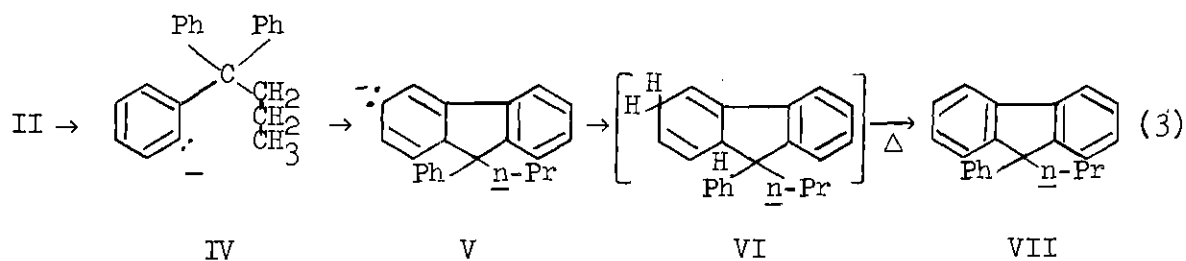
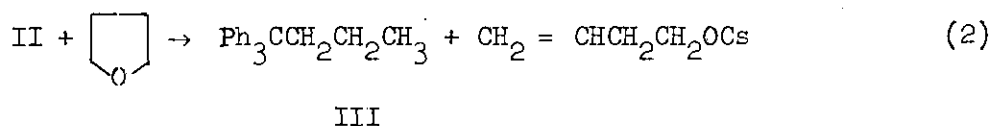
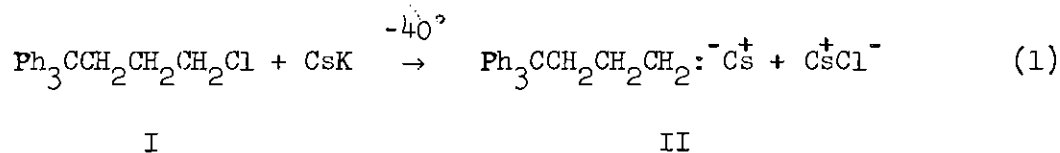
Reaction of cesium-potassium alloy with 4-chloro-1,1,1-triphenylbutane at -40° followed by protonation gave ca. 40 percent of 9-phenyl-9-n-propylfluorene, 20 percent 1,1,1-triphenylbutane, 10 percent 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (and/or 1,1,4-triphenylbutane), and 20 percent of a hydrocarbon which is believed to be 9-phenyl-9-n-propyl-dihydrofluorene because it was converted to 9-phenyl-9-n-propylfluorene on heating. 9-Phenyl-9-n-propylfluorene was identified by comparisons of melting point, mixed melting point, infrared spectrum, and ultraviolet spectrum with an authentic sample.

In conclusion, there are two significant accomplishments in this work. First, a technique of carrying out the synthesis of organocesium compounds in tetrahydrofuran solution at low temperature (-40°) was discovered.



It is hoped that this technique will prove of value in studying the chemistry of organoalkali compounds in homogeneous solution. Second, it was

discovered that the reactive carbanion (II), formed at -40° from the reaction of the corresponding chloride (I) with cesium-potassium alloy is reasonably stable toward protonation by the solvent (ca. 20 percent yield of 1,1,1-triphenylbutane (III) was obtained); some 60 percent of this carbanion underwent reaction (3) to give after addition of methanol a mixture of about one part of VI and two parts of VII. Compound VI is believed to have the structure of a 9-phenyl-9-n-propyldihydrofluorene since upon heating it is converted into 9-phenyl-9-n-propylfluorene (VII). Under these conditions, carbanion II also gave about 10 percent of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (IX).



Reaction of 1,1,1-triphenyl-4-chlorobutane (I) with molten potassium in tetrahydrofuran at 65° for some 10 minutes gave after carbonation chiefly hydrocarbons (90 percent yield) and a low yield of carboxylic acids (10 percent). The hydrocarbon consisted of 84 percent of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (IX) and 14 percent of 1,1,1-triphenylbutane (III).

CHAPTER I

INTRODUCTION

The purpose of this research was to study the reaction products of 4-chloro-1,1,1-triphenylbutane with various alkali metals to determine if rearrangements of the carbon skeleton involving 1,4-shifts of phenyl occur in the carbanion.

Many reactions between the common alkali metals and organic halides have been previously studied, but analogous reactions between cesium metal and organic halides have been studied less.

The reactions^{1,2} of 2,2,2-triphenylethyl chloride with sodium, lithium, potassium, and sodium-potassium alloy have been found to involve a 1,2-shift of the phenyl group to give, upon carbonation, 2,2,3-triphenylpropanoic acid. A 1,2-shift of a biphenyl group has also been observed by Wentworth³ in the reaction of 2-chloro-1,m-biphenyl-1,1-bis(p-biphenyl)ethane with lithium.

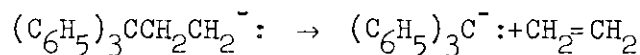
The reaction of 3,3,3-triphenylpropyl iodide with sodium in liquid ammonia followed by hydrolysis has been reported to give triphenylmethane and it was shown to be due to the molecular rearrangement of the sodium

(1) E. Grovenstein, Jr. and L. P. Williams, Jr., J. Am. Chem. Soc., **83**, 412 (1961).

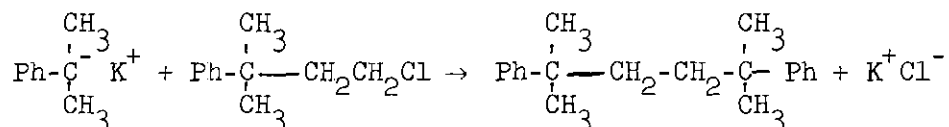
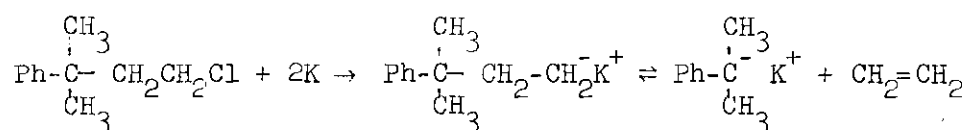
(2) L. P. Williams, Jr., Ph.D. Thesis, Georgia Institute of Technology, June, 1962, pp. 24, 28.

(3) Gary Wentworth, Ph.D. Thesis, Georgia Institute of Technology, March, 1966, p. 103.

triphenylpropide accompanied by a spontaneous cleavage:⁴



Pines and Schaap⁵ reported that a small amount of 1,1-dimethylindan was produced when 3-methyl-3-phenyl-chlorobutane was treated with potassium in refluxing cyclohexane. The major product of this reaction was identified as 2,5-dimethyl-2,5-diphenylhexane:



Rogers⁶ has studied a similar reaction in which $\text{Ph}_3\text{CCH}_2\text{CH}_2\text{NMe}_3\text{I}$ was reacted with sodium in liquid ammonia and the yields of 67.5 percent and 12.0 percent have been reported for 1,1,1-triphenylpropane and triphenylmethane, respectively.

The reaction of $\text{Ph}_3\text{CCH}_2\text{NMe}_3\text{I}$ with sodium in dioxane, followed by

(4) C. B. Wooster and R. A. Morse, *J. Am. Chem. Soc.*, **56**, 1735 (1934).

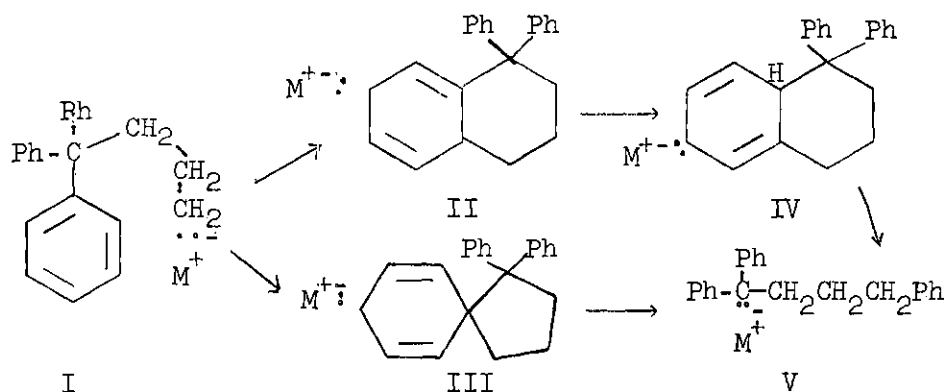
(5) Herman Pines and L. Schaap, *J. Am. Chem. Soc.*, **80**, 4378 (1958).

(6) L. C. Rogers, M.S. Thesis, Georgia Institute of Technology, 1963, pp. 60-72.

carbonation, was reported by Rogers to give only amine and neutral material. The yields of $\text{Ph}_2\text{CHCH}_2\text{Ph}$, Ph_3CCH_3 , and $\text{Ph}_2\text{C}=\text{CHPh}$ were said to be 4.84 percent, 22.02 percent, and 11.95 percent, respectively.⁶

From the examples cited above it is of interest to study the reactions of different alkali metals with the halide 4-chloro-1,1,1-triphenylbutane, which contains one more carbon atom than those used by Rogers⁶ and Wooster and Morse,⁴ to see whether there will be any rearrangement of the corresponding carbanion.

In this research, 4-chloro-1,1,1-triphenylbutane was reacted with lithium, potassium, sodium-potassium alloy, cesium, and cesium-potassium alloy. The 4,4,4-triphenylbutyl anion formed was expected to undergo rearrangement through an intramolecular mechanism involving cyclic intermediates or transition states:



The carbanion V should be more stable than the carbanion I due to the delocalization of the negative charge.

Most of the products from the alkali metal reactions were allowed

to react with carbon dioxide to convert the organoalkali compounds to carboxylic acids except in the case of two of the cesium-potassium alloy reactions. In the latter two reactions, the organoalkali compounds were protonated by methanol.

CHAPTER II

REAGENTS AND SOLVENTS

Acetyl Chloride

Matheson Coleman & Bell, Inc., practical grade acetyl chloride (b.p. 50-52°) was used without further purification.

Acetone

Commercial grade acetone was redistilled at 56° from potassium permanganate.

Ammonium Chloride

Baker reagent grade ammonium chloride was used without further purification.

Ammonia

Matheson Company, Inc., anhydrous ammonia was distilled from the cylinder through a barium oxide drying tube and condensed in the reaction vessel in which it was to be used.

Benzene

Industrial grade (thiophene free) benzene was stored over sodium wire.

Benzophenone

Eastman white label grade benzophenone was used without further purification.

Benzhydryl Chloride

Matheson & Company practical grade benzhydryl chloride was redistilled at 173° and 19 mm from a Claisen flask.

Benzyl Chloride

Eastman white label grade benzyl chloride was used without further purification.

Bromobenzene

Unmarked brown-bottled bromobenzene (recorded b.p. 154.5-155°, student preparation) from the organic stock room of the Georgia Institute of Technology was redistilled at 150° through a 70 cm Vigreux column.

1-Bromo-3-chloropropane

Eastman white label grade 1-bromo-3-chloropropane was redistilled at 140-141° through a 60 cm vacuum jacketed column packed with glass helices.

1-Bromo-3-phenylpropane

Eastman white label grade 1-bromo-3-phenylpropane was redistilled at 118-119.5° and 20 mm from a Claisen flask.

Carbon Tetrachloride

Baker analyzed reagent grade carbon tetrachloride was used without further purification.

Cesium

MSA Research Corporation, 99.9 percent purity minimum, cesium was used.

1-Chloro-3-phenylpropane

Columbia Organic Chemicals Company grade was redistilled at 81-82° and 7 mm through a 60 cm vacuum jacketed column packed with glass halices.

1-Chloropropane

Fisher reagent grade 1-chloropropane redistilled at 46.5-47.0° by Gary Wentworth⁷ was used.

Crotonic Acid

Crotonic acid (m.p. 168-170°, student preparation) from the organic stock room of Georgia Institute of Technology was used without further purification.

Cyclohexane

Commercial grade cyclohexane was used without further purification.

Deuteriochloroform

Merck, Sharp & Dohme of Canada, Ltd., 99.5 percent pure deuteriochloroform was used without further purification.

m-Dibromobenzene

Eastman white label m-dibromobenzene was redistilled at 64° and 5 mm from a Claisen flask.

Diethyl Ether

Baker reagent grade anhydrous ether, stored over sodium wire, was used without further purification.

(7) Gary Wentworth, Ph.D. Thesis, Georgia Institute of Technology, March, 1966, p. 13.

Diphenylacetic Acid

A sample prepared by Gary Wentworth was recrystallized from benzene to give white solid of m.p. 148-148.5°.

Dimethyl Sulfoxide

Matheson, Coleman, Bell reagent grade dimethyl sulfoxide was used without further purification.

Dimethyl Formamide

Technical grade dimethyl formamide was redistilled at 35° and 24 mm through a 60 cm spinning-band column.

Diphenylmethane

Matheson practical grade diphenylmethane was redistilled at 136-137° and 18 mm through a 60 cm vacuum jacketed column packed with glass halices.

Lithium

Lithium Corporation of America, 0.05 percent sodium maximum, lithium wire was used.

Lithium Aluminum Hydride

Metal Hydride, Inc., 95 percent, lithium aluminum hydride was used without further purification.

Methanol

Commercial grade methanol was purified by treatment of a 1000 ml portion with magnesium at reflux for 40 minutes and then distilled at 64°.

Magnesium

Eastman white label magnesium was used without further purification.

2-Phenylbutanoic Acid

Eastman white label grade 2-phenylbutyric acid was used without further purification.

4-Phenylbutanoic Acid

Eastman white label grade 4-phenylbutyric acid was used without further purification.

Potassium

Baker reagent grade potassium was used without further purification.

Sodium

Baker reagent grade sodium was used without further purification.

Sodium Aluminum Hydride

Metal Hydrides, Inc., pure grade sodium aluminum hydride was used without further purification.

Sodium Cyanide

Baker analyzed grade sodium cyanide was used without further purification.

Tetrahydrofuran

Anhydrous tetrahydrofuran was prepared by drying a commercial grade of tetrahydrofuran over sodium wire.

Triphenylmethane

Eastman white label grade triphenylmethane was used without further purification.

Triphenylmethanol

Eastman white label grade triphenylmethanol was recrystallized from carbon tetrachloride to give white solid of m.p. 162-164.5°.

CHAPTER III

INSTRUMENTAL ANALYSES

Ultraviolet spectra were obtained on the Cary 14 recording spectrophotometer.

All n.m.r. spectra were obtained on the Varian Associates Model A-60 spectrometer using tetramethylsilane as an internal standard unless otherwise specified.

Infrared spectra were taken on the Perkin-Elmer Grating Infrared spectrophotometer model 237 B using carbon tetrachloride solutions with a 0.1 mm sodium chloride cell and were calibrated with the 6.238 μ band of polystyrene film. In the case of the unknown methyl ester, the sample was in the form of potassium chloride pellet.

The qualitative analyses of most of the reaction mixtures were accomplished by vapor-phase chromatography on F & M Research Chromatograph Model 810. The columns were 6 ft long, 1/4 in diameter, packed with 10 percent Silicone Gum Rubber (SE30) on 60-80 Mesh Chromosorp G-AW-DMCS. (Chromosorp G, acid washed and treated with dimethyldichlorosilane.)

In the case of the last two cesium-potassium alloy reactions, 12 ft long, 1/4 in diameter columns were packed with 10 percent Silicone Gum Rubber (SE30) on 60-80 mesh Diatoport S.

In one of the cesium-potassium alloy reactions, a set of 12 ft, 1/2 in columns packed with 20 percent Silicone Gum Rubber on 45-60 mesh Chromosorp W-AW-DMCS (Chromosorp W, acid washed and treated with dimethyl-

dichlorosilane) was used for the separation of the methyl esters.

The following two methods were used for the identification of reaction mixtures by vapor-phase chromatography. In method A, a known quantity of the authentic sample was mixed with the unknown mixture to make the peak height nearly twice as big as it was when there was no known compound added. In method B, the retention time of each component in the mixture was compared with the retention time of the authentic sample under identical analytical conditions.

Compound [4] in lithium run 4 was identified as compound [4] in cesium run 2 by vpc method A.

Compound [8] in lithium run 4 was identified as compound [8] in cesium run 1 by vpc method B.

Compound [8] in potassium run 1 was identified as compound [8] in potassium run 3 by vpc method A and was identified as the methyl ester of 2,2-diphenylpentanoic acid by the same method.

Compound [9] in potassium run 1 was identified as compound [9] in potassium run 3 by vpc method A.

Compound [10] in potassium run 1 was identified as compound [10] in potassium run 3 by vpc method A.

Compound [10] in lithium run 4 was identified as compound [10] in cesium run 1 by vpc method B and the latter was identified as compound [10] above by vpc method A.

Compound [12] in potassium run 1, potassium run 3, cesium run 1, and cesium run 2 was identified as methyl triphenylacetate by vpc method A.

Compound [14] in potassium run 1, potassium run 3, cesium run 1,

and cesium run 2 was identified as methyl 2,2,5-triphenylpentanoate by vpc method A.

Compound [16] in potassium run 1 was identified as compound [16] in potassium run 3 and as compound [16] in cesium run 2 by vpc method A.

Compound [21] in cesium run 1 was identified as compound [21] in cesium run 2 by vpc method A. Compound [21] in potassium run 3 was identified as compound [21] in cesium run 2 by the same method.

Compound [23] in cesium run 1 was identified as compound [23] in cesium run 2 by vpc method A. This compound [23] was conceivably 9-n-propylfluorene.

Compound [25] in potassium run 3 and cesium run 2 was identified as triphenylmethane by vpc method B.

Compound [26] in potassium run 1 was identified as compound [26] in potassium run 3 and as compound [26] in cesium run 2 by vpc method B.

Compound [28] in lithium run 4, in potassium run 1, and in cesium runs 1, 2, 5, and 6 was identified as 1,1,1-triphenylbutane by vpc method A. The identification of this compound [28] in potassium run 3 was based on vpc method B.

Compound [29] in cesium runs 1, 2, 5, and 6 was identified as 9-phenyl-9-n-propylfluorene by vpc method A.

Compound [30] in cesium run 5 was identified as compound [30] in cesium run 6 by vpc method B. This compound was believed to be 9-phenyl-9-n-propyldihydrofluorene.

Compound [31] in lithium run 4, potassium run 1, potassium run 3, and cesium runs 1, 2, 5, and 6 was identified as 1,1-diphenyl-1,2,3,4-

tetrahydronaphthalene and/or 1,1,4-triphenylbutane by vpc method A.

Compound [32] in lithium run 4 and in potassium run 3 was identified as 4-chloro-1,1,1-triphenylbutane by vpc method A.

CHAPTER IV

EXPERIMENTAL DETAILS

Synthesis of 4-Chloro-1,1,1-triphenylbutaneTriphenylchloromethane

This chloride was prepared according to the method described in Organic Syntheses.⁸ The reaction of 254 g (0.977 mole) of triphenylcarbinol in 80 ml of benzene with 100 ml of acetyl chloride gave 135 g (0.484 mole) of triphenylchloromethane (49.5 percent yield), m.p. 111-112.5° (with previous softening). In another preparation, an 82 percent yield was observed. A 93-95 percent yield is reported⁸ in Organic Syntheses.

4-Chloro-1,1,1-triphenylbutane

The synthesis of 4-chloro-1,1,1-triphenylbutane was first attempted by the reaction of triphenylmethylpotassium with trimethylene chloride. Into a 1-l Morton flask fitted with a high-speed stirrer was distilled from lithium aluminum hydride 600 ml of tetrahydrofuran, which had previously been dried over sodium wire. Under an atmosphere of nitrogen, potassium (16.7 g, 0.43 g-atom) was added into the container and the solution was stirred at reflux. A solution of 55.8 g (0.20 mole) of triphenylmethyl chloride in 100 ml of tetrahydrofuran was added over a period

(8) E. C. Hornig (Editor-in-chief), Organic Syntheses, Collective Vol. III, John Wiley & Sons, Inc., New York, 1962, p. 941.

of two and one-half hours. The first portion of halide added caused a red color to appear and the final color was like that of bromine. The resulting solution was stirred at reflux for an additional 40 minutes. After being cooled with an ice water bath, the red colored contents were siphoned into a 3-l three-necked round-bottomed flask containing 700 ml of trimethylene chloride. No appreciable color change was observed for this coupling reaction. Methanol (50 ml) was added to destroy any unreacted potassium. The next day, 100 ml of methanol and then 100 ml of water were added. After separation from the organic portion, the aqueous portion was extracted with three portions of ether (a total of 200 ml). The organic solutions were combined, dried over anhydrous magnesium sulfate and solvents removed in vacuo to give 54.66 g of dark brown tarry material. The attempted isolation of the desired 4-chloro-1,1,1-triphenylbutane by the recrystallization of a small sample of this above tarry material from cyclohexane and ethanol and by column chromatography failed.

Triphenylmethylsodium was prepared by the procedure of Renfrow and Hauser⁹ from powdered sodium amalgam (12.7 g of sodium and 524.0 g of mercury) and triphenylchloromethane (69.7 g, 0.25 mole) in 200 ml of anhydrous ether. The triphenylmethylsodium was siphoned under a nitrogen atmosphere from the mercury and added over a ten minute period to 440 ml of 1-bromo-3-chloropropane at $12 \pm 3^\circ$. The red color of the triphenylmethylsodium disappeared almost instantly upon contact of this reagent

(9) A. H. Blatt, Organic Syntheses, Collective Volume II, John Wiley & Sons, Inc., New York, 1961, p. 607.

with 1-bromo-3-chloropropane and the reaction mixture became warm. The resulting solution was filtered and solvent was removed in vacuo to give 51.0 g (63.6 percent based on triphenylchloromethane used) of light yellow crystals of m.p. 125-170°. Recrystallization from acetone and subsequent sublimation gave 26.29 g of nearly pure 4-chloro-1,1,1-triphenylbutane, m.p. 129-131.5° (reported¹⁰ m.p. 130°).

Anal.* Calcd. for $C_{22}H_{21}Cl$: C, 82.35; H, 6.60; Cl, 11.05.

Found: C, 81.92, 81.89; H, 6.59, 6.53; Cl, 11.29, 11.25.

During the preparation and purifications, 2.28 g of a substance, m.p. 164-167° and 3.62 g of a substance, m.p. 205-230°, were obtained. In another preparation similar to the above but with 3.4 times the quantity of reactants, 165.9 g (68.7 percent yield) of product, m.p. 115-131°, was obtained. Recrystallization from acetone yielded 120.50 g of nearly pure 4-chloro-1,1,1-triphenylbutane, m.p. 129-131°.

In another preparation, triphenylmethylsodium prepared from 69.7 g (0.250 mole) of triphenylchloromethane with sodium amalgam (12.7 g sodium, 523 g mercury) in 200 ml of ether was reacted with 400 ml of trimethylene chloride. After filtration, the solvent and unreacted trimethylene chloride were removed in vacuo to give some light yellow crystals contaminated by oily material, which was washed with n-pentane four times to give 23.4 g (0.0731 mole, 29.2 percent yield) of light yellow crystals, m.p. 122-125°.

(10) J. C. Charlton, I. Dostrovsky, and E. D. Hughes, Nature, 167, 986-7 (1951).

* Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

One recrystallization from acetone gave 15.9 g of colorless crystals, m.p. 123-128.5°, of which a sample of 6.50 g was recrystallized twice from acetone and sublimed at 170 microns and 145° to give 2.16 g of nearly pure 4-chloro-1,1,1-triphenylbutane, m.p. 129-131.5°. This compound was found to be identical with the compound obtained from the reaction of 1-chloro-3-bromopropane by comparison of infrared spectra (mixed melting point showed no depression).

Synthesis of 5,5,5-Triphenylpentanoic Acid

5,5,5-Triphenylpentanenitrile

This nitrile was prepared following the general procedure of Cope and Mehta.¹¹ In a typical preparation, 2.00 g (0.00605 mole) of 4-chloro-1,1,1-triphenylbutane, 0.471 g (0.00962 mole) of sodium cyanide and 0.922 g (0.00615 mole) of sodium iodide were dissolved in 180 ml dimethyl sulfoxide in a 250 ml round-bottomed flask, and the resulting solution stirred at room temperature for twenty-five and a half days. After filtration, the orange-colored reaction mixture was poured into 100 ml water in a 400 ml beaker. The solid formed was filtered and washed with 100 ml water to give 1.798 g (95.3 percent yield based on the 4-chloro-1,1,1-triphenylbutane used), m.p. 147-149°. Two recrystallizations of 1.622 g of this crude product from acetone gave 0.930 g of solid, m.p. 149-150° (new compound).

Anal.* Calcd. for C₂₃H₂₁N: C, 88.70; H, 6.80; N, 4.50.

(11) A. C. Cope and A. S. Mehta, J. Am. Chem. Soc., 86, 5626 (1964).

* Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee

Found: C, 88.24, 88.06; H, 6.98, 6.82; N, 4.71, 4.72.

In another run, a yield of 96.7 percent of this nitrile was observed by stirring the mixture at room temperature for ten days.

5,5,5-Triphenylpentanoic Acid

The synthesis of this acid was carried out by the treatment of the corresponding nitrile with base according to the general procedure given in Organic Syntheses.¹² A solution of 0.615 g (1.97 mmole) of 5,5,5-triphenylpentanenitrile and 0.34 g (6.1 mmole) of KOH in 20 ml of ethylene glycol was heated at 220° for six hours. After the solution had cooled to room temperature, it was diluted with 25 ml of water and extracted with ether. The ether extracts were combined and washed with water. The combined aqueous phases were acidified with HCl and the solid which separated from solution was isolated by filtration. This solid was dissolved in ether and dried over anhydrous MgSO₄. After filtration, the ethereal solution was allowed to evaporate to dryness leaving 0.609 g of light blue solid, m.p. 220-223° (93.7 percent yield). A recrystallization of this material from benzene followed by vacuum sublimation gave 0.145 g of white solid 5,5,5-triphenylpentanoic acid, m.p. 223-224.5° (with decomposition). An acid with a melting point of 222-223° produced from the reaction of 1,1,1,6,6,6-hexaphenylhexane-2-one with potassium hydroxide in methanol was believed by Piehl and Brown¹³ to have the structure of 5,5,5-triphenylpentanoic acid.¹³

(12) Norman Rabjohn, Organic Syntheses, Collective Volume IV, John Wiley & Sons, Inc., New York, 1963, p. 95.

(13) F. J. Piehl and W. G. Brown, J. Am. Chem. Soc., 75, 5023-6 (1953).

Anal.* Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71.

Found: C, 84.79, 84.61; H, 6.92, 6.83.

In a second run, a yield of 97.3 percent of the desired acid was observed by hydrolyzing the corresponding nitrile at 200° for 12 hours.

Methyl 5,5,5-Triphenylpentanoate

An ether solution of diazomethane was prepared by the method of deBoer and Backer.¹⁴ A solution of 7.25 g (0.03 mole) of N-methyl-N-nitroso-p-toluene sulfonamide in 45 ml of ether was added dropwise to a solution of 1.75 g of KOH in 2.7 ml of water and 8.3 ml of 95 percent ethanol at 65°. The diazomethane co-distilled with the ether, and part of the resulting solution was added to a solution of 0.722 g (2.19 mmoles) of 5,5,5-triphenylpentanoic acid in 70 ml of ether at 0°. The solution was allowed to evaporate to dryness and the residue (0.604 g), after a recrystallization from MeOH, gave 0.580 g (1.69 mmoles, 77.2 percent yield) of colorless crystals, m.p. 91-97°. A sample of 0.0912 g was recrystallized from absolute alcohol to give 0.0417 g of sheet-like crystals, m.p. 97-97.7° (new compound).

Anal.* Calcd. for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02.

Found: C, 83.59, 83.38; H, 7.02, 7.06.

Synthesis of 2,2-Diphenylpentanoic Acid

This acid was prepared following the general method outlined by

(14) T. J. deBoer and H. J. Backer, Rec. trav. chim., 73, 229 (1954).

* Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Hauser,¹⁵ in which the potassium salt of ethyl diphenylacetate is alkylated with an alkyl halide. In a 1-l three-necked round-bottomed flask fitted with a stirrer, dropping funnel, and Dry Ice-acetone condenser, was condensed 400 ml of anhydrous ammonia. Under an atmosphere of nitrogen, 1.258 g (0.032 g-atom) of potassium was added in 12 pieces. After the first piece of potassium had dissolved, a small crystal of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to catalyze the formation of potassium amide. The blue color of potassium in liquid ammonia changed to grey after 25 minutes of stirring. A solution of 7.041 g (0.0311 mole) of methyl diphenyl acetate in 40 ml of anhydrous ether was added dropwise over a period of 17 minutes and the resulting solution stirred for 33 minutes. A solution of 3.85 g (0.0313 mole) of 1-bromopropane in 35 ml of anhydrous ether was added dropwise over a period of 15 minutes and the resulting solution stirred for two hours. Solid ammonium chloride (2.52 g, 0.047 mole) was added to neutralize unreacted potassium amide. The ammonia was allowed to evaporate from the mixture. The next day, the mixture was extracted with two 100 and one 150 ml portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, and allowed to evaporate to dryness, to give 7.77 g of oily material. A sample of 2.30 g of this crude product was refluxed with 2.55 g of KOH in 50 ml absolute alcohol for 24 hours. After three-fourths of the solvents had been removed under partial vacuum, 50 ml of water was added to the residue and the mixture was extracted with three 30 ml portions of ether. The aqueous fraction

(15) W. G. Kenyon, R. B. Meyer, and C. R. Hauser, J. Org. Chem., 28, 3108 (1963).

was acidified with 10 percent HCl and the white solid formed was separated by filtration to give 2.53 g of light yellow crystals; one recrystallization from absolute alcohol gave 0.91 g of colorless crystals, m.p. 153-157° (reported¹⁶ m.p. 155.5°). A small sample of this acid was converted to the liquid methyl ester for vapor-phase chromatography.

Attempted Synthesis of 2,2,5-Triphenylpentanoic Acid

Methyl Diphenylacetate

This ester was synthesized according to the general procedure given in Organic Syntheses.¹⁷ The reaction of 9.33 g (0.0440 mole) of diphenylacetic acid with 100 ml of methanol and 5 ml of concentrated H₂SO₄ at steam-bath temperature for five hours gave 7.76 g (0.0343 mole) of methyl diphenylacetate (78.4 percent yield, based on diphenylacetic acid), m.p. 55-59°. One recrystallization from petroleum ether gave 6.10 g of colorless crystals, m.p. 59.5-60.5° (reported melting point of methyl diphenylacetate: 60°¹⁸). The reaction was repeated at the same temperature for 62 hours; a 94.4 percent yield was observed after one recrystallization from petroleum ether. In another reaction at the same temperature for 48 hours, the yield was 92.3 percent.

2,2,5-Triphenylpentanoic Acid

The synthesis of this acid was first attempted following the general

(16) A. L. Mndzhoyan, G. T. Tatevosyan, S. G. Agbalyan, and R. Kh. Bostandzhyan, Doklady. Akad. Nauk. Armyan. S.S.R., 28, No. 1, 11 (1959).

(17) E. C. Horning, Organic Syntheses, Collective Volume III, John Wiley & Sons, Inc., New York, 1962, p. 605.

(18) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, 1943, p. 1014.

method outlined by Hauser,¹⁵ in which the potassium salt of ethyl diphenylacetate is alkylated with a halide. In a 1-l, three-necked, round-bottomed flask, fitted with a mechanical stirrer, a dropping funnel, and a Dry Ice-acetone condenser, 600 ml of anhydrous ammonia was condensed. Under an atmosphere of dry nitrogen, 2.36 g (0.060 g-atom) of potassium was added rapidly in pieces of about 0.2 g each. After the first piece of potassium had dissolved, a small crystal of ferric nitrate was added to catalyze the formation of potassium amide. The blue color of potassium in liquid ammonia changed to grey-green after 100 minutes of stirring. A solution of 12.02 g (0.0532 mole) of methyl diphenylacetate in 90 ml of anhydrous ether was added over a period of 30 minutes and the resulting solution stirred for 55 minutes. A solution of 8.28 g (0.053 mole) of 1-chloro-3-phenylpropane in 20 ml of anhydrous ether was added dropwise over a period of 20 minutes and the resulting solution stirred for two hours. Solid ammonium chloride (3.5 g, 0.065 mole) was added to neutralize unreacted potassium amide. The ammonia was allowed to evaporate from the mixture. Some 3.96 g of unreacted methyl diphenylacetate, m.p. 59.5-61°, was recovered from the ether extract. Vapor-phase chromatography of the ether solution after the isolation of methyl diphenylacetate showed the presence of three major components, two of which were confirmed to be unreacted 1-chloro-3-phenylpropane and methyl diphenylacetate. The third one, which constituted 0.6 percent of the mixture, was conceivably the desired methyl ester of 2,2,5-triphenylpentanoic acid.

In a second run, potassium amide was prepared in 500 ml of liquid ammonia from 3.23 g (0.085 g-atom) of potassium in the same manner as in

the first run. A solution of 16.9 g (0.0748 mole) of methyl diphenylacetate in 90 ml of tetrahydrofuran (distilled from sodium aluminum hydride) was added dropwise over a period of 30 minutes and the resulting solution stirred for 30 minutes. A solution of 10.62 g (0.0748 mole) of 1-chloro-3-phenylpropane in 50 ml of tetrahydrofuran was added dropwise over a period of 10 minutes, and the resulting solution stirred for 30 minutes at Dry Ice-acetone bath temperature. The Dry Ice-acetone bath was removed and ammonia was allowed to evaporate for two hours and then 150 ml of tetrahydrofuran was added to the mixture over a period of 40 minutes. The yellowish suspended mixture was heated at reflux for nine hours and cooled to room temperature in seven and one-half hours and stirred at reflux again for 89 hours. The mixture was allowed to separate into two phases and then these were separated by filtration. The solid portion was extracted with three 50 ml portions of tetrahydrofuran. The tetrahydrofuran solutions were combined and filtered again. Solvents and unreacted chloride were removed under vacuum to give 4.3 g of a tarry material which was analyzed by vapor-phase chromatography. This chromatography showed that it contained approximately seven percent of a new ester, presumably the desired methyl ester.

In the third run, potassium amide was prepared in 600 ml of liquid ammonia from 3.89 g (0.0997 g-atom) of potassium in the usual manner and the Dry Ice-acetone bath was removed as soon as the formation of potassium amide was completed. A solution of 20.72 g (0.0921 mole) of methyl diphenylacetate in 70 ml of tetrahydrofuran was added over a period of 45 minutes. The yellowish grey solution turned green. The mixture was stirred at re-

flux for 30 minutes. A solution of 14.89 g (0.0951 mole) of 1-chloro-3-phenylpropane in 50 ml of tetrahydrofuran was added dropwise over a period of five minutes and the resulting solution was stirred at reflux for seven hours. Solid ammonium chloride (5.84 g, 0.108 mole) was added to destroy the unreacted potassium amide. The next day, the solid material was isolated by filtration and the filtrate was subjected to vapor-phase chromatography and found to contain only two percent of the desired methyl ester. The solution was added dropwise to potassium amide, prepared from 5.06 g (0.130 g-atom) of potassium in 350 ml of liquid ammonia, over a period of 18 minutes. The resulting solution was brown after one-third of the reaction mixture had been added and it changed to green at the completion of the addition. A solution of 4.5 g (0.00292 mole) of 1-chloro-3-phenylpropane in 100 ml of tetrahydrofuran was added over a period of 20 minutes and the resulting solution was stirred at reflux for 24 hours. Vapor-phase chromatography of this above solution showed that it contained seven percent of the desired methyl ester. Solid ammonium chloride (7.0 g, 0.13 mole) was added to decompose unreacted potassium amide and the reaction mixture was stirred for 24 hours. This final mixture was subjected to vapor-phase chromatography and found to contain 0.58 percent of the desired methyl ester. (The reason for the decrease in the percentage of the desired methyl ester was not clear.)

Synthesis of 2,2,5-Triphenylpentanoic Acid

1,1,4-Triphenylbutanol-1

To a solution of 3-phenylpropyllithium, prepared from 48.94 g (0.317 mole) of 1-chloro-3-phenylpropane and 4.72 g (0.680 g-atom) of

lithium in 600 ml of tetrahydrofuran at -50° , was added 19.77 g (0.109 mole) of benzophenone dissolved in 80 ml of tetrahydrofuran. The addition was made at $-5 \pm 5^{\circ}$ over a period of 70 minutes with stirring at room temperature for an additional seven hours. The reaction mixture was poured into 500 ml saturated aqueous ammonium chloride with stirring. The organic layer was extracted with ether and the ether extract gave 49.17 g of amorphous product. One recrystallization from light petroleum ether gave 21.53 g (65.3 percent) of feather-like crystals, m.p. $73-75^{\circ}$ (T. W. Campbell and W. G. Young report m.p. $72-73^{\circ}$ ¹⁹; Kharasch and Weinhouse reported m.p. 74° ²⁰).

In another preparation, this compound was made from 3-phenylpropylmagnesium chloride and benzophenone according to the general procedure given in Organic Syntheses.²¹ In the usual apparatus for alkali-metal reactions was placed 7.48 g (0.304 g-atom) of magnesium turnings and a crystal of iodine. The flask was heated with a flame and swept with dry nitrogen for 30 minutes. After cooling to room temperature, 50 ml of anhydrous ether was added to cover the magnesium. Approximately five percent of a solution of 47.15 g of 1-chloro-3-phenylpropane in 100 ml of dry ether was added and the mixture was heated until reflux was attained. After 30 minutes at reflux temperature, no reaction was apparent, and another five

(19) T. W. Campbell and W. G. Young, J. Am. Chem. Soc., 69, 3066-8 (1947).

(20) M. S. Kharasch and S. Weinhouse, J. Org. Chem., 1, 209 (1936).

(21) A. H. Blatt, Organic Syntheses, Collective Volume II, John Wiley & Sons, Inc., New York, 1961, p. 606.

percent of halide solution and 50 ml of anhydrous ether were added and the mixture was swept with N_2 . A third portion of five percent of the halide solution and 100 ml of ether were added in ten minutes and the initiation of the reaction was attempted by stirring and heating at reflux for 90 minutes. As soon as the more vigorous reflux of the solvents was noticed when heating was discontinued, the remaining halide solution was added dropwise over a period of 50 minutes. After the addition of the chloride was completed, the mixture was stirred at reflux temperature for two hours. A solution of 38.63 g (0.213 mole) of benzophenone in 100 ml of anhydrous ether was added over a period of 40 minutes, and the resulting orange solution was stirred at reflux for five hours. Six hours later, the reaction mixture was acidified with 500 ml of a mixture of saturated aqueous ammonium chloride and crushed ice. The mixture was extracted with three 150 ml portions of ether and the ether extract was allowed to evaporate to dryness. Total weight of product isolated by this procedure was 49.05 g (0.162 mole, 76.4 percent yield based on benzophenone used) of a light yellow solid.

In the third preparation, the mixture of 7.49 g of magnesium turnings with a small crystal of iodine was heated with a flame under nitrogen atmosphere in the usual apparatus and swept with nitrogen for five minutes. One-tenth of a solution of 60.65 g (0.305 mole) of 3-phenylpropyl bromide was added and formation of 3-phenylpropylmagnesium bromide was initiated in 25 minutes. The remaining bromide was added over a period of 45 minutes. After the addition of the bromide was completed, the mixture was stirred at reflux for two and a half hours. A solution of approximately 17 g of

3-phenylpropyl chloride in 50 ml of anhydrous ether was added over a period of 35 minutes to react with the remaining magnesium. The mixture was stirred at reflux for 50 minutes. A solution of 40.96 g (0.222 mole) of benzophenone in 50 ml of ether was added over a period of 35 minutes and the resulting mixture was stirred at reflux for four hours. The next day, the reaction mixture was poured into 800 ml of a mixture of saturated ammonium chloride solution and crushed ice. The ether extract was allowed to evaporate to dryness. The oily product was washed with petroleum ether to give 19.80 g of unreacted benzophenone, m.p. 162-170°, 15.05 g of 1,1,4-triphenylbutanol, m.p. ca. 74°, and 4.42 g of low melting material, m.p. 49-65°. One recrystallization of the fraction with m.p. ca. 74° from pentane gave 8.83 g of material, m.p. 74-75°.

2,2,5-Triphenylpentanoic Acid

The 1,1,4-triphenylbutanol-1 was converted to its methyl ether by the general procedure of Ziegler and co-workers.²² 1,1,4-Triphenylbutanol-1 (18.09 g, 0.0600 mole) was dissolved in 85 ml of anhydrous methanol and 0.9 ml of concentrated sulfuric acid was added to this solution. The ether precipitated at the end of 15 minutes and, after standing one hour at room temperature, the contents of the reaction flask completely solidified. An additional 55 ml of methanol was added and the mixture was stirred and allowed to stand three hours. Then 250 ml of methanol was added and the ether was isolated by filtration. One recrystallization from methanol yielded 11.14 g (58.9 percent yield) of 1-methoxy-1,1,4-triphenylbutane,

(22) K. Ziegler, K. Richter, and B. Schnell, Ann., 443, 177 (1925).

m.p. 80-81.5°. (The purification of this compound was difficult; therefore, it was not analyzed.)

When drying of 5.30 g of the ether was attempted at 45 microns pressure and room temperature for 30 minutes, some substance melting from 70-73° was obtained. The attempted drying of another sample of this ether at 45 microns pressure and room temperature for one and a half hours resulted in the evolution of a gas and the formation of an oily material. The ultraviolet spectrum of this oily product [ϵ max = 1.55×10^3 (calculated for $C_{23}H_{24}O$) at λ max 257 μ] indicated that it contained an appreciable amount of unsaturated compound with conjugated double bonds (therefore likely $Ph_2C = CHCH_2CH_2Ph$ was formed by elimination of methanol). The attempted conversion of this molten substance back into the methyl ether by reflux with methanol and concentrated sulfuric acid was unsuccessful.

The 1-methoxy-1,1,4-triphenylbutane was cleaved by potassium by a procedure similar to that of Ziegler and co-workers²³ except that, rather than shaking with Na-K alloy, stirring the molten potassium with the Morton stirrer was employed. In a 500 ml Morton flask fitted with a high-speed stirrer, a Vigreux column and a dropping funnel, 250 ml of tetrahydrofuran which had previously been dried over sodium wire, was distilled from lithium aluminum hydride. The whole system was under a nitrogen atmosphere. Potassium, 2.91 g (0.0745 g-atom), was added in pieces of about 0.4 g each. The mixture was heated and was refluxed for one hour with vigorous stirring.

(23) K. Ziegler, F. Crossmann, H. Kleiner, and O. Schafer, Ann., 473, 27 (1929).

A solution of 9.73 g (0.0308 mole) of 1-methoxy-1,1,4-triphenylbutane in 35 ml of tetrahydrofuran was added dropwise over a period of 31 minutes. A red color appeared in one minute and the final color was that of bromine. Stirring was continued for one and a half hours at the reflux temperature of tetrahydrofuran and then the reaction mixture was forced onto pulverized solid carbon dioxide. The next day, 200 ml of water was added to the mixture and the solvents were removed in vacuo at steam-bath temperature. A 3.0 g portion of neutral material was extracted with ether. Acidification and extraction with ether gave, in the ether extract, 6.66 g (68.1 percent yield) of acidic material, m.p. 162-168°. One recrystallization of 6.65 g of this acid from cyclohexane gave 4.51 g, m.p. 164-169°, 1.74 g of which was recrystallized from chloroform to give 1.06 g, m.p. 168-169.5° (with decomposition)(new compound).

Anal.* Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71.

Found: C, 83.63, 83.55; H, 6.63, 6.52.

Synthesis of Triphenylacetic Acid

About half of the triphenylmethylsodium prepared from 72.3 g (0.259 mole) of triphenylchloromethane with sodium amalgam in anhydrous ether following the method of Renfrow and Hauser,⁹ as mentioned in the preparation of 1,1,1-triphenyl-4-chlorobutane, was reacted with crushed solid carbon dioxide in an atmosphere of nitrogen. The next day, 200 ml of water was added to the mixture and the resulting mixture was acidified with 10 percent H_2SO_4 . Some 45.8 g of yellow solid, m.p. 252-253° (with

* Analysis by Alfred Bernhardt, Analytical Laboratories, West Germany.

premelting) was isolated by filtration. A sample of 15.15 g of this crude acid was extracted with ether to give 3.89 g of insoluble material, m.p. 268-270° (with premelting), which was extracted with benzene at reflux. The residue from the benzene extraction was recrystallized from 95 percent ethanol to give 3.26 g of light yellow crystals, m.p. 272-275° (with decomposition)(reported²⁴ m.p. 269-271°).

A small quantity of this acid was converted into the methyl ester by the reaction of diazomethane in ether; the methyl ester obtained had an m.p. of 188-189° (with decomposition)(reported²⁵ m.p. 184-185°).

Synthesis of 1,1,1-Triphenylbutane

The synthesis of this hydrocarbon was first attempted by reacting a solution of triphenylmethylsodium with propyl chloride in diethylether. The remainder of the sodium triphenylmethane prepared in the synthesis of triphenylacetic acid mentioned above was reacted with 100 ml of 1-chloropropane under an atmosphere of nitrogen. After removing the solvent and unreacted chloride in partial vacuo, some 18.69 g of oil was obtained. The isolation of 1,1,1-triphenylbutane by recrystallization from 95 percent ethanol was unsuccessful.

A solution of propylmagnesium bromide in 180 ml of diethyl ether was prepared by the reaction of 18.35 g (0.1505 mole) of 1-bromopropane

(24) J. L. Greene, D. Abraham, and H. D. Zook, J. Org. Chem., 24, 132-4 (1959).

(25) K. Bowden, N. B. Chapman, and J. Shorter, J. Chem. Soc., 3372 (1964).

with 3.67 g (0.1505 g-atom) of magnesium turnings at reflux temperature under a nitrogen atmosphere. A solution of 29.6 g (0.106 mole) of chlorotriphenylmethane in 220 ml of diethyl ether was added dropwise to the Grignard reagent at 25° over a period of 40 minutes. After filtration, the ether solution was washed with water and evaporated to dryness to give 4.46 g of 1,1,1-triphenylbutane, m.p. 78-80° (reported²⁶ m.p. 79°).

Synthesis of 1,1,4-Triphenylbutane

The synthesis of this hydrocarbon was first attempted by reacting a solution of 3-phenylpropylmagnesium bromide in diethyl ether with a solution of benzhydryl chloride in diethyl ether. The resulting solution was stirred at reflux for one hour. Some 40.4 percent of 1,1,2,2-tetraphenylethane, m.p. 211-213°, was isolated. In another attempt to synthesize the hydrocarbon, the general procedure of Hauser¹⁵ was followed.

Diphenylmethyl potassium was prepared in liquid ammonia from a solution of 5.45 g (32.4 mmoles) of diphenylmethane in 30 ml of ether and potassium amide made from 1.52 g (0.0389 g-atom) of potassium with liquid ammonia. The red organopotassium compound was reacted with three-fourths of a solution of 3-phenylpropyl bromide (6.24 g, 31.4 mmole) in 30 ml of ether until the red color of the potassium diphenylmethane disappeared. After neutralization with solid ammonium chloride and separation from the aqueous fraction, the ether portion was evaporated to give 7.14 g of a light yellow oily material. Vapor-phase chromatography of this crude product showed the presence of two compounds. One of them constituted

(26) M. Gomberg and L. H. Cone, Ber., 39, 2957 (1906).

84 percent of the mixture and had a longer retention time than the starting diphenylmethane, which constituted the remaining 16 percent. The isolation of solid 1,1,4-triphenylbutane was unsuccessful (reported²⁷ m.p. 79°).

Synthesis of 1,1-Diphenylbutane

The synthesis of this hydrocarbon was carried out following the general method outlined by Hauser.¹⁵

In a 500 ml Morton flask fitted with a high-speed stirrer, a Dry-Ice-acetone condenser, and a dropping funnel, 220 ml of anhydrous ammonia was condensed. Under an atmosphere of nitrogen, 1.627 g (0.042 g-atom) of potassium was added in pieces over a period of 15 minutes. After the first piece of potassium had been added and dissolved, a small crystal of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to catalyze the formation of potassium amide. Every piece of potassium was added after the blue color of potassium in liquid ammonia had changed to grey-brown. The mixture was stirred at reflux for 35 minutes. A solution of 6.11 g of diphenylmethane in 30 ml of ether was added over a period of 15 minutes. The addition of the first portion of diphenylmethane caused the solution to turn red. The red solution was stirred at reflux for two hours. Approximately three-fourths of a solution of 4.61 g of 1-bromopropane in 30 ml of ether was added over a period of ten minutes, causing the red color to disappear. The resulting solution was stirred for two hours. Solid ammonium chloride (2 g, 0.04

(27) F. Bergmann, S. Israelashvili, and D. Gottlieb, J. Chem. Soc., 2522 (1952).

mole) was added to neutralize any unreacted potassium amide and the ammonia was allowed to evaporate from the mixture. The next day, the mixture was extracted three times with 150 ml portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, and allowed to evaporate to give 5.78 g of oily material. Vapor-phase chromatography showed that it contained 89 percent of conceivably 1,1-diphenylbutane and 11 percent of diphenylmethane. This compound has been reported as a liquid,²⁸ b.p. 145° (16 mm).

Synthesis of 1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene

This hydrocarbon was prepared by the procedure of Linstead and co-workers.²⁹ In the first attempt, 1.43 g of 1,1,4-triphenylbutanol was treated with 12 ml of 85 percent sulfuric acid at ice-water bath temperature for 30 minutes. At the end of the reaction, the mixture was poured into 50 ml of water and extracted with petroleum ether. The petroleum ether extract was washed with 85 percent sulfuric acid, followed by saturated sodium carbonate solution and water. The petroleum ether solution was evaporated to dryness to give some solid which was washed with absolute alcohol to give a 0.562 g yield of white crystals, m.p. 39-65° and a 0.47 g yield of light yellow crystals, m.p. 39-45°.

The preparation of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene was attempted by the same method except that 92 percent sulfuric acid was used

(28) V. N. Ipatieff, Herman Pines, and R. E. Schaad, J. Am. Chem. Soc., 66, 816-7 (1944).

(29) E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, J. Chem. Soc., 3127 (1960).

instead of 85 percent sulfuric acid. In a typical preparation, a sample of 0.4396 g of 1,1,4-triphenylbutanol was treated with 10 ml of cold 92 percent sulfuric acid and the reaction mixture was worked up as usual to give 0.1180 g (25 percent yield) of a white solid, m.p. 120-126°. In another preparation by the same method, 1.4 g of carbinol was reacted to give 1.3 g of oil which was recrystallized from absolute alcohol to give 0.1458 g of solid material, m.p. 120-125°. Vacuum sublimation at 60 microns pressure and 100° of 0.2338 g of the substance melting from 120-126° gave 0.169 g of white crystals, m.p. 122-125°. One recrystallization of this hydrocarbon from absolute alcohol gave 0.1198 g of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene, m.p. 125-126° (reported²⁹ m.p. 125°).

Synthesis of 1,1,2-Triphenylbutene-1

Methyl 2-Phenylbutanoate

This methyl ester was prepared following the procedure given in Organic Syntheses.¹⁷ The reaction of 24.54 g of 2-phenylbutanoic acid with 100 ml of methanol and 4 ml of concentrated H₂SO₄ at steam-bath temperature for 24 hours yielded 18.06 g of methyl 2-phenylbutanoate, b.p. 101-102° (12 mm)(reported b.p. 225-226°³⁰ and 228°³¹). Attempted recrystallization of a small portion of this methyl ester was unsuccessful. (A m.p. of 77-78° was reported by Mary M. Rising and Tsoh-Wu Zee.³⁰)

(30) Mary M. Rising and Tsoh-Wu Zee, J. Am. Chem. Soc., 50, 1211 (1928).

(31) K. Neure, Ann., 250, 140 (1888).

1,1,2-Triphenylbutene-1

The authentic sample of 1,1,2-triphenylbutene-1 was prepared from 1,1,2-triphenylbutanol-1 which was made from phenylmagnesium bromide and methyl 2-phenylbutanoate following the general method of C. F. H. Allen and S. Converse.³² In the usual apparatus for alkali-metal reactions was placed 10.8 g (0.443 g-atom) of magnesium turnings and a crystal of iodine, and 100 ml of anhydrous ether. A total of 69.14 g (0.442 mole) of bromobenzene and 50 ml of ether were added dropwise over a period of 65 minutes after a tenth part of the bromobenzene had been used for the initiation of the reaction. The reaction was initiated by heating with a small flame locally. After addition of the bromide was completed, the reaction mixture was stirred at reflux for two hours. Then 18.0 g (0.101 mole) of methyl 2-phenylbutanoate in 50 ml of dry ether was added over a period of 16 minutes and stirring at reflux was continued for an additional one and a half hours. After hydrolysis with an ammonium chloride solution (20 g of ammonium chloride in 60 ml of water at 25°), the combined ether extracts yielded 28.3 g of a solid material, m.p. 65-93°. A portion of 11.3 g of the crude carbinol prepared above was heated with 40 ml of 20 percent H₂SO₄ at an oil bath temperature of 150° for one hour. The reaction yielded 10.8 g (96 percent recovery) of somewhat impure 1,1,2-triphenylbutanol-1, m.p. 73-87° (identified by infrared spectrum). Some 2.83 g of this recovered carbinol was vacuum sublimed at 30 microns and 90° to give 2.21 g of white solid, m.p. 85.5-89.2°; 1.74 g was recrystal-

(32) Gilman and Blatt, Organic Syntheses, Collective Volume I, John Wiley & Sons, Inc., New York, 1948, p. 226.

lized from absolute ethanol to give 0.062 g of white crystals, m.p. 94-97° (mixed m.p. with the purified starting carbinol showed no depression). The mother liquor was evaporated to dryness to give 1.46 g of a solid which was subjected to vacuum sublimation at 200 microns and 190° to give 1.407 g of a solid, m.p. 91-93° (reported melting point for 1,1,2-triphenylbutanol-1: 93-94°).³³ Some 1.34 g of this sublimate was heated again with 5 ml of 30 percent H₂SO₄ at a bath temperature of 200° for two hours. After cooling to room temperature, 50 ml of water was added to the mixture and the solution was extracted with ether. The ether extracts were combined and evaporated to dryness to give 1.32 g of light yellow crystals; 1.30 g of this material was subjected to vacuum sublimation at 25 microns pressure and 105° bath temperature to give 1.19 g (94.4 percent yield based on 1,1,2-triphenylbutanol used) of 1,1,2-triphenylbutene-1, m.p. 79-82°. A sample of 0.759 g of this was recrystallized from absolute ethanol to give 0.388 g of essentially pure 1,1,2-triphenylbutene-1, m.p. 83-83.8° (reported³³ m.p. 80-81° and 91-92°³⁴). Two portions of 0.138 g, m.p. 82.5-83.5° and 0.127 g, m.p. 81-82°, were obtained from the mother liquor.

Synthesis of 1-Methyl-2,3-diphenylindene

1-Methyl-2,3-diphenylindene was prepared following the procedure of

(33) E. C. Dodds, L. Goldberg, E. I. Grunfeld, W. Lawson, C. M. Saffer, Jr., and Robert Robinson, Proc. Roy. Soc. (London), 132B, 95 (1944).

(34) I. A. D'yakonov and N. B. Vinogradova, Zhur. Obsheei Khim, 23, 244-251 (1953).

C. F. Koelsch and P. R. Johnson.³⁵

2,3-Dibromobutanoic Acid

In a 250 ml. round-bottomed flask, fitted with a condenser and a drying tube, was placed 11.51 g (0.134 mole) of crotonic acid and 70 ml of anhydrous ether. The mixture was stirred at 10 to 15° and 11.1 ml (0.134 mole) of bromine was added dropwise over a period of 30 minutes. The resulting brown solution was stirred at this temperature for 10 minutes and then the solvents were removed under reduced pressure. Some orange semi-solid remained and this was washed with light petroleum ether to give 21.90 g of light yellow crystals, m.p. 72-85°.

2,3-Diphenylbutanoic Acid

The above 21.80 g of crude dibromobutanoic acid was placed in a 1-l round-bottomed flask provided with a condenser and a drying tube. The dibromobutanoic acid was covered with 200 ml of dry benzene and 28 g of aluminum chloride was added. The resulting solution was stirred at reflux for one hour and then poured into 200 ml of water. After removing the solvent with steam, a light yellow tarry material was obtained and, after extraction with ether, gave 17.66 g of a yellowish semi-solid. A sample of 17.31 g of this crude product was recrystallized from benzene to give 4.47 g of a solid substance, m.p. 189-190° (reported³⁵ m.p. 182-183°).

3-Methyl-2-phenylindanone

A 4.46 g portion of 2,3-diphenylbutanoic acid prepared above was placed in a 250 ml round-bottomed flask and covered with 50 ml of benzene.

(35) C. F. Koelsch and P. R. Johnson, J. Am. Chem. Soc., 65, 571 (1943).

To the mixture was added 4.0 g of phosphorous pentachloride and the resulting mixture was refluxed for 15 minutes. Aluminum chloride (4.0 g) was added and the resulting mixture was refluxed for 30 minutes. The reaction mixture was poured into 100 ml of crushed ice and hydrochloric acid and extracted with two 50 ml portions of ether. The ether extracts were combined and washed with water and evaporated to dryness to give 4.10 g (0.0185 mole, 99.5 percent yield) of light yellow crystals. One recrystallization from methanol gave 2.88 g of soft amber crystals, m.p. 83-85° (reported³⁵ m.p. 84.5-86°).

1-Methyl-2,3-diphenylindene

A solution of 2.85 g of 3-methyl-2-phenylindanone, prepared above, in 50 ml of anhydrous ether was reacted with 30 ml of 1.138 M phenylmagnesium bromide* and the resulting solution was stirred at reflux for 15 minutes. After the container had been cooled with ice water, a solution of 1.5 g of ammonium chloride in 1 ml of water was added. The ether fraction was isolated and the remaining pasty material was dissolved in a five percent HCl solution and extracted with ether. The ethereal solutions were combined and washed with water and then evaporated to dryness. The resulting semi-solid was warmed at steam-bath temperature with 20 ml of one percent H₂SO₄ in glacial acetic acid for one hour then cooled with an ice bath. The solid material formed was isolated by filtration and washed with water to give 5.77 g of light yellow crystals, m.p. 99-103°. One recrystallization from absolute alcohol gave 1.25 g of cream colored

* The author is indebted to Simon Yu for his supply of this reagent.

soft crystals, m.p. 107-108.5° (reported³⁵ m.p. 106.5°).

Synthesis of 9-Phenyl-9-n-propylfluorene

9-Phenylfluorene

This hydrocarbon was prepared following the procedure of Kliegl.³⁶ The reaction of 21.04 g (0.0809 mole) of triphenylcarbinol with 47.88 g of 85 percent phosphoric acid gave 15.31 g (0.0633 mole, 78.2 percent yield) of orange solid, m.p. 138-144° (with premelting at 100°). One recrystallization from absolute alcohol gave 2.405 g of pink crystals, m.p. 148-150° (reported melting point for 9-phenylfluorene: 145.5°).

9-Phenyl-9-n-propylfluorene

This hydrocarbon was prepared following a modified general procedure of Hauser.³⁷ In the first attempt, to potassium amide, prepared from 0.777 g (0.0199 g-atom) of potassium in 200 ml of anhydrous commercial liquid ammonia under nitrogen atmosphere, was added 9-phenylfluorene (2.40 g, 9.94 mmole) in 100 ml anhydrous ether over a period of ten minutes. The orange colored solution was stirred for 20 minutes and a solution of 3.8 ml of n-propyl chloride in 50 ml ether was added dropwise over a period of 15 minutes. The resulting solution was stirred for another 20 minutes. Since no color change was observed, additional n-propyl chloride (10 ml) was added over a period of five minutes and stirring was continued for an additional 150 minutes. No obvious color change was observable. Solid

(36) A. Kliegl, Ber., 38, 284 (1905).

(37) W. S. Murphy and C. R. Hauser, J. Org. Chem., 31, 85 (1966).

ammonium chloride (1.07 g, 0.02 mole) was added and the resulting solution was stirred for 30 minutes. After removing ammonia, 200 ml of water was added to the residue and the mixture was extracted with ether to give 2.46 g of orange solid, m.p. 133-145°. One recrystallization of this orange solid from ethanol gave 1.714 g of essentially pure 9-phenylfluorene, m.p. 148-150°, and 0.186 g of less pure material, m.p. 146-148°.

In the second run, a solution of 1.667 g (0.00689 mole) of 9-phenylfluorene recovered from the previous run in 100 ml dry ether was added over a period of ten minutes into a solution of potassium amide prepared from 2.86 g (0.0733 g-atom) of potassium in 200 ml of dry ammonia. The resulting brown solution was stirred at reflux ammonia for 55 minutes, while no evidence of additional darkening in color was observable. A solution of 7.5 ml (0.0823 mole) of n-propyl bromide in an equal volume of anhydrous ether was then added dropwise over a period of 20 minutes. No obvious color change was observable. The resulting solution was stirred for another two hours, and, while there was no appreciable color change, dry ether (100 ml) was added and liquid ammonia was allowed to evaporate over a period of 55 minutes. Then, 10 ml more of n-propyl bromide was added and the color of the resulting solution seemed to gradually disappear over a period of ten minutes. Stirring was continued for another two and a half hours. Ammonium chloride (4.0 g, 0.074 mole) was added to decompose unreacted potassium amide. The usual work up gave 1.631 g of light yellow crystals (83.7 percent yield) which was washed with petroleum ether to give 0.896 g of white solid, m.p. 112-115° (some melted at 100°). From the petroleum ether solution was recovered 0.767 g of light yellow solid, m.p. 45-100°. The above 0.896 g of white solid was recrystallized from

ethanol to give 0.716 g of colorless crystals, m.p. 115-116°.

Reaction of 4-Chloro-1,1,1-triphenylbutane with Lithium at -60°

In run 1, the reaction of lithium with 4-chloro-1,1,1-triphenylbutane was carried out according to the procedure of Grovenstein and Williams.¹ Tetrahydrofuran (250 ml) was distilled from NaAlH_4 directly into a 500 ml Morton flask equipped with a Morton high-speed stirrer. Under an atmosphere of nitrogen, 0.63 g (0.090 g-atom) of lithium and 0.1 ml of methyl iodide were added. After cooling to -15° , about 4 ml of a solution of 8.86 g (0.0276 mole) of 4-chloro-1,1,1-triphenylbutane in 35 ml of dry tetrahydrofuran was added. The mixture turned pink after stirring at $-7 \pm 5^\circ$ for 37 minutes; the solution changed to orange in ten minutes. The temperature was lowered to -60° and the remainder of the chloride was added dropwise over a period of 15 minutes. The reaction mixture was stirred at $-60 \pm 5^\circ$ for three hours. The solution was allowed to warm to -40° and was stirred at this temperature for one hour; then the reaction mixture was forced onto pulverized solid carbon dioxide. The next day, 200 ml of water was added to decompose the remainder of the lithium and then the solvents were removed in vacuo at steam-bath temperature. The residue was extracted with ether and ether extract was evaporated to dryness to give 6.23 g of neutral material (approximately 2 g of the neutral material was lost due to spillage during evaporation), which was washed with pentane to give 4.06 g of solid, m.p. 126-131° (mixed m.p. with 4-chloro-1,1,1-triphenylbutane 128-130°). Acidification and extraction with ether gave, in the ether extract, 0.39 g of crude acids, m.p. 212-245°.

In run 2, reaction between 4-chloro-1,1,1-triphenylbutane and li-

thium metal at -60° was carried out on the same scale and by the same technique as in run 1. Approximately half of the chloride was lost during the reaction because of stopcock loosening. The remainder of the chloride was added at -50° over a period of 10 minutes. The reaction mixture was stirred at -58° for three hours and 15 minutes before carbonation. After removing the unreacted lithium by filtration, 200 ml of water was added and the reaction mixture was worked up in the same manner as the first run. The yield was 3.03 g of neutral material and 1.22 g of acidic material, m.p. $180-230^{\circ}$. One recrystallization of the acidic material from benzene gave 0.864 g of acid, m.p. $222-225^{\circ}$ (with decomposition); a second recrystallization from benzene yielded 0.609 g of acid, m.p. $221-224^{\circ}$ (with decomposition). A 0.247 g portion of this acid was recrystallized from 95 percent ethanol followed by vacuum sublimation at 50 microns pressure and at 180° oil-bath temperature to give 0.139 g of acid, m.p. $221-223.5^{\circ}$ (with decomposition). Another sample of 0.362 g was recrystallized from benzene to give 0.113 g of the material, m.p. $223-224^{\circ}$ (with decomposition). [Mixed m.p. of this acid with authentic 5,5,5-triphenylpentanoic acid: $223-224^{\circ}$ (soften ca. 220°)]

In run 3, a small portion of 7.53 g (0.0235 mole) of 4-chloro-1,1,1-triphenylbutane in 35 ml of tetrahydrofuran and 0.20 ml of methyl iodide were added to 0.51 g of lithium in 250 ml of tetrahydrofuran. After 78 minutes of stirring at $-5 \pm 5^{\circ}$, the solution turned pink and then red. The stirring was continued at -5° for three hours and 43 minutes. The reaction temperature was lowered to -60° and the remainder of the chloride was added over a period of 25 minutes. Stirring was continued for an ad-

ditional three hours at $-60 \pm 5^\circ$. The reaction mixture was then allowed to warm with stirring to $-5 \pm 5^\circ$ and stirred at 0° for two hours before carbonation. The usual workup yielded 1.28 g of acidic material, m.p. $207-220^\circ$ and 7.21 g of neutral material. One recrystallization of the acidic material from benzene gave 0.489 g of acid, m.p. $217-223^\circ$ (mixed m.p. of this acid with that obtained in the second run showed no depression). A second recrystallization of 0.395 g of this acid from benzene gave 0.249 g of acid, m.p. $217-222^\circ$. One recrystallization of the neutral material from acetone gave 1.35 g of white crystals, m.p. $115-124^\circ$.

In run 4,* about one-tenth of 10.0 g (0.0311 mole) of 4-chloro-1,1,1-triphenylbutane in 70 ml tetrahydrofuran and 0.20 ml of methyl iodide were added to 0.644 g (0.0925 g-atom) of lithium in 250 ml of tetrahydrofuran at -10° . The mixture was stirred at $-5 \pm 5^\circ$ for four hours and 40 minutes and a pale color appeared. The reaction temperature was lowered to -60° and the remainder of the chloride was added over a period of 40 minutes. Stirring was continued for four more hours. The reaction mixture was then allowed to warm to 25° and stirred at $25 \pm 2^\circ$ for two hours followed by carbonation. This reaction yielded 9.11 g of neutral material and 0.373 g of acidic material. This 0.373 g of acidic material was methylated with diazomethane and analyzed by vapor-phase chromatography. The chromatography showed that the acidic material contained 45.3 percent 5,5,5-triphenylpentanoic acid and 11.7 percent of an acid which was not triphenylacetic acid. Another major component,

* The flask was previously flame-dried under a stream of dry nitrogen.

which constituted 17.3 percent of the acidic material, was found not to be 2,2,5-triphenylpentanoic acid. The vapor-phase chromatography of the above 9.11 g of neutral material showed it contained 86.5 percent 1,1,1-triphenylbutane, 10.11 percent 4-chloro-1,1,1-triphenylbutane and 3.38 percent 1,1,4-triphenylbutane or 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (see Table 1). The identifications are based on VPC method A.* A sample of 2.04 g of this neutral material was vacuum sublimed at 10 microns and 103° to give 1.23 g of white solid material, m.p. 55-74°. One recrystallization of a sample of 1.13 g of this solid material from absolute ethanol gave 0.675 g of colorless crystals, m.p. 74-79°. Second recrystallization of a sample of 0.520 g from absolute ethanol gave 0.433 g, m.p. 77-79°. This purified hydrocarbon was further identified as 1,1,1-triphenylbutane by comparisons of m.p., mixed m.p., and infrared spectrum with an authentic sample.

Reaction of 4-Chloro-1,1,1-triphenylbutane with Potassium
and Sodium-Potassium Alloy

In run 1, into a 500 ml Morton flask (previously flame dried under a stream of dry nitrogen), equipped with a Morton high-speed stirrer, a Vigreux column, and a dropping funnel, was distilled from lithium aluminum hydride 250 ml of tetrahydrofuran, which had been previously dried over sodium wire. To the flask was added 3.44 g (0.0882 g-atom) of freshly cut potassium metal. The apparatus was kept under a nitrogen atmosphere. The solvent was heated to the boiling point, stirring was started, and

* See Instrumental Analyses.

Table 1. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Lithium in Tetrahydrofuran at 25° (Run 4)

Relative Retention Time	Area, Percent	Code No. (Method)	Identification	(Method)
A. Acidic Material (as Methyl Esters)				
0.300	3.70	[4] (A)		
0.375	17.27	[5] (B)		
0.400		[6] (B)		
0.475		[8] (B)		
0.575		[9] (B)		
0.725	2.47	[10] (B)		
1.000	11.73	[11] (A)		
1.675	17.27	[13] (A)	Not 2,2,5-Triphenylpentanoic Acid	(A)
2.075	46.30	[15] (A)	5,5,5-Triphenylpentanoic Acid	(A)

VPC conditions used: Temperature, 289°; Flow A, 24 mm; Pressure 30 lb/in²

B. Neutral Material

1.000	86.52	[28] (A)	1,1,1-Triphenylbutane	(A)
1.34	3.37	[31] (A)	1,1,4-Triphenylbutane or 1,1-Diphenyltetrahydronaphthalene	(A)
1.87	10.11	[32] (A)	4-Chloro-1,1,1-triphenylbutane	(A)

VPC conditions used: Temperature, 272°; Flow A, 33 mm; Pressure 30 lb/in²

the mixture was refluxed for 50 minutes. A solution of 10.08 g (0.0314 mole) of 4-chloro-1,1,1-triphenylbutane in 70 ml of dry tetrahydrofuran was then added over a period of 10 minutes. The first portion of the halide added caused the solution to turn a deep red which then changed to a final color, which was like that of bromine. After cooling to room temperature in ten minutes, the contents of the flask were forced onto a large excess of crushed solid carbon dioxide. A 300 ml portion of absolute ethanol was added to destroy any unreacted potassium. The next day, solvents were removed under partial vacuo and the residue was extracted with ether. The ether extract was evaporated to dryness to give 9.49 g of a white semi-solid. Gas chromatography of this neutral fraction showed it contained 83.8 percent of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene, 14.2 percent of 1,1,1-triphenylbutane, 0.78 percent of 1,1-diphenylbutane, and 0.39 percent of triphenylmethane. The identifications of the first two compounds were performed by VPC method A; the latter two compounds were identified by VPC method B* (see Table 2). The possible presence of 1,1,4-triphenylbutane cannot be excluded because this compound has the same retention time as 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene and a mixture of equal quantity of these two compounds shows only one peak under the VPC conditions investigated.

The aqueous portion was acidified with 10 percent HCl. Ether extraction gave 1.08 g of an oily acid mixture which was converted into the methyl esters and analyzed by vapor-phase chromatography (see Table 2). This chromatography showed that the acidic material contained only

* See Instrumental Analyses.

Table 2. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Potassium in Refluxing Tetrahydrofuran (Run 1)

Relative Retention Time	Area, Percent	Code No. (Method)	Identification	(Method)
A. Acidic Material as Methyl Esters				
0.381	0.76	[5] (A)	Diphenylacetic Acid	(A)
0.524	4.53	[8] (A)	2,2-Diphenylpentanoic Acid	(A)
0.583	46.72	[9] (A)		
0.667	5.02	[10] (A)		
1.000	2.66	[12] (A)	Triphenylacetic Acid	(A)
1.618	1.14			
1.785	5.70	[14]	2,2,5-Triphenylpentanoic Acid	(A)
2.095	28.50	[16] (A)		
2.955	4.94	[18] (A)		
VPC conditions: Temperature, 284°; Flow A, 24 mm; Pressure, 30 lb/in ²				
B. Neutral Material				
0.41	0.78	[24] (B)	1,1-Diphenylbutane	(B)
0.65	0.39	[26] (B)		
1.00	14.23	[28] (A)	1,1,1-Triphenylbutane	(A)
1.33	83.79	[31] (A)	1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene (and possible 1,1,4-triphenylbutane)	(A)
VPC conditions: Temperature, 272°; Flow A, 33 mm; Pressure, 30 lb/in ²				

4.5 percent 2,2-diphenylpentanoic acid, 27 percent triphenylacetic acid and 5.7 percent 2,2,5-triphenylpentanoic acid. The identifications were performed by VPC method A.* A sample of 7.31 g of the neutral material was vacuum sublimed at 300 microns pressure and 102° to give 3.71 g of white solid, m.p. 80-115°. One recrystallization of 1.89 g of this hydrocarbon from absolute ethanol gave 1.108 g of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene, m.p. 125-126° (reported²⁹ m.p. 125°). This compound was further confirmed by m.p., mixed m.p., and infrared spectral comparisons with an authentic sample prepared by the method of Linstead²⁹ and nuclear magnetic resonance spectroscopy. Nuclear magnetic resonance spectrum of the isolated hydrocarbon showed 15.3 hydrogen atoms at 2.88 τ (aromatic), 4.2 hydrogen atoms at 7.3 τ (methylene) and 2.6 hydrogen atoms at 8.3 τ (methylene).

In run 2, tetrahydrofuran (300 ml) was distilled from sodium aluminum hydride into the usual apparatus (previously flame-dried under a stream of dry nitrogen) for organoalkali metal reactions. To the flask was added 3.3 g (0.0085 g-atom) of freshly cut potassium metal. The apparatus was kept under an atmosphere of nitrogen. The solvent was heated to the boiling point, stirring was started, and the mixture was refluxed for 45 minutes. A solution of 10.0 g (0.0311 mole) of 4-chloro-1,1,1-triphenylbutane in 75 ml of tetrahydrofuran was added dropwise over a period of 30 minutes. (The first half of the halide added caused the solution to turn deep red and the final color was like that of bromine.) The resulting solution was stirred at reflux for 75 minutes and then al-

* See Instrumental Analyses.

lowed to cool to room temperature before carbonation. The next day, 250 ml of 95 percent ethanol was added to destroy unreacted potassium. After removing the solvents in partial vacuo, some brown oily material was obtained which was acidified with 10 percent HCl and extracted with one 250 ml and three 150 ml portions of ether. The ethereal extracts were combined and extracted with one 150 ml, one 100 ml, and two 70 ml portions of five percent sodium hydroxide solution. During the extractions some oily material appeared between the two main phases and was insoluble in either phase.

The aqueous portion was acidified and extracted with ether to give some brown oily material which was recrystallized from benzene and pentane to give 0.187 g of grey solid, m.p. 263-285° (with decomposition), 0.83 g light yellow solid, m.p. 130-160°, 0.258 g orange colored solid, m.p. 154-160°, and 1.18 g of tarry material. A sample of 0.64 g of the solid with m.p. 130-160° was recrystallized from benzene to give 0.061 g of white solid, m.p. 285-286° (with decomposition).

The oily material which was between the neutral ether layer and the acidic aqueous layer was acidified with 10 percent HCl and extracted with ether to give 4.82 g of brown tarry material. Recrystallizations of this tarry material from cyclohexane gave 0.40 g of brown solid, m.p. 115-130°, 0.018 g of white solid, m.p. 285-295°, and 1.1 g of yellow solid, m.p. ca. 90°. The vapor-phase chromatography of a mixture of equal proportion of each of these fractions showed that it contained 5.5 percent of triphenylacetic acid, 3.3 percent of 2,2,5-triphenylpentanoic acid, 16.0 percent of an acid which was proved to be not 5,5,5-triphenylpentanoic acid, and 38.1 percent of an acid which had a higher retention time than

that of 5,5,5-triphenylpentanoic acid. The identifications were performed by VPC method A.*

In run 3, liquid sodium-potassium alloy was prepared in the usual apparatus** from 10.3 g of potassium and 3.1 g of sodium in 250 ml of tetrahydrofuran, heated at reflux with stirring. The mixture was cooled to ice bath temperature (approximately 15°) and a solution of 10.0 g (0.0311 mole) of 4-chloro-1,1,1-triphenylbutane in 70 ml of tetrahydrofuran was added over a period of 40 minutes. The first portion of halide added caused the solution to change from grey to red and finally to a color like that of bromine. The mixture was stirred at ice bath temperature for an additional hour and then carbonated. The usual work-up of the reaction mixture yielded 3.00 g of a light yellow sticky neutral material and 3.64 g of an acidic material (some 3.4 g of acidic material was lost because of spillage during evaporation of the solvents). The above 3.00 g of hydrocarbon was analyzed by vapor-phase chromatography and found to contain 31.5 percent 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene and/or 1,1,4-triphenylbutane, 15.0 percent unreacted 4-chloro-1,1,1-triphenylbutane (VPC method A*). A sample of 0.742 g of the acidic material was esterified with diazomethane and analyzed by vapor-phase chromatography. This chromatography showed that the acidic material contained 21.9 percent 2,2-diphenylpentanoic acid, 3.7 percent triphenylacetic acid and 5.5 percent 2,2,5-triphenylpentanoic acid (VPC method A*)(see Table 3).

* See Instrumental Analyses.

** Previously flame-dried under a stream of dry nitrogen.

Table 3. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Sodium-Potassium Alloy in Tetrahydrofuran at 15° (Run 3)

Relative Retention Time	Area, Percent	Code No. (Method)	Identification	(Method)
A. Acidic Material (as Methyl Esters)				
0.16 } 0.18 } 0.21 } 0.32 }	1.22			
0.39	0.61	[6] (B)		
0.45	21.95	[8] (A)	2,2-Diphenylpentanoic Acid	(A)
0.52	38.40	[9] (A)		
0.62	15.85	[10] (A)		
0.84	0.61			
1.00	3.66	[12] (A)	Triphenylacetic Acid	(A)
1.96	5.49	[14] (A)	2,2,5-Triphenylpentanoic Acid	(A)
2.30	12.19	[16] (A)	Not 5,5,5-Triphenylpentanoic Acid	(A)
VPC conditions used: Temperature, 272°; Flow A, 33 mm; Pressure 30 lb/in ²				
B. Neutral Material				
0.21 } 0.22 }	35.2	[21] (B) [22] (B)		
0.57	2.9	[25] (B)	Triphenylmethane	(B)
0.67	1.9	[26] (B)		
0.89	4.8	[27] (B)		
1.00	Trace	[28] (B)	1,1,1-Triphenylbutane	(B)
1.34	31.5	[31] (A)	1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene*	(A)
1.77	15.0	[32] (A)	4-Chloro-1,1,1-triphenylbutane	(A)
VPC conditions used: Temperature, 272°; Flow A, 33 mm; Pressure 30 lb/in ²				

* The possible presence of 1,1,4-triphenylbutane could not be excluded because this compound has the same retention time as 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene and a mixture of equal quantity of these two compounds shows only one peak under the VPC conditions investigated.

Reaction of 4-Chloro-1,1,1-triphenylbutane with Cesium
and Cesium-Potassium Alloy

The apparatus* and general procedure for conducting the reactions with cesium were similar to those for the potassium experiments. In run 1, into 250 ml of freshly distilled tetrahydrofuran was placed 4.09 g (0.0308 g-atom) of cesium metal. The solution was blue when stirring was started. The solvent was heated to 50° over a 50 minute period and was stirred at 40 ± 5° for 35 minutes; 5.01 g (15.6 mmole) of 4-chloro-1,1,1-triphenylbutane was dusted into the reaction mixture over a period of four minutes at 33°. The first portion of the halide added caused the solution to turn brown and finally dark red. The mixture was stirred at 40° for an additional 11 minutes before carbonation. The next day, 200 ml of water was added and the mixture was worked up in the usual manner to give 1.22 g of acidic material and 3.98 g of neutral product. A sample of 0.141 g of the acidic material was converted into methyl esters and subjected to vapor-phase chromatography. The acidic material contained 6.4 percent 2,2-diphenylpentanoic acid, 4.8 percent triphenylacetic acid, and 6.1 percent 2,2,5-triphenylpentanoic acid. The above 3.99 g of neutral material was analyzed by vapor-phase chromatography and found to contain 45.1 percent 1,1,1-triphenylbutane, 35.3 percent 9-phenyl-9-n-propylfluorene, and 7.84 percent 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene or 1,1,4-triphenylbutane (see Table 4). The identifications were performed by VPC method A.**

* Previously flame-dried under a stream of dry nitrogen.

** See Instrumental Analyses.

Table 4. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-Triphenylbutane and Cesium in Tetrahydrofuran at 35° (Run 1)

Relative Retention Time	Area, Percent	Code No. (Method)	Identification	(Method)
A. Acidic Material (as Methyl Esters)				
0.34	1.61	[5] (B)	Diphenylacetic	(B)
0.40	6.45	[8] (A)	2,2-Diphenylpentanoic Acid	(A)
0.66	3.22	[10] (A)		
1.00	4.84	[12] (A)	Triphenylacetic Acid	(A)
1.61	26.45	[13] (A)		
1.90	6.12	[14] (A)	2,2,5-Triphenylpentanoic Acid	(A)
2.25	35.15	[17]		
3.08	16.13	[19]		
VPC conditions used: Temperature, 278°; Flow A, 33 mm; Pressure, 30 lb/in ²				
B. Neutral Material				
0.21	6.65	[21] (A)		
0.42	5.11	[23] (A)	{ Not 1,1-Diphenylbutane conceivably 9-Propylfluorene*	(A)
1.000	45.10	[28] (A)		1,1,1-Triphenylbutane
1.050	35.30	[29] (A)	9-Phenyl-9-n-propylfluorene	(A)
1.425	7.84	[31] (A)	1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene (or 1,1,4-triphenylbutane)	(A)
VPC conditions used: Temperature, 273°; Flow A, 31-35 mm; Pressure 30 lb/in ²				

* Compound unavailable for confirmation.

In run 2, liquid cesium-potassium alloy was prepared in the usual apparatus (previously flame-dried under a stream of dry nitrogen) from 1.16 g of potassium and 3.93 g of cesium in 250 ml of tetrahydrofuran, heated at reflux with stirring. The solution changed from blue to greenish-black when the heating commenced. After heating at $39 \pm 5^\circ$ for one hour, the mixture was cooled to 30° and 4.45 g (13.9 mmole) of the chloride in 50 ml of dry tetrahydrofuran was placed in the dropping funnel attached to one of the side arms of the reaction vessel. The apparatus was swept with dry nitrogen for five minutes and then the mixture was cooled to -25° in 16 minutes. As the chloride solution was added dropwise over a period of 30 minutes, the solution turned red and this color developed into a color like that of bromine. The stirring was continued at $-25 \pm 3^\circ$ for an additional 34 minutes before carbonation. The next day, 50 ml of absolute ethanol was added to decompose unreacted metals and the mixture was worked up in the usual manner to give 0.787 g of neutral material, and some oily acidic material which gave, after seven hours of drying in a vacuum desiccator, 4.15 g of light yellow powder, m.p. $70-160^\circ$.

This acidic material and the neutral material were analyzed by vapor-phase chromatography and the results are given in Table 5. A sample of 3.7 g of this acidic material was converted into the methyl esters by diazomethane and subjected to preparative vapor-phase chromatographic separation to give as a first fraction 0.1 g of an oily material, which was not further investigated. A second fraction (retention time related to methyl triphenylacetate: 0.40) of 0.30 g, m.p. $90-105^\circ$, was vacuum sublimed at 60 microns and 67° to give 0.22 g of colorless crystals, m.p. $106-112^\circ$ (premelted at ca. 93°). Several recrystallizations of this methyl

Table 5. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at $-25 \pm 3^\circ$ (Run 2)

Relative Retention Time	Area, Percent	Code No. (Method)	Identification	(Method)
A. Acidic Material (as Methyl Esters)				
0.15	8.43	[1]	4-Phenylbutanoic Acid	(B)
0.21	11.23	[2]		
0.28	3.27	[4] (A)	Not diphenylacetic Acid	(A)
0.40	33.35	[7] (A)	Not 2,2-Diphenylpentanoic Acid	(A)
1.00	10.83	[12] (A)	Triphenylacetic Acid	(A)
2.02	14.05	[14] (A)	2,2,5-Triphenylpentanoic Acid	(A)
2.45	7.63	[16] (A)	Not 5,5,5-Triphenylpentanoic Acid	(A)
2.83	2.05	[18] (A)		
5.75	9.24	[20] (A)		
VPC conditions used: Temperature, 273° ; Flow A, 33 mm; Pressure, 30 lb/in ²				
B. Neutral Material				
0.21	2.10	[21] (A)	Diphenylmethane	(B)
0.22	1.15	[22] (A)		
0.40	54.5	[23] (A)	Not 1,1-Diphenylbutane Conceivably 9-Propylfluorene*	(A)
0.58	1.63	[25] (B)	Triphenylmethane	(B)
0.64	1.63	[26] (B)		
0.88	0.81	[27] (B)		
1.00	21.0	[28] (A)	1,1,1-Triphenylbutane	(A)
1.05	8.25	[29] (A)	9-Phenyl-9-n-propylfluorene	(A)
1.33	8.94	[31] (A)	1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene (or 1,1,4-Triphenylbutane)	(A)
VPC conditions used: Temperature, 274° ; Flow A, 33 mm; Pressure 30 lb/in ²				

* Compound unavailable for confirmation.

ester [7] from absolute alcohol gave 0.11 g of sheet-like colorless crystals, m.p. 118.5-119.5°. A purified sample of melting point 119.0-119.8° was analyzed for C,H contents and molecular weight..

Anal. * Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70; Mol. Wt. 212. Calcd. for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39; Mol. Wt. 224. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.25; Mol. Wt. 226.

Found: C, 79.43; H, 5.85; Mol. Wt. 204.

A third fraction (retention time 4.7, relative retention time 1.00, compound [12]) of 0.18 g of glassy material was recrystallized from ethanol-pentane to give 0.026 g, m.p. 187-189° which after further purification was identified as methyl triphenylacetate by comparisons of m.p., mixed m.p. with an authentic sample, and nuclear magnetic resonance. Nuclear magnetic resonance showed that it had 14.5 hydrogen atoms at 2.6 τ (aromatic) and 3.5 hydrogen atoms at 6.0 τ (methoxy). A fourth fraction of 1.18 g of oily material was subjected to a second preparative vapor-phase chromatographic separation to give six fractions, among which only the last fraction of 0.082 g, m.p. 140-179°, was purified to give 0.018 g, m.p. 192.5-196°.

In run 3, liquid cesium-potassium alloy prepared as above from 4.65 g of cesium and 1.29 g of potassium was treated in 250 ml of tetrahydrofuran at -30° with 4.51 g of solid 4-chloro-1,1,1-triphenylbutane by adding the latter to the solution over a period of 10 minutes. The chloride was not completely dissolved. The stirring was continued at $-26 \pm 3^\circ$ for an addi-

* Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

tional 70 minutes and then the mixture was forced onto crushed solid carbon dioxide. The usual work-up gave 0.804 g of neutral material and 1.06 g of acidic material. About two-thirds of the acidic material was lost because of spillage during the ether extractions. Vapor-phase chromatographic analyses of the neutral material and the acidic material (as methyl esters) are given in Table 6.

In run 4 of the cesium metal reaction,^{*} 5.89 g (0.0443 g-atom) of cesium metal in 250 ml of tetrahydrofuran was heated to 48° with stirring for one hour and then cooled to -10°; the solution was blue when the temperature was 32° and it turned a yellowish green at higher temperatures. A 1.48 g (5.93 g-atom) portion of potassium was added in four pieces at -10° and the apparatus was swept with nitrogen. The mixture was heated to 54° and stirred at $46 \pm 4^\circ$ for one hour and then the temperature was lowered to -40° in 35 minutes. A solution of 5.93 g (18.5 mmole) of the chloride in 30 ml ether solution was added over a period of 30 minutes and stirring was continued at $-41 \pm 4^\circ$ for 30 minutes before carbonation. The addition of the first portion of the halide turned the solution deep red. Near the middle of the halide addition, some tiny particles of metal were observed. The mixture was brown and became viscous below -35°. The usual work-up gave 5.51 g of acidic material and 0.846 g of neutral material. Vapor-phase chromatographic analysis of the acids (as methyl esters) is given in Table 7.

In run 5, the reaction^{*} of 6.12 g of 4-chloro-1,1,1-triphenylbutane

* The flask was previously flame-dried under a stream of dry nitrogen.

Table 6. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at $-26 \pm 3^\circ$ (Run 3)

Relative Retention Time	Area, Percent	Code No. (Method)	Identification	(Method)
A. Acidic Material (as Methyl Esters)				
0.20	7.77	[1] (B)	4-Phenylbutanoic Acid	(B)
0.22	3.02			
0.25	7.34			
0.28	1.72	[4] (B)		
0.31	0.90			
0.37	1.29			
0.45	23.73	[7] (A)	Not 2,2-Diphenylpentanoic Acid	(A)
0.64	0.65			
0.75	0.65			
1.00	3.89	[12] (A)	Triphenylacetic Acid	(A)
1.26	0.97			
1.82	0.97			
1.96	19.46	[14] (A)	2,2,5-Triphenylpentanoic Acid	(A)
2.36	8.44	[16] (A)		
3.18	1.30			
3.95	7.14			
5.15	10.72	[20] (B)		

VPC conditions used: Temperature, 273° ; Flow A, 33 mm; Pressure, 30 lb/in²

Table 6. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at $-26 \pm 3^\circ$ (Run 3) (Concluded)

Relative Retention Time	Area, Percent	Code No. (Method)	Identification	(Method)
B. Neutral Material				
0.18 } 0.24 }	7.86			
0.29	2.24			
0.41	47.15	[23] (A)	Not 1,1-Diphenylbutane conceivably 9-propyl-fluorene*	(A)
0.56	3.37	[25]		
0.66	16.85	[26]	Triphenylmethane	(A)
0.88	2.24	[27] (B)		
1.00	6.74	[28] (A)	1,1,1-Triphenylbutane	(A)
1.07	3.37	[29] (B)	9-Ph-9-n-pr-fluorene	(B)
1.32	10.11	[31] (A)	1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene (or 1,1,4-triphenylbutane)	(A)

VPC conditions used: Temperature 273° ; Flow A, 33 mm; Pressure 30 lb/in²

* Compound unavailable for confirmation.

Table 7. Vapor-Phase Chromatographic Analysis of the Methyl Esters of the Acidic Material Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at $-41 \pm 4^\circ$ (Run 4)

Relative Retention Time	Area, Percent	Code No. (Method)	Identification	(Method)
0.31	0.28			
0.40	3.04		2,2-Diphenylpentanoic Acid	(A)
0.50	0.41			
0.62	0.14			
1.00	13.81	[12] (B)	Triphenylacetic Acid	(A)
1.46	0.14			
1.70	1.24			
2.14	27.64	[14] (B)	2,2,5-Triphenylpentanoic Acid	(A)
2.60	32.05	[16] (B)		
2.90	5.53	[18] (B)		
3.20	1.80			
3.60	1.10			
4.00	1.10			
4.60	3.87			
5.20	1.10	[20] (B)		
6.10	6.77			

VPC conditions used: Temperature 275° ; Flow A, 33 mm; Pressure 30 lb/in²

with cesium-potassium alloy made from 5.72 g of cesium and 1.47 g of potassium was carried out in the usual manner at -40° . The deep colored solution was stirred at $-42 \pm 2^{\circ}$ for 40 minutes and then 50 ml of methanol was added in one minute; the red solution cleared immediately. An additional 4 ml portion of methanol was added to the mixture and stirring was continued at -50° for 30 minutes. The next day, 100 ml of water was added to the reaction mixture and the mixture was extracted with ether to give 5.64 g of crude product (92.14 percent yield). Vapor-phase chromatography of this mixture showed the presence of eight compounds, among which the peaks of the four major components overlapped with each other (see Table 8). Compound [28] was confirmed to be 1,1,1-triphenylbutane and compound [31] was confirmed to be either 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (and/or 1,1,4-triphenylbutane) by VPC method A.*

One dehydrogenation of 0.257 g of this mixture by heating with 0.029 g of sulfur in 15 ml of dimethyl formamide at reflux for five and one-half hours was attempted. After washing with water, the organic fraction was evaporated to give 0.194 g of brown tar. This mixture was analyzed by vapor-phase chromatography and found to contain essentially every compound in the original mixture except [29]. Another attempted dehydrogenation of the above reaction mixture was carried out treating 0.209 g of the mixture in 10 ml of m-dibromobenzene at 215° with 0.16 ml of 2.49 percent (by volume) bromine solution in m-dibromobenzene for five minutes, followed by heating at 215° for two and a half hours. After extracting with 10 percent

* See Instrumental Analyses.

Table 8. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at -42° Followed by Addition of Methanol (Run 5)

Retention Time (Minutes)	Area, Percent	Code No. (Method)	Identification	(Method)
1.9	1.0			
3.1	0.6			
4.6	0.4			
5.4	0.2			
7.4	1.2			
9.2	0.8			
10.5	31.8	[28] (A)	1,1,1-Triphenylbutane	(A)
10.9	30.3	[29] (A)	9-Phenyl-9-n-propylfluorene	(A)
11.5	20.2	[30] (B)	conceivably 9-Phenyl-9-n-propyldihydrofluorene	
11.8	8.0	[31] (A)	1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene (or 1,1,4-Triphenylbutane)	(A)

VPC conditions: Temperature, 250° -4 min; 250° to 300° at $10^{\circ}/\text{min}$; 300° -12 min; Flow A, 35 mm; Pressure, 50 lb/in²

sodium bicarbonate and washing with water, the organic fraction was analyzed by vapor-phase chromatography and it was found to contain the same major components as prior to treatment with bromine but in a different composition (most of [29] disappeared). This mixture was again treated with 0.3 ml more of 2.5 percent bromine solution in m-dibromobenzene for an additional two and a half hours at 216°. Vapor-phase chromatography showed no further change in composition. This mixture was mixed with another batch of reaction mixture obtained from the treatment of 0.103 g of the protonation mixture with the same bromination solution at reflux temperature for 24 hours. This mixture was evaporated to give 0.288 g of brown tar. This tar was combined with 0.186 g of the reaction mixture obtained in the sulfur reaction mentioned above. The mixture was vacuum sublimed at 100° and 50 microns pressure to give 0.206 g of a semi-solid. One recrystallization of 0.152 g of this vacuum sublimate from absolute ethanol gave 0.036 g of light yellow crystals, m.p. 113.0-113.8° (with premelting at 105°).

In run 6, a solution of 6.65 g (20.7 mmole) of 4-chloro-1,1,1-triphenylbutane in 30 ml of tetrahydrofuran was reacted with cesium-potassium alloy made from 6.39 g (0.0480 g-atom) of cesium and 1.61 g (0.0411 g-atom) of potassium at -45° in the usual manner* except approximately 10 percent of the halide was accidentally added to the container at room temperature before the reflux of the solvent. The reaction mixture was stirred at $-45 \pm 3^\circ$ for 30 minutes and then forced into 110 ml of

* The flask was previously flame-dried under a stream of dry nitrogen.

methanol in a Dry-Ice-acetone bath at -55° . The temperature of both the reaction vessel and the flask containing methanol was increased to approximately -30° due to the delay in operation. The mixture was neutralized with a five percent HCl solution. The usual work-up gave 4.95 g of white oily material. This crude product was analyzed by vapor-phase chromatography and the results are given in Table 9. A sample of 0.346 g of this crude product was vacuum sublimed at 40 microns pressure and $100-130^{\circ}$ to give 0.233 g of sublimate, 0.199 g of which was recrystallized from absolute ethanol to give 0.0390 g of crystals, m.p. $112.5-113.3^{\circ}$ (premelting ca. 107°) and 0.0308 g of pale yellow crystals, m.p. $113-115^{\circ}$. Vacuum sublimation of another 3.44 g of the reaction mixture at 100° and 10 microns gave 2.69 g of volatile material. One recrystallization of 1.90 g of this sublimate from absolute ethanol gave 0.843 g of a mixture of colorless and light yellow crystals, m.p. $108-114^{\circ}$. A sample of 0.174 g of this crystalline material was subjected to vacuum sublimation at 100° and 10 microns to give 0.163 g of white crystals, m.p. $110-113^{\circ}$, of which 0.156 g was recrystallized from absolute ethanol to give 0.0357 g of colorless crystals, m.p. $114.5-115.3^{\circ}$. A fairly pure compound, 0.0968 g, m.p. $114.3-115.3^{\circ}$ (with premelting $\sim 113^{\circ}$), was recovered from the mother liquor. A 0.0234 g sample of the material with m.p. $115-115.8^{\circ}$ (compound [29]) was used for C,H analysis.

Anal. * Calcd. for $C_{22}H_{20}$: C, 92.93; H, 7.09; Mol. Wt., 284.

* Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Table 9. Vapor-Phase Chromatographic Analyses of Products Resulting from Reaction of 4-Chloro-1,1,1-triphenylbutane and Cesium-Potassium Alloy in Tetrahydrofuran at -30° to -45° Followed by Addition of Methanol (Run 6)

Retention Time (Minutes)	Area, Percent	Code No. (Method)	Identification	(Method)
1.9	2.6			
3.1	1.1			
4.6	3.3			
7.4	1.9			
10.5	9.5	[28] (A)	1,1,1-Triphenylbutane	(A)
10.9	54.7	[29] (A)	9-Phenyl-9-n-propylfluorene	
11.5	15.0	[30] (B)	conceivably 9-Phenyl-9-n-propyldihydrofluorene	
11.8	10.9	[31] (A)	1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene (or 1,1,4-triphenylbutane)	(A)

VPC conditions: Temperature, 250° -4 min; 250° to 300° at 10/min; 300° -12 min; Flow A, 35 mm; Pressure 50 lb/in²

Found: C, 93.37; H, 6.76; Mol. Wt., 268. (Molecular weight by mass spectrometer, * 284)

The nuclear magnetic resonance spectrum of compound [29] showed a broad unsymmetrical peak at 9.15-9.45 τ , which is assigned to an ethyl group, a peak at 7.6-8.0 τ , which is assigned to the methylene group (a peak at 7.3-7.5 τ was found in the present work for the methylene group at C-2 in 1,1,1-triphenylbutane) adjacent to the 9-phenylfluorene nucleus, as well as complex absorption of aromatic hydrogens (see Table 10 in Chapter V).

Compound [29] was finally identified as 9-phenyl-9-n-propylfluorene by comparisons of melting point, mixed melting point (m.p. of a sample of compound [29]: 114.5-115°, m.p. of a synthetic sample of 9-phenyl-9-n-propylfluorene: 115-116°, mixed m.p. 114-115°), infrared spectra, and ultraviolet spectra (see Tables 11 and 12 in Chapter V).

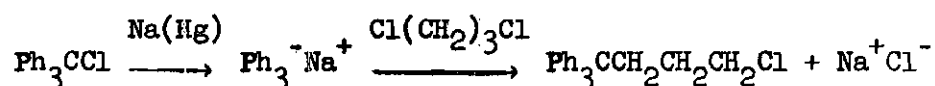
* Analysis by Department of Biochemistry and Nutrition, University of Pittsburgh, Pittsburgh, Pennsylvania.

CHAPTER V

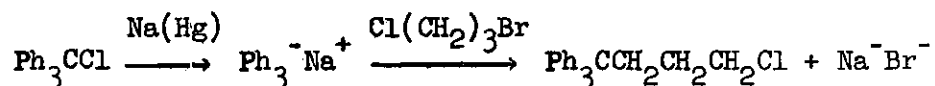
DISCUSSION

Syntheses4-Chloro-1,1,1-triphenylbutane

This chloride was prepared in 29 percent yield from the reaction of triphenylmethylsodium with trimethylene chloride



A yield of 63-68 percent was observed from the reaction of triphenylmethylsodium with 1-bromo-3-chloropropane*



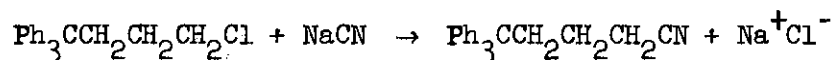
This chloride was further proved by C, H, Cl analysis and by the formation of 1,1,1-triphenylbutane in the alkali metal reactions.

5,5,5-Triphenylpentanenitrile

This nitrile was prepared following the general procedure of Cope and Mehta.¹¹ The reaction of 4-chloro-1,1,1-triphenylbutane with sodium

* This reaction was mentioned by Hughes and co-workers,¹⁰ but details were not given.

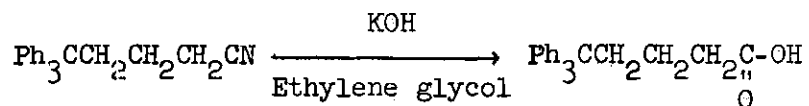
cyanide in dimethylsulfoxide at room temperature gave 95-97 percent yield of 5,5,5-triphenylpentanenitrile



This nitrile was further identified by C, H, and N analysis.

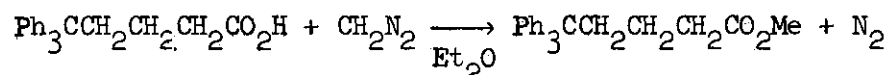
5,5,5-Triphenylpentanoic Acid

This acid was prepared by basic hydrolysis of 5,5,5-triphenylpentanenitrile. An average yield of 95 percent was observed.



Methyl 5,5,5-Triphenylpentanoate

This methyl ester was prepared from the reaction of 5,5,5-triphenylpentanoic acid with diazomethane in diethyl ether. A 77 percent yield of methyl 5,5,5-triphenylpentanoate was observed.

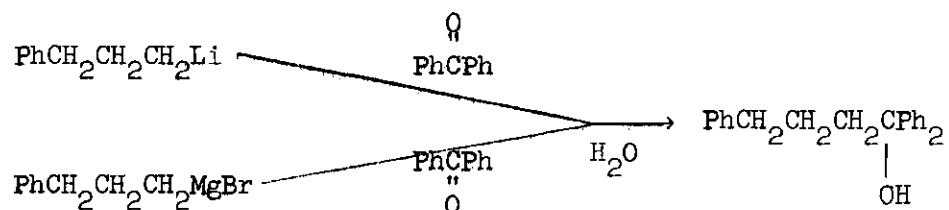


This methyl ester was further identified by C, H analysis.

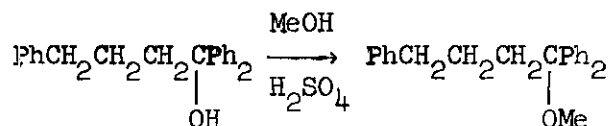
2,2,5-Triphenylpentanoic Acid

This acid was prepared following the synthetic route shown below. A 30 percent yield of 1,1,4-triphenylbutanol-1 was observed from the reaction of benzophenone with 3-phenylpropyllithium. The reaction of 3-

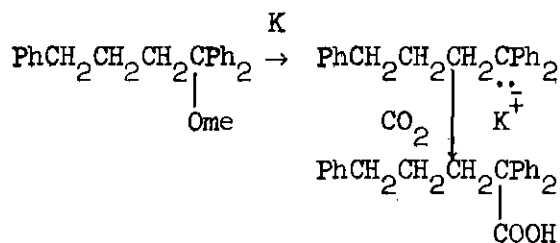
phenylpropylmagnesium bromide with benzophenone gave better yields (65 percent) of the carbinol:



1-Methoxy 1,1,4-triphenylbutane was prepared following the modified general procedure of Ziegler and co-workers.²² The reaction of 1,1,4-triphenylbutanol-1 with methanol at room temperature gave 58.9 percent of 1-methoxy 1,1,4-triphenylbutane. The drying of this methyl ether at room temperature and 45 microns pressure resulted in partial loss of methanol, apparently because of the presence of traces of acid catalyst.



Cleavage of 1-methoxy-1,1,4-triphenylbutane by potassium, followed by carbonation, gave the desired acid in a 68.1 percent yield.



Four attempts to synthesize this acid from the reaction of potassium diphenyl acetic acid methyl ester with 3-phenyl-1-chloro propane were unsuccessful. This failure was apparently due to complicated side reactions, such as the cleavage of the expected product by potassium amide, rearrangement of the expected product, and the coupling reactions of the organopotassium compounds with the halide.

Reactions

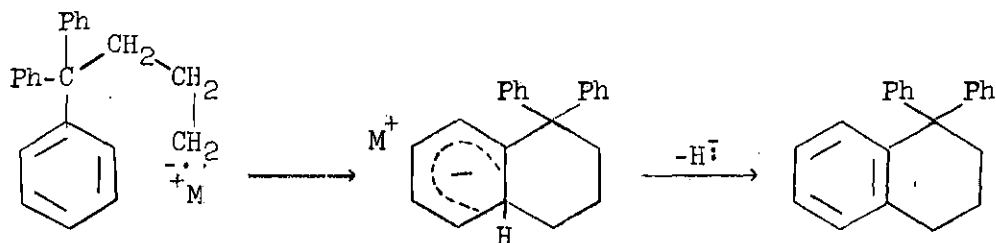
Reaction of 4-Chloro-1,1,1-triphenylbutane with Lithium

The reaction of lithium metal with 4-chloro-1,1,1-triphenylbutane in tetrahydrofuran at -10° produced a pink solution which changed to orange after stirring for another 10 minutes at $-7 \pm 5^{\circ}$. (A deep red solution was observed by Williams² from the reaction of lithium metal with 2-chloro-1,1,1-triphenylethane in the same solvent.) This solution was stirred at -60° for three hours and, after no obvious color change was observed, the reaction temperature was increased to -40° and stirring was continued at this temperature for one hour followed by carbonation. The acidic material, which had a melting point of $212-245^{\circ}$, constituted only ca. four percent of the overall reaction mixture. Another reaction was run at a temperature of -58° for three and one-fourth hours and then carbonated to give a 29 percent yield of acidic material, 70 percent of which was found to be 5,5,5-triphenylpentanoic acid. A reaction of 4-chloro-1,1,1-triphenylbutane at $-5 \pm 5^{\circ}$ for five hours and at -60° for an additional three hours followed by stirring at 0° for another two hours gave, after carbonation, 15 percent of acidic material which was mainly 5,5,5-triphenylpentanoic acid.

A similar reaction was carried out at -60° for four and two-thirds hours and was then warmed to 25° for two hours before carbonation. The resulting four percent yield of carboxylic acids was shown to contain 46 percent 5,5,5-triphenylpentanoic acid and a complex mixture of unidentified acids. The 96 percent yield of neutral material was shown to contain 87 percent 1,1,1-triphenylbutane and 10 percent unreacted 4-chloro-1,1,1-triphenylbutane. Thus, 4,4,4-triphenylbutyllithium is decomposed readily at higher temperatures to give 1,1,1-triphenylbutane before it rearranges.

Reaction of 4-Chloro-1,1,1-triphenylbutane with Potassium and Sodium-Potassium Alloy

The reaction of 4-chloro-1,1,1-triphenylbutane with potassium in boiling tetrahydrofuran for a period of 20 minutes gave, after carbonation, a 90 percent yield of neutral material. Vapor-phase chromatography of this neutral material showed that it contained 84 percent of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene, which was identified by nuclear magnetic resonance spectroscopy, infrared spectroscopy, and melting point, and mixed melting point comparison with the authentic compound. The neutral material also contained 14 percent of 1,1,1-triphenylbutane. Obviously, under the reaction conditions, most of the 4,4,4-triphenylbutyl carbanion formed from the reaction of potassium and 4-chloro-1,1,1-triphenylbutane cyclized intramolecularly, and the intermediate formed was unstable and readily eliminated KH to give 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene.



The remaining 14 percent of 1,1,1-triphenylbutane in the neutral portion is due to protonation of the 4,4,4-triphenylbutyl anion by the solvent.

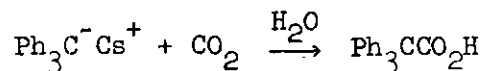
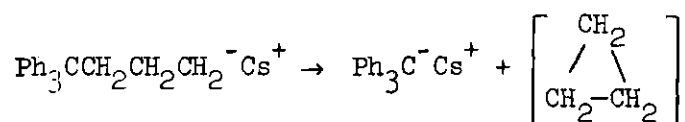
The reaction of 4-chloro-1,1,1-triphenylbutane with potassium in reflux tetrahydrofuran for 105 minutes followed by carbonation gave mainly acidic material, but the recrystallization of this acidic material did not give any appreciable amount of single compound. Obviously, the reaction between 4-chloro-1,1,1-triphenylbutane and potassium in reflux tetrahydrofuran was complicated due to prolonged reaction time.

The reaction of 4-chloro-1,1,1-triphenylbutane with liquid sodium-potassium alloy in tetrahydrofuran at 15° for 100 minutes gave a higher yield of acidic material (70 percent), but this acidic mixture was rather complicated. Vapor-phase chromatography indicated that it contained 22 percent 2,2-diphenylvaleric acid, 3.7 percent triphenylacetic acid, and 5.5 percent 2,2,5-triphenylpentanoic acid. The neutral fraction contained 15 percent of unreacted 4-chloro-1,1,1-triphenylbutane and 31 percent 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (and/or 1,1,4-triphenylbutane) from vapor-phase chromatography.

Reaction of 4-Chloro-1,1,1-triphenylbutane with Cesium and Cesium-Potassium Alloy

The reaction of cesium metal with 4-chloro-1,1,1-triphenylbutane

in tetrahydrofuran at 35° produced a deep red solution. This solution was stirred at 40° for 11 minutes and then carbonated. This reaction gave a 20 percent yield of an acid mixture which consisted of 6.4 percent 2,2-diphenylpentanoic acid, 4.8 percent triphenylacetic acid, 6.1 percent 2,2,5-triphenylpentanoic acid, and a complex mixture of unidentified acids. The neutral material contained 45.1 percent 1,1,1-triphenylbutane, 35.3 percent 9-phenyl-9-n-propylfluorene and 7.8 percent 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (and/or 1,1,4-triphenylbutane). Triphenylacetic acid apparently comes from triphenylmethyl anion which could result from cleavage of a carbon-carbon bond of the 4,4,4-triphenylbutyl anion by intramolecular cyclization of cyclopropane



The 1,1,1-triphenylbutane obviously resulted from the protonation of 4,4,4-triphenylbutyl anion by the solvent.

Further reactions of 4-chloro-1,1,1-triphenylbutane with cesium were carried out at lower temperatures to see if the yield of the acidic material could be increased and if the reaction mixture could be simplified. The reaction was studied with liquid cesium-potassium alloy in tetrahydrofuran at $-25 \pm 3^\circ$ and gave an 82 percent yield of acids and an 18 percent yield of neutral material. Vapor-phase chromatography of the

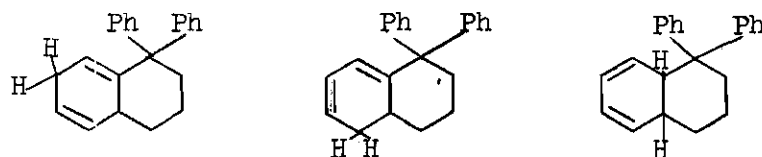
acidic material (as their methyl esters) gave 28 ± 5 percent of an acid which displayed the same retention time as 2,2-diphenylpentanoic acid, 7 ± 3 percent of triphenylacetic acid, and 17 ± 2 percent of another acid which has the same retention time as 2,2,5-triphenylpentanoic acid. The acid which has the same retention time as 2,2-diphenylpentanoic acid was isolated as its methyl ester by preparative vapor-phase chromatography and purified to give a colorless crystalline solid with a melting point of 119° and was found to be not 2,2-diphenylpentanoic acid. The triphenylacetic acid was isolated by the same method and identified as triphenylacetic acid by mixed melting point with an authentic sample and by nuclear magnetic resonance spectroscopy.

Vapor-phase chromatography of the neutral products in these cesium-potassium reactions indicates the presence of 1,1,1-triphenylbutane, 9-phenyl-9-n-propylfluorene and 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene in appreciable amounts.

In order to try to further simplify the reaction mixture, two reactions of cesium-potassium alloy with 4-chloro-1,1,1-triphenylbutane in tetrahydrofuran were carried out at -40° and the resulting mixtures were then reacted with methanol. Vapor-phase chromatography indicated that the products contained 9-32 percent hydrocarbon [28], 30-55 percent hydrocarbon [29], 15-20 percent hydrocarbon [30], and 8-11 percent hydrocarbon [31]. Hydrocarbons [28] and [31] were identified as 1,1,1-triphenylbutane and 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene, respectively, by VPC method A.* Compounds [29] and [30] were initially believed to be either

* See Instrumental Analyses.

two of



If this assumption is correct, it should be possible to dehydrogenate any one of them to give 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene. Hydrocarbon [30] was found to disappear after the original mixture was treated either with sulfur in dimethyl formamide at 120° for five and a half hours or heating the original mixture with bromine in *m*-dibromobenzene at 215° for two and a half hours. The relative amount of hydrocarbon [29] was found to increase by the above treatments. There was no evidence for the increase of the relative amount of hydrocarbon [31]. Therefore, the assumption made above was proved to be incorrect. The above mentioned analyses were all performed by VPC method B.*

In a later work, hydrocarbon [30] was more conveniently converted to hydrocarbon [29] by vacuum sublimation at 100° and 50 microns. Hydrocarbon [29] was eventually isolated and purified by vacuum sublimation and subsequent recrystallizations from absolute alcohol.

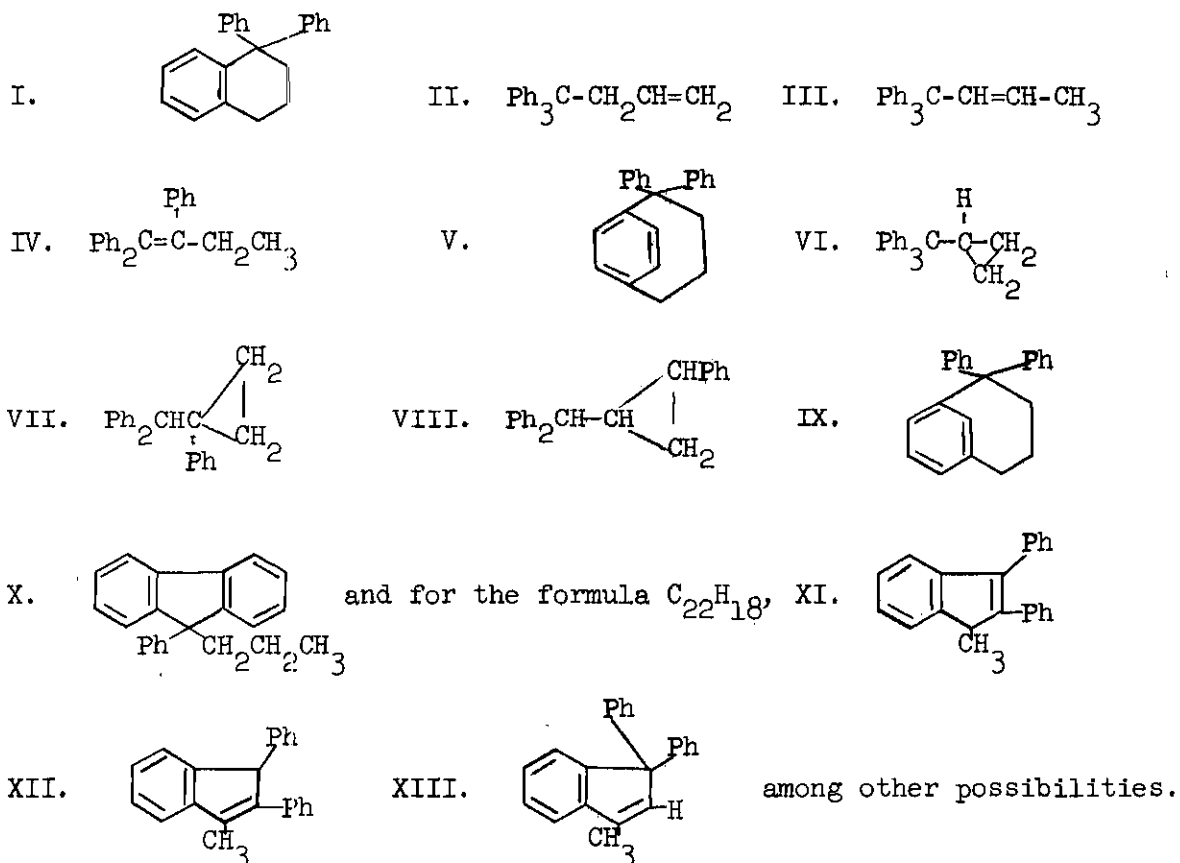
Identification of the Unknown Hydrocarbon [29] from Cesium-Potassium Alloy

Reactions

The C, H analysis and molecular weight determination (see Table 16) of this hydrocarbon [20] indicated that this compound could have the molecular formula $C_{22}H_{20}$, $C_{22}H_{18}$, or $C_{21}H_{18}$; the last one was ruled out because it is rather unlikely from a chemical point of view to split off

* See Instrumental Analyses.

one carbon atom even though it has the most satisfactory C, H analysis and molecular weight determination. The following chemically interpretable structures could be postulated: for the formula $C_{22}H_{20}$,



This hydrocarbon [29] displayed a melting point of 115-115.8°.

The ultraviolet spectrum (see Table 11) of this hydrocarbon showed the presence of conjugated double bonds and, therefore, the structures I, V, VI, VII, VIII, and IX were ruled out.

From the nuclear magnetic resonance spectrum of this hydrocarbon [29] which did not show any vinyl type hydrogen, structures II, III, and XIII could also be ruled out. XII was also ruled out by nuclear magnetic resonance spectroscopic evidence (see Table 10).

From the above argument, there were only three structures, IV, X, and XI, left to be proved or disproved.

The unknown hydrocarbon [29] had a melting point of 115-115.8° (from ethanol) and the melting points of 1,1,2-triphenylbutene-1 (IV) and 1-methyl-2,3-diphenylindene (XI) are 93° and 107°, respectively. From the comparison of the melting points, the structure of this unknown hydrocarbon [29] could be neither IV nor XI but, in order to make sure, the ultraviolet, infrared, and nuclear magnetic resonance spectroscopic data were compared (see the spectroscopic data for the three hydrocarbons in Tables 10-14). Thus, the possibilities of structures IV and XI were also ruled out as that of the unknown hydrocarbon.

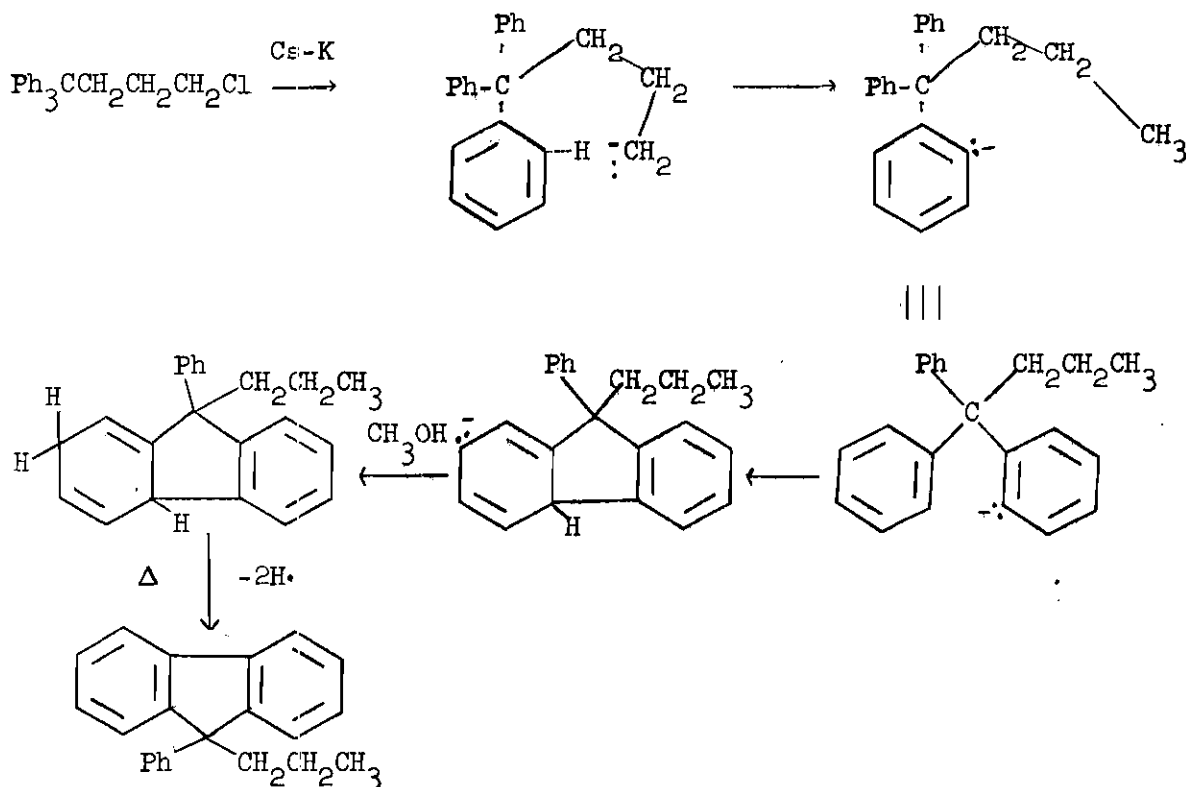
The ultraviolet spectrum of this unknown hydrocarbon [29] (see Table 11) was very similar to the spectrum of fluorene and its derivatives.^{38,39} Fluorene itself showed three bands at λ_{\max} 263 m μ ($\log \epsilon_{\max} = 4.31$), λ_{\max} 290 m μ ($\log \epsilon_{\max} = 3.80$), and λ_{\max} 300 m μ ($\log \epsilon_{\max} = 4.00$) and 9-phenylfluorene showed three bands at λ_{\max} 267 m μ ($\log \epsilon_{\max} = 4.23$), λ_{\max} 292 m μ ($\log \epsilon_{\max} = 3.72$), λ_{\max} 303 m μ ($\log \epsilon_{\max} = 3.87$). The infrared spectrum (see Table 12) of the unknown hydrocarbon [29] showed the presence of an ethyl group and the nuclear magnetic resonance spectrum of this unknown hydrocarbon had an abnormally large band in the methyl group region (see Table 10). These spectroscopic

(38) Charles K. Bradsher and L. U. Wissow, J. Am. Chem. Soc., **68**, 2150 (1946).

(39) Robert A. Friedel and Milton Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, 1955, pp. 311-318.

data together with the C, H analysis strongly support the structure of the unknown hydrocarbon as being 9-phenyl-9-n-propylfluorene. This hydrocarbon [29] was finally identified as 9-phenyl-9-n-propylfluorene by the comparisons of melting point, mixed melting point, infrared spectra, and ultraviolet spectra with an authentic sample prepared by a modified general method of Hauser.³⁷

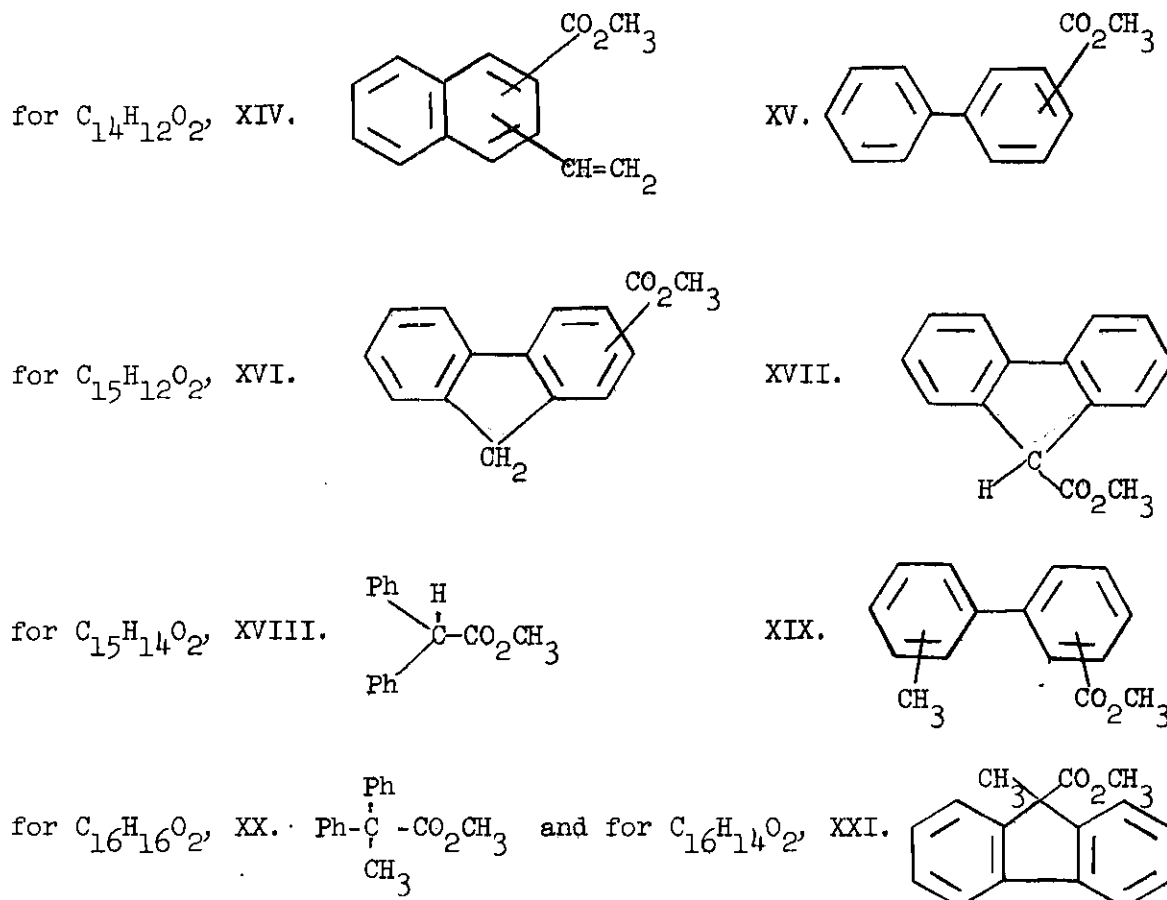
The formation of 9-phenyl-9-n-propylfluorene from the reaction of cesium-potassium alloy could be rationalized as shown below



Attempted Identification of the Unknown Methyl Ester [7] from Cesium-Potassium Reactions

The C, H analysis and molecular weight determination suggested that the methyl ester [7] with a melting point of 119° from the cesium-

potassium reactions could have the molecular formula $C_{14}H_{12}O_2$, $C_{15}H_{12}O_2$, $C_{15}H_{14}O_2$ (see Table 16). Structures XIV through XXI could be postulated:



Any of these structures could have as strong an ultraviolet absorption as that of the unknown methyl ester [7], except structures XVIII and XX. The nuclear magnetic resonance spectrum of the unknown methyl ester showed that a methyl group band almost of equal size as that of the methoxyl methyl group, therefore, structures XIV through XVIII were ruled out. Based solely on the nuclear magnetic resonance spectrum of the unknown methyl ester, structures XIX, XX, and XXI were considered. Struc-

ture XX was ruled out as one of the possibilities because of its physical properties (reported as a liquid, b.p. $144^{\circ}/1$ mm). Compound XXI has a melting point of $108-109^{\circ}$ and its ultraviolet spectrum must be similar to that of fluorene and dissimilar to that of the unknown methyl ester. The structure of the unknown methyl ester could not be identified on the basis of the infrared, ultraviolet, and nuclear magnetic resonance spectroscopic data listed in Tables 10, 11, and 15.

Table 10. Nuclear Magnetic Resonance Spectroscopic Data* of the Unknown Hydrocarbon [29] from the Cesium-Potassium Alloy Reactions, 1-Methyl-2,3-diphenylindene, 1,1,2-Triphenylbutene, and the Unknown Methyl Ester [7]

Compound	τ ppm	Percent Area	No. of Hydrogens			Assignment
The unknown hydrocarbon [29]	3.45	67.7	12.2	13.5	14.9	Aromatic hydrogens
	7.80	8.5	1.5	1.7	1.9	Methylene
	9.33	<u>23.8</u>	<u>4.3</u>	<u>4.8</u>	<u>5.2</u>	Ethyl
	Total	100.0	18.0	20.0	22.0	
1,1,2-Triphenylbutene	3.0	73.0	14.6			Aromatic hydrogens
	7.5	10.1	2.0			Methylene
	9.1	<u>16.8</u>	<u>3.4</u>			Ethyl
	Total	99.9	20.0			
1-Methyl-2,3-diphenylindene	2.85	77.6	13.7			Aromatic hydrogens
	6.10	5.8	1.4			
	8.75	<u>16.6</u>	<u>2.9</u>			Methyl
	Total	100.0	18.0			
The unknown methyl ester with m.p. 119°** [7]	1.62	62.2	10.0	8.7	7.5	Aromatic hydrogens
	2.25					
	5.84	18.1	2.9	2.5	2.2	Methoxyl methyl
	7.67	<u>19.4</u>	<u>3.1</u>	<u>2.7</u>	<u>2.3</u>	
	Total	99.7	16.0	13.9	12.0	

* Carbon tetrachloride was used as solvent.

** External TMS standard was used. All other n.m.r. spectra used TMS as internal standard.

Table 11. Ultraviolet Absorption Maxima of the Unknown Hydrocarbon [29] from the Cesium-Potassium Alloy Reactions, 9-Phenyl-9-n-propylfluorene, 1-Methyl-2,3-diphenylindene, 1,1,2-Triphenylbutene, 1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene, and Unknown Methyl Ester [7]

Compound	λ_{max} m μ	Optical Density	Molar Extinction Coefficient	Solvent
The Unknown Hydrocarbon [29]	266		1.43×10^4	95% EtOH
	294		5.31×10^3	
	306		8.90×10^3	
9-Phenyl-9-n- propylfluorene	266		1.42×10^4	95% EtOH
	294		5.33×10^3	
	306		8.89×10^3	
1-Methyl-2,3 diphenylindene	237		2.26×10^4	95% EtOH
	295		1.86×10^4	
1,1,2-Triphenyl- butene-1	225		1.46×10^4	95% EtOH
	260		9.77×10^3	
1,1-Diphenyl-1,2,3,4- tetrahydronaphthalene	258		6.99×10^2	95% EtOH
	263		8.43×10^2	
	269		6.13×10^2	
	274		2.93×10^2	
The Unknown Methyl Ester [7] with m.p. 119°	272	0.75		0.00535 g in one l 95% EtOH

Table 12. Infrared Spectroscopic Data of Unknown Hydrocarbon [29]

Range cm^{-1}	Intensity	Possible Assignment ^{40, 41}
900	W	$-\text{CH}_2-\text{CH}_3$
910	W	$-\text{CH}_2-\text{CH}_3$
935	W	$-\text{CH}_2-\text{CH}_3$
950	W	$-\text{CH}_2-\text{CH}_3$
1035	M	$-\text{CH}_2-\text{CH}_3$
1045	M	$-\text{CH}_2-\text{CH}_3$
1100	W	$-\text{CH}_2-\text{CH}_3$
1125	W	
1165	W	
1385	W	$\text{CH}_3-\text{C} \quad \text{CH}_2$
1450	S	$\text{CH}_3-\text{C} \quad \text{CH}_2$
1470	W	
1600-2000	W	Aromatic
1600-2000	W	
2850	W	$-\text{CH}_2-$
2870	S	CH_3- (CH Stretching Frequency)
2935	W	$-\text{CH}_2-$
2960	S	CH_3- (CH Stretching Frequency)
3020	W	Aromatic
3040	W	Aromatic (C-H Stretching)
3070	M	Aromatic

(40) John E. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965.

(41) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, 1954.

Table 13. Infrared Spectroscopic Data of 1-Methyl-2,3-diphenylindene

Range cm^{-1}	Intensity	Possible Assignment ^{40, 41}
920		1,2-Substituted Aromatic
1040		1,2-Substituted Aromatic
1080		
1095	W	1,2-Substituted Aromatic
1105	W	
1150	W	1,2-Substituted Aromatic
1350	M	CH Deformation -CH-
1370	W	C-CH ₃
1440, 1460	S	C-CH ₃
1770	W	
1870	W	
1935	W	
2865	M	CH Stretching Frequency CH ₃ or CH ₂
2915	M	CH Stretching Frequency CH ₂
2950-3050 (four)	S	CH Stretching Frequency CH ₃

Table 14. Infrared Spectroscopic Data of 1,1,2-Triphenylbutene-1

Range cm^{-1}	Intensity	Possible Assignment ^{40, 41}
700	M Assym.	CH out of plane deformation
890	W	
910	W	
1030	M	
1075	M Assym.	
1100		
1175-1290		
1375	M	CH deformation, $\text{CH}_3\text{-C}$
1440	S	$\text{CH}_3\text{-C}$
1460	W	$\text{-CH}_2\text{-}$
1480	M	-C=C- vibration in Benzene ring
1670	W	$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$
1750	W	
1800	W	
1860-1880	W	
1925-1960	M	
2850	S	CH stretching, $\text{CH}_3\text{-}$ or CH_2
2910	S	CH stretching, CH_2
2950	S	CH stretching, $\text{CH}_3\text{-}$
3005	S	=C-H stretching vibration of Benzene
3040	M	=C-H stretching vibration of Benzene
3060	M	=C-H stretching vibration of Benzene
3080	W	=C-H stretching vibration of Benzene

Table 15. Infrared Spectroscopic Data of Unknown Methyl Ester [7]

Range cm^{-1}	Intensity	Possible Assignment ⁴⁰
660	W	
700	M	Monosubstituted benzene
750	S(Broad)	Monosubstituted, ortho disubstituted benzene
835	M	
850	S	Para disubstituted benzene
935	W	
950, 970	M	Ortho disubstituted benzene
1010	M	Para disubstituted benzene
1025	M	Monosubstituted, para disubstituted benzene
1100	S(Broad)	Benzoates
1170	W	Monosubstituted benzene
1185	W	
1195	W	Ortho disubstituted benzene
1210	W	
1275	S(Broad)	Benzoates
1320	M	
1350	W	CH_3^-
1370	W	
1405	M	CH_3^-
1440	M	CH_3^-
1455	W	
1485	M	Monosubstituted, ortho disubstituted benzene
1540	W	
1570	W	
1585	W	Monosubstituted, ortho disubstituted benzene

Table 15. Infrared Spectroscopic Data of Unknown Methyl Ester [7]
(Concluded)

Range cm^{-1}	Intensity	Possible Assignment ⁴⁰
1605	M	Monosubstituted, ortho disubstituted benzene
1710	S(Broad)	Benzoate
2100	W(Broad)	
2525	VW	
2855	W	
2965	W	
3005	W	
3040	VW	
3070	VW	

Table 16. The Calculated and Analytical Found C, H Contents and Molecular Weights of Hydrocarbon [29] and Methyl Ester [7]

Compound	Carbon	Hydrogen	Molecular Weight
Hydrocarbon [29]			
Calcd. for $C_{22}H_{18}$	93.58	6.42	282
Calcd. for $C_{22}H_{20}$	92.93	7.09	284
Calcd. for $C_{21}H_{18}$	93.39	6.71	270
Found	93.37	6.76	284
Methyl Ester [7]			
Calcd. for $C_{14}H_{12}O_2$	79.23	5.70	212
Calcd. for $C_{15}H_{12}O_2$	80.34	5.39	224
Calcd. for $C_{15}H_{14}O_2$	79.62	6.25	226
Calcd. for $C_{16}H_{14}O_2$	80.08	5.88	238
Calcd. for $C_{16}H_{16}O_2$	78.37	8.57	245
Found	79.43	5.85	204

CHAPTER VI

RECOMMENDATIONS

It will be of great interest to apply the technique discovered in this work of the synthesis of organo-cesium compound at low temperatures to the studies of some simpler systems like n-butylcesium, 4-phenylbutylcesium, 4,4-diphenylbutylcesium, or many other similar compounds.

It would also be interesting to study the reaction of potassium or sodium salt of methyl diphenylacetate with alkyl halides in liquid ammonia in order to understand more about carbanion reactions since the author has failed in the preparation of 2,2,5-triphenylpentanoic acid following the general method outlined by Hauser.¹⁴

LITERATURE CITED*

1. E. Grovenstein, Jr. and L. P. Williams, Jr., J. Am. Chem. Soc., 83, 412 (1961).
2. L. P. Williams, Jr., Ph.D. Thesis, Georgia Institute of Technology, June, 1962, pp. 24,28.
3. Gary Wentworth, Ph.D. Thesis, Georgia Institute of Technology, March, 1966, p. 103.
4. C. B. Wooster and R. A. Morse, J. Am. Chem. Soc., 56, 1735 (1934).
5. H. Pines and L. Schaap, J. Am. Chem. Soc., 80, 4378 (1958).
6. L. C. Rogers, M.S. Thesis, Georgia Institute of Technology, 1963, pp. 60-72.
7. Gary Wentworth, Ph.D. Thesis, Georgia Institute of Technology, March, 1966, p. 13.
8. E. C. Horning (Editor-in-chief), Organic Syntheses, Collective Volume III, John Wiley & Sons, Inc., New York, 1962, p. 941.
9. A. H. Blatt, Organic Syntheses, Collective Volume II, John Wiley & Sons, Inc., New York, 1961, p. 607.
10. J. C. Charlton, I. Dostrovsky, and E. D. Hughes, Nature, 167, 986-7 (1951).
11. A. C. Cope and A. S. Mehta, J. Am. Chem. Soc., 86, 5626 (1964).
12. Norman Rabjohn, Organic Syntheses, Collective Volume IV, John Wiley & Sons, Inc., New York, 1963, p. 95.
13. F. J. Piehl and W. G. Brown, J. Am. Chem. Soc., 75, 5023-6 (1953).
14. T. J. deBoer and H. J. Backer, Rec. trav. chim., 73, 229 (1954).
15. W. G. Kenyon, R. B. Meyer, and C. R. Hauser, J. Org. Chem., 28, 3108 (1963).

* For the complete titles of all journals referred to, see Chemical Abstracts, 50, 1 J (1956).

LITERATURE CITED (Continued)

16. A. L. Mndzhoyan, G. T. Tatevosyan, S. G. Agbalyan, and R. Kh. Bostandzhyan, Doklady Akad. Nauk Armyan. S. S. R., 28, No. 1, 11 (1959).
17. E. C. Horning, Organic Syntheses, Collective Volume III, John Wiley & Sons, Inc., New York, 1962, p. 605.
18. I. M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, 1943, p. 1014.
19. T. W. Campbell and W. G. Young, J. Am. Chem. Soc., 69, 3066-8 (1947).
20. M. S. Kharasch and S. Weinhouse, J. Org. Chem., 1, 209 (1936).
21. A. H. Blatt, Organic Syntheses, Collective Volume II, John Wiley & Sons, Inc., New York, 1961, p. 606.
22. K. Ziegler, K. Richter, and B. Schnell, Ann., 443, 177 (1925).
23. K. Ziegler, F. Crossmann, H. Kleiner, and O. Schafer, Ibid., 473, 27 (1929).
24. J. L. Greene, D. Abraham, and H. D. Zook, J. Org. Chem., 24, 132-134 (1959).
25. K. Bowden, N. B. Chapman, and J. Shorter, J. Chem. Soc., 1964, 3372.
26. M. Gomberg and L. H. Cone, Ber., 39, 2957 (1906).
27. F. Bergmann, S. Israelashvili, and D. Gottlieb, J. Chem. Soc., 2522 (1952).
28. V. N. Ipatieff, Herman Pines, and R. E. Schaad, J. Am. Chem. Soc., 66, 816-7 (1944).
29. E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, J. Chem. Soc., 3127 (1960).
30. Mary M. Rising and Tsoh-Wu Zee, J. Am. Chem. Soc., 50, 1211 (1928).
31. K. Neure, Ann., 250, 140 (1888).
32. Gilman and Blatt, Organic Syntheses, Collective Volume I, John Wiley & Sons, Inc., New York, 1948, p. 226.

LITERATURE CITED (Concluded)

33. E. C. Dodds, L. Goldberg, E. I. Grunfeld, W. Lawson, C. M. Saffer, Jr., and Robert Robinson, Proc. Roy. Soc. (London), 132B, 95 (1944).
34. I. A. D'yakonov and N. B. Vinogradova, Zhur. Obshchei Khim, 23, 244-251 (1953).
35. C. F. Koelsch and P. R. Johnson, J. Am. Chem. Soc., 65, 571 (1943).
36. A. Kliegl, Ber., 38, 284 (1905).
37. W. S. Murphy and C. R. Hauser, J. Org. Chem., 31, 85 (1966).
38. C. K. Bradsher and L. U. Wissow, J. Am. Chem. Soc., 68, 2150 (1946).
39. R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, 1955, pp. 311, 318.
40. John R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965.
41. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, 1954.