THE REACTION OF THE MONO ETHYL ENOL ETHER OF DIHYDRORESORCINOL WITH o-, m- AND p-TOLYLMAGNESIUM BROMIDES

By

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ACKNOWLEDGEMENT

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Also, the author wishes to express her thanks to Mr. Willis H. Waldo for his helpful criticism and aid in typing the copy.

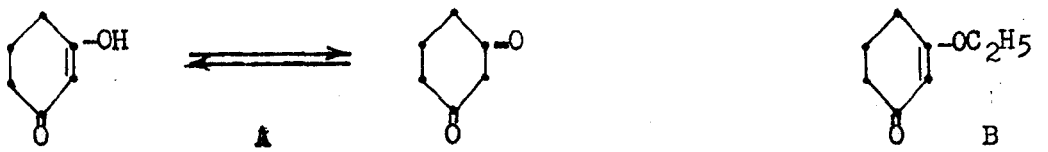
TABLE OF CONTENTS

Page

Page

INTRODUCTION

A study of the preparation of dihydroresorcinol (A) was undertaken on order to shorten the procedure of syntheses by eliminating the preliminary preparation of the catalyst. The dihydroresorcinol was an intermediate in the work herein presented which involved the reaction of the mono ethyl enol ether of dihydroresorcinol (B) with various Grignard reagents and a study of the products derived therefrom.



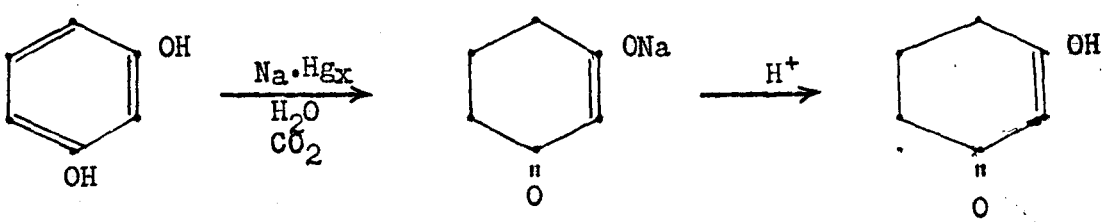
A B

The major portion of this work was the preparation and study of the 2,3', 3,3' and 4,3' dimethylbiphenyls. In order to prove that the structures were correct and to extend the utilization of these reactions, the three dimethylbiphenyls were oxidized to known compounds, the three corresponding dicarboxybiphenyls. The ultraviolet absorption curves for both the dimethylbiphenyls and dicarboxybiphenyls were investigated. The study of the decarboxylation products of 2,3' dicarboxybiphenyl was also undertaken. It was thus shown that the mono ethyl enol ether of dihydroresorcinol can be utilized in the synthesis of meta-arylalkyl benzenes.

HISTORICAL

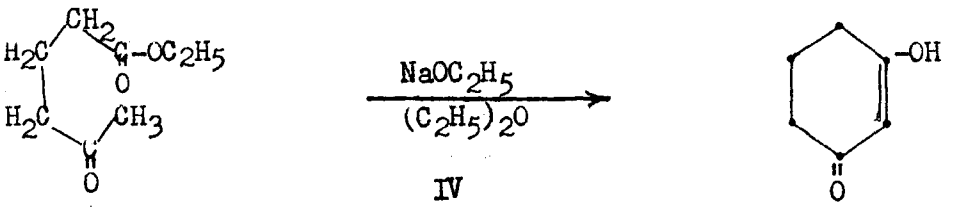
The Preparation of Dihydroresorcinol

Dihydroresorcinol was first reported in a German patent (1) in 1893, and shortly after, Merling (2) described a means of preparation of it from resorcinol that was the same as that given in the patent. The method consisted (III) of treating a boiling water solution of resorcinol with a 2% sodium amalgam while a stream of carbon dioxide was passed into the solution. The sodium salt of dihydroresorcinol was thus produced, which was treated with sulfuric acid, and the free dihydroresorcinol which resulted was extracted with ether. By use of this method, Merling obtained 35 grams of dihydroresorcinol from 100 grams of resorcinol and 5000 grams of sodium amalgam. Approximately 16 liters of ether were used.



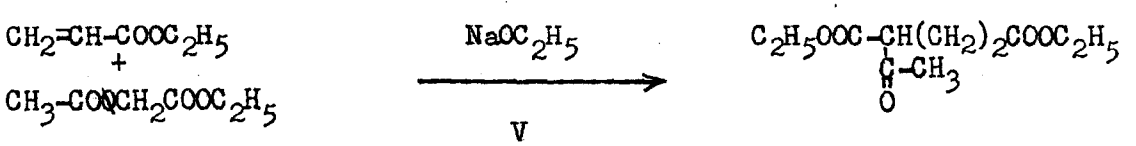
III

Vorländer (3) gave a method of preparation of dihydroresorcinol by the intramolecular condensation (IV) of γ-acetobutyric acid ester. By using an acetoacetic ester synthesis of ethyl β-iodopropionate this keto acid was obtained. Condensation of 50 grams of ethyl γ-acetobutyrate was performed with 42 grams of ethanol-free sodium ethylate in an ether solution. The yield was not stated.

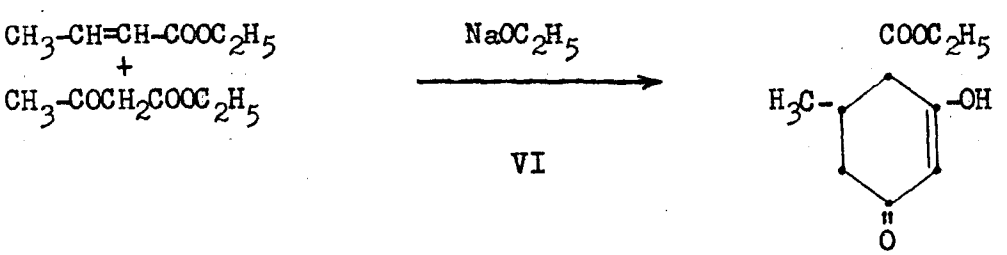


IV

v. Shilling and Vorländer (4) attempted to prepare dihydroresorcinol through a series of reactions beginning with a Michael condensation (V) of ethyl acrylate and acetoacetic ester. The condensation producing diethyl α-acetoglutarate was satisfactory, but the subsequent ring closure that was expected to give 4-carbethoxycyclohexanedione-1,3 did not take place. Ethyl crotonate (VI), under identical conditions, yielded 4-carbethoxy-5-methylcyclohexanedione-1,3, which gave rise to v. Shilling's expectation. The latter dione was hydrolyzed and decarboxylated to the dihydroresorcinol derivative.



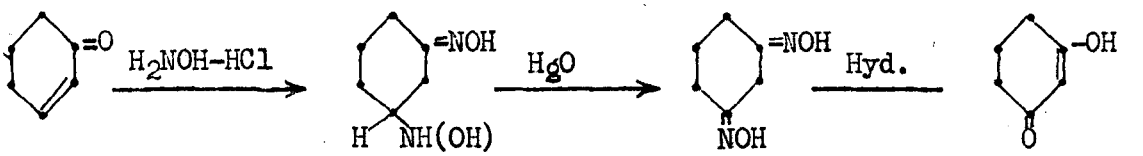
V



VI

Dihydroresorcinol was prepared by Kötz and Grethe (5) by reacting (VII) 2 moles of hydroxyamine hydrochloride with 1 mole of Δ^2-cyclohexenone giving 3-(hydroxyamino)-cyclohexanoneoxime. This substance was oxidized by mercuric oxide to the dioxime and then hydrolyzed to dihydroresorcinol. Yields were not stated, but for oxidation of 5 grams of the N-hydroxylamino compound, Kötz used 30-40 grams of

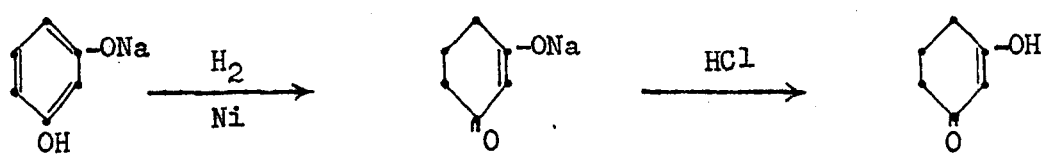
mercuric oxide.



VII

Thiele and Jaeger (6) gave a method of synthesis of dihydroresorcinol starting with "oxyhydroquinone". When treating an aqueous solution of this trihydroxybenzene with a 3% sodium amalgam in a current of hydrogen gas, one of the oxygen atoms was removed by hydrogenolysis, and dihyreoresorcinol was produced in about 35% yield. Thiele and Jaeger made the report that "oxyhydroquinonecarbonic acid" treated similarly also yielded dihydroresorcinol.

Thompson (7) gave a working procedure for a method of preparing dihydroresorcinol according to the patent granted to Klingenfuss (8) in 1934. By this method better than a 95% yield of dihydroresorcinol was carried out in the presence of one equivalent of sodium hydroxide and Raney nickel as the catalyst. A high pressure hydrogenation bomb was (VIII) employed and the reaction arrested itself when one mole of hydrogen had been absorbed. The dihydroresorcinol was isolated from the solution of its sodium salt by the addition of concentrated hydrochloric acid while cooling in an ice bath. The product, which was removed by filtration and was contaminated with sodium chloride, could be used directly or purified by recrystallization from benzene.

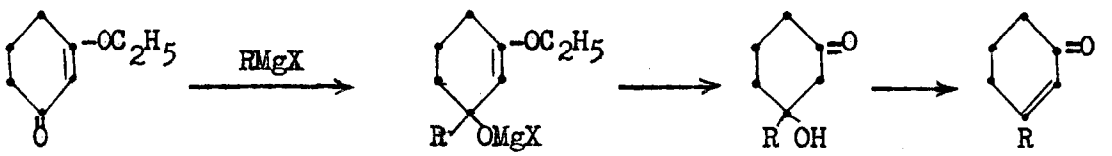


VIII

The Uses of 3-Ethoxy-Δ^2-cyclohexenone

(Mono Ethyl Enol Ether of Dihydroresorcinol)

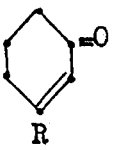
A. The Preparation of 3-Alkyl-Δ^2-cyclohexenones. The mono ethyl ether of dihydroresorcinol reacted (IX) with alkylmagnesium halides as was shown by Woods, Griswold, Armbrecht, Blumenthal and Plapinger (9).



IX

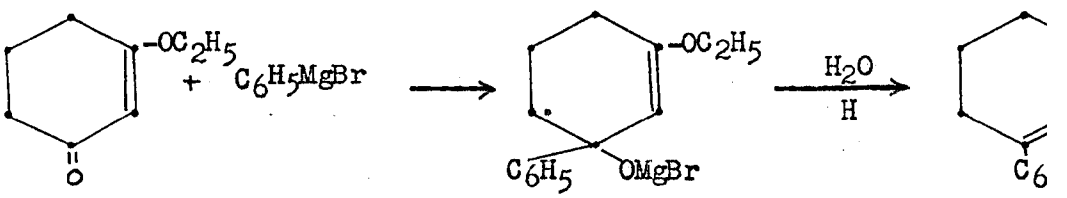
Table I contains the list of 3-alkyl-Δ^2-cyclohexenones and data related to them which have been obtained where R has been varied from methyl to the t-butyl group. This method of preparation thus constitutes an excellent procedure for the synthesis of this type of substance. Woods, et al. point out that the yield of the 3-alkyl-Δ^2-cyclohexenones as observed in Table I are rather normal in the sense that increasing complexity of the Grignard reagents leads to lower yields of normal products. The notable exception to the preceding is the surprisingly low yield of 3-methyl-Δ^2-cyclohexenone which these workers were unable to increase by varying the conditions and the mode of isolation of the reaction product of the Grignard reagent (CH_3MgBr and CH_3MgCl) with the ketone. The Grignard reaction solution always developed marked color and after isolation of the product a large amount of presumably polymeric substance was observed.

TABLE I

Physical Values for 

R	B. P.° C.	mm.	Yield %	n_D^{25}
CH_3	40	0.8	34	1.4945^{20}
C_2H_5	56-57	0.8	75	1.4913^{20}
n-C_3H_7	59-60	0.4	75	1.4876
i-C_3H_7	59-60	0.3	12	1.4842
n-C_4H_9	82-89	0.3	85	1.4865
i-C_4H_9	83-84	1-1.5	43	1.4840
s-C_4H_9	57-58	0.3	15	1.4948
t-C_4H_9	70	0.3	13	1.4875

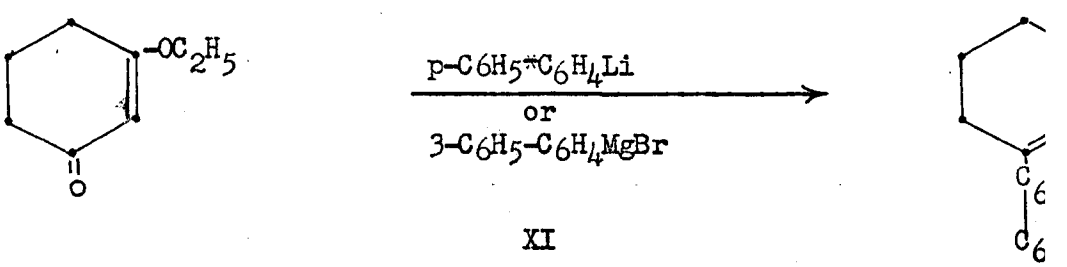
B. The Preparation of 3-Aryl-Δ^2-cyclohexenones. Woo and Tucker (10) prepared 3-phenyl-Δ^2-cyclohexenone by the reactio (X) of dihydroresorcinol ethyl enol ether with phenylmagnesium bro



X

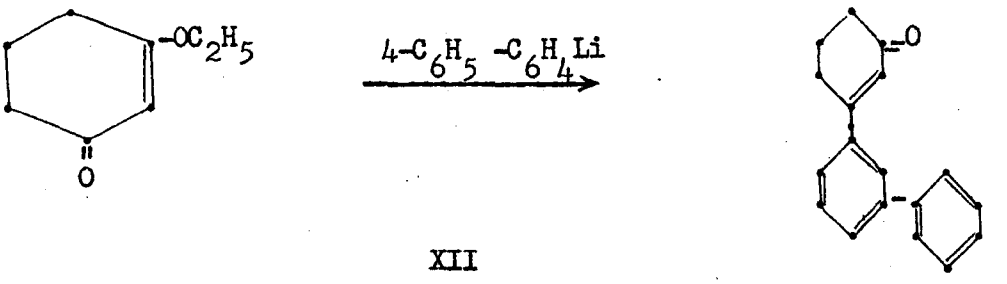
This product was obtained in 80-85% yield, and was the same as the 3-phenyl-Δ^2-cyclohexenone these workers had prepared by the react of dihydroresorcinol with phenylmagnesium bromide.

During the study of meta diarylbenzenes, Woods and Tucke (11) reacted (XI) dihydroresorcinol ethyl enol ether with p-biphen lithium or with 3-biphenylmagnesium bromide and from this reaction 3-(4-biphenyl)-Δ^2-cyclohexenone was obtained in a 90% yield.



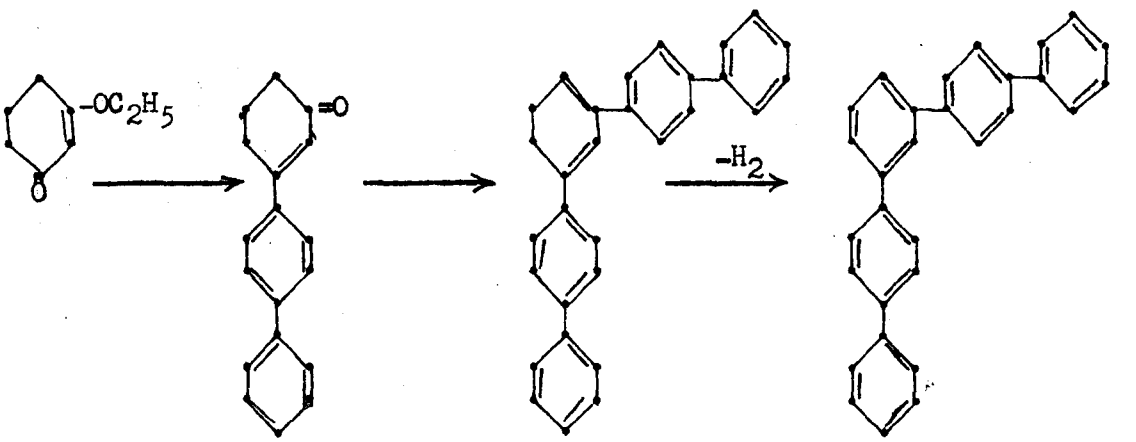
XI

Woods and Reed (12) prepared 3-(3-xenyl)-Δ^2-cyclohexeno by reacting dihydroresorcinol ethyl enol ether with a dry ether so of 3-xenylmagnesium bromide. Attempts to crystallize the 3-(3-xen cyclohexenone were unsuccessful.



XII

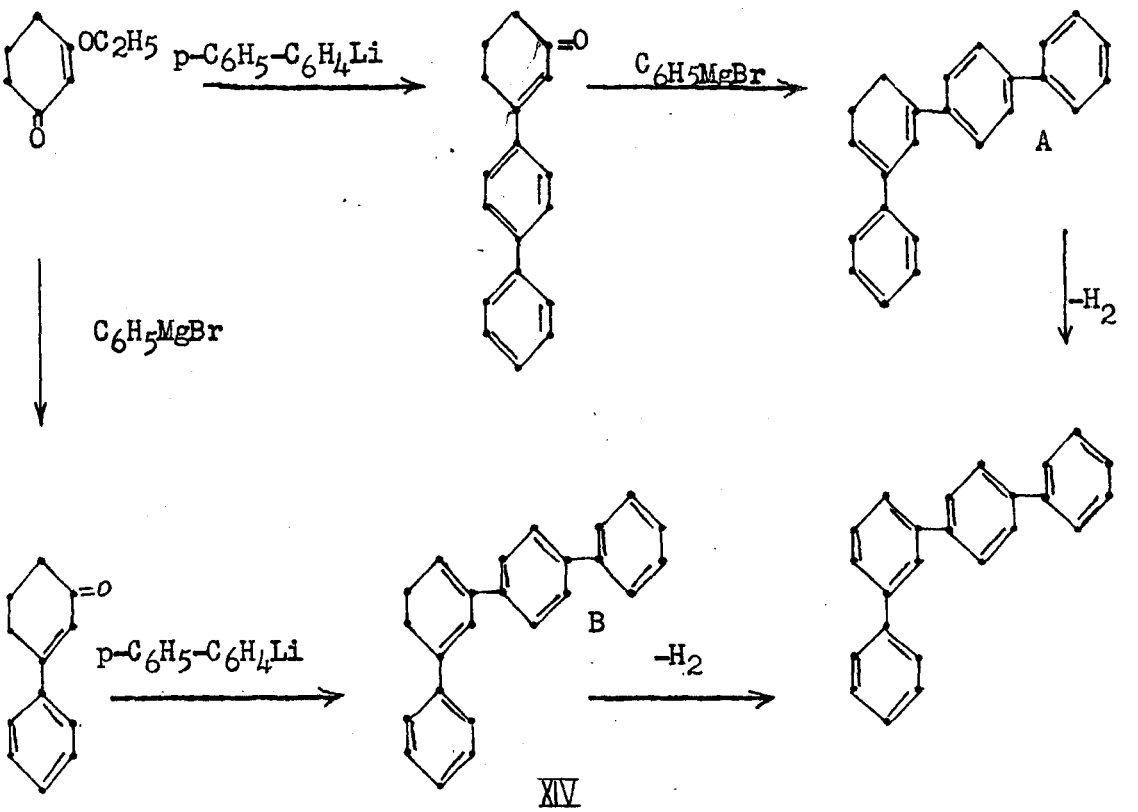
C. The Preparation of 3-Diarylbenzenes. Dihydroresorcinol ethyl enol ether reacted readily with p-biphenyllithium and from this reaction 3-(4-biphenyl)- Δ^2-cyclohexenenone was obtained according to the method of Woods and Tucker (11). This ketone when treated with p-diphenyllithium produced (XIII) 1,3-di-(4-biphenyl)-cyclohexadiene-1,3. This diene was dissolved in phenetole, to which had been added a small amount of palladinized carbon, and refluxed for three hours. Upon crystallization from toluene 4-di-(4biphenyl)-benzene precipitated.



XIII

Reaction (XIV) of the biphenyl- Δ^2-cyclohexenone with phenylmagnesium bromide afforded 1-phenyl-3-(4-biphenyl)-cyclohexadiene-1,3, and aromatization of this latter substance yielded 3-phenyl-(4-biphenyl)-benzene. This same hydrocarbon was obtained by treatment of phenyl- Δ^2-

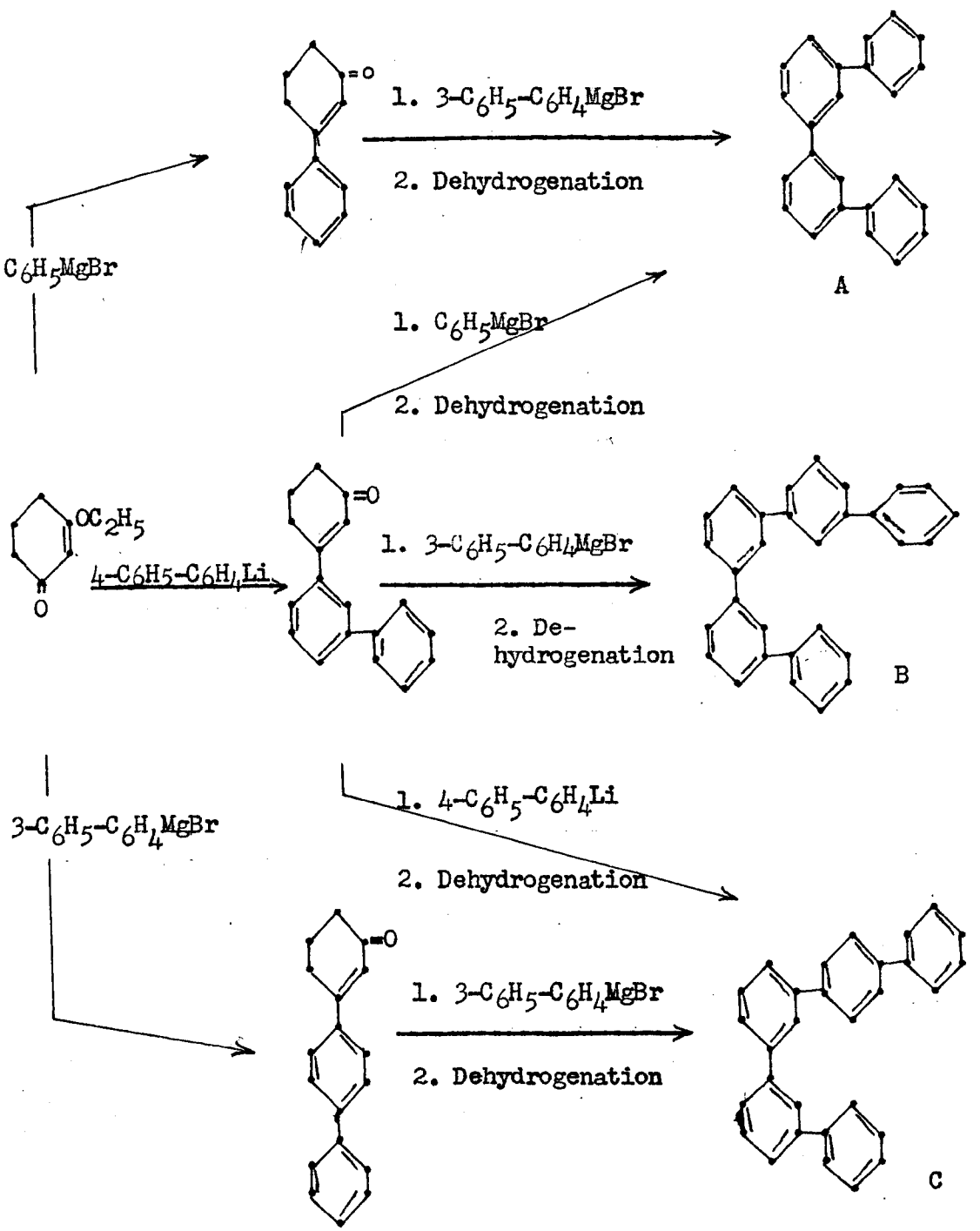
cyclohexenone with p-biphenyllithium and subsequently aromatizing the diene.



XV

It is interesting to note that the reaction of dihydroresorcinol ethyl enol ether with the same organometallic reagents, but in the reverse order of use, led ultimately to the same aromatic compound but did so with a different diene, 3-phenyl-1(4-biphenyl)-cyclohexadiene-1,3 (A), which is isomeric to 1-phenyl-3-(4-biphenyl)-cyclohexadiene-1,3 (B), in the position of the ethylenic links.

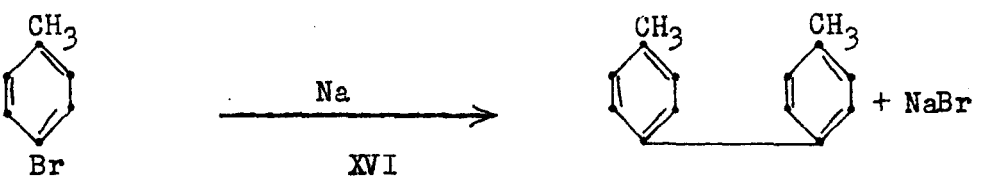
Recently Woods and Reed (12) studied the preparation (XV) of three more m-diaryl benzenes using essentially the method of Woods and Tucker (11).


=O
1. 3-C6H5-C6H4MgBr
2. Dehydrogenation
A
C6H5MgBr
1. C6H5MgBr
2. Dehydrogenation
OC2H5
O
4-C6H5-C6H4Li
=O
1. 3-C6H5-C6H4MgBr
2. De-
hydrogenation
B
3-C6H5-C6H4MgBr
1. 4-C6H5-C6H4Li
2. Dehydrogenation
=O
1. 3-C6H5-C6H4MgBr
2. Dehydrogenation
C

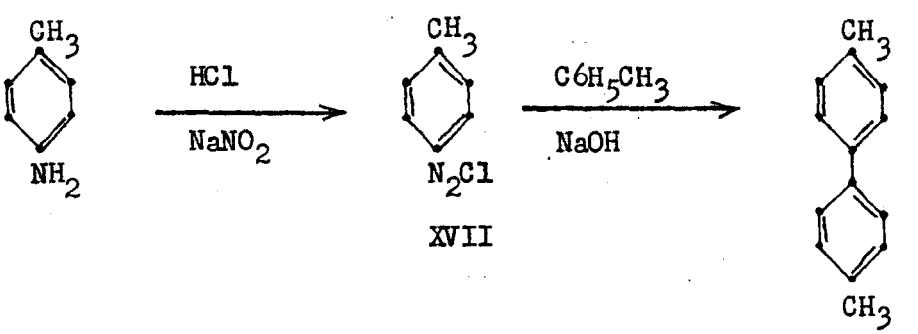
1-Phenyl-3-(3-xenyl)-benzene, (A), was best prepared by the reaction of phenyl-Δ^2-cyclohexenone with 3-xenylmagnesium bromide with subsequent dehydrogenation rather than by the alternate route since a Wurtz type of reaction takes place with 3-xenylmagnesium bromide giving A as a product. Substance C was best prepared by treating biphenyl-Δ^2-cyclohexenone with 3-xenylmagnesium bromide rather than by the alternate method. Substance B could only be prepared by the series of reactions indicated.

Previous Preparations of the Dimethylbiphenyls

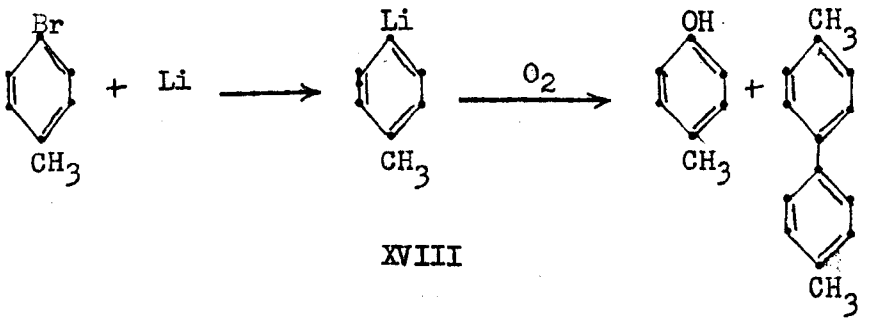
In 1876 Doebner and de Clereq (13) prepared 4,4' ditolyl by the Fittig synthesis (XVI), that is, by dissolving p-bromotoluene in benzene containing small pieces of sodium. After repeated extractions with benzene good yields of the prismatic crystals of 4,4' ditolyl were obtained. By this same procedure Weiler (14) made 4,4' ditolyl. Also he found a small amount of the 3,4' ditolyl along with some dibenzyl present in the final products.



Gomberg and Pernert (15) found coupling (XVII) 4-toluidine with toluene gave 4,4' dimethylbiphenyl and 2,4' dimethylbiphenyl. An Ullman reaction was carried out by heating 4-iodo-toluene with finely divided copper and 4,4' dimethylbiphenyl was prepared.



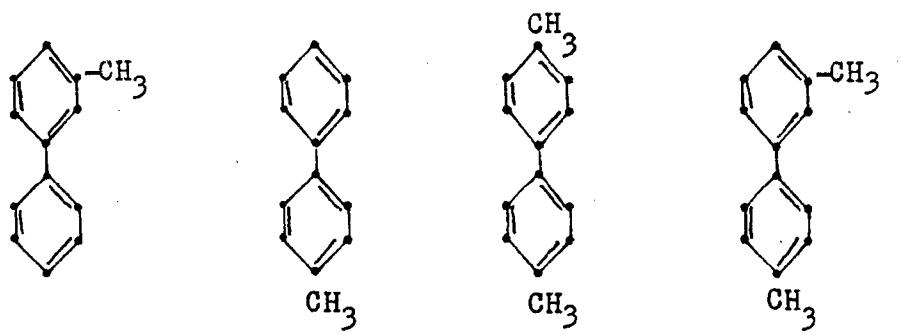
During the study of lithium Grignard reactions Müller and Töpel (16) prepared (XVIII) the 4,4' ditolyl.



XVIII

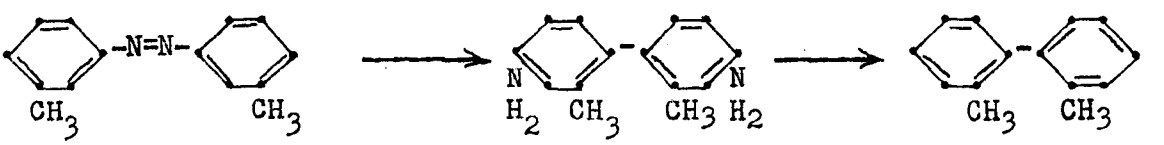
p-Bromotoluene was dissolved in dry ether and this solution was poured into a swirling tube with pieces of lithium. The reaction was run in a nitrogen atmosphere. When the reaction had subsided a stream of oxygen was passed through the ether solution. p-Cresol was obtained from the phenolic material and 4,4' ditolyl from the neutral part. To synthesize 3,3' ditolyl, Müller and Töpel (16) prepared the organolithium compound in a manner analogous to the p-lithium tolyl compound described above. A yield of 17% of 3,3' ditolyl was reported. o-Tolyllithium was prepared in a similar manner and from the neutral portion of the reaction mixture 2,2' ditolyl was obtained in about 15% yield.

Kruber (17), in his study of the compounds in coal tar oils, found these homologs of the biphenyls in the 270-290° C. boiling range.



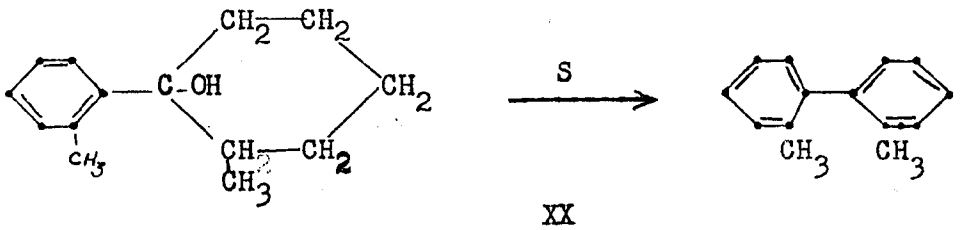
3-Methylbiphenyl and 4-methylbiphenyl were in the lower boiling fraction; 4,4' dimethylbiphenyl boiled around 290° C. and was a solid at room temperature; 3,4' dimethylbiphenyl was a liquid at room temperature. The sulfonation products of this fraction (270-290° C.) stood for a long time in the cold. There were two hydrocarbons in the mixture of sulfonic acids, which were recognized as dimethylbiphenyls. The solid sulfonic acids were transformed into the sodium salts, which had no definite crystalline form. These were then treated with 70% sulfuric acid and left in an ice-water bath. Two solid hydrocarbons crystallized out. The first was recrystallized from ethanol and was identified as 4,4' dimethylbiphenyl having a melting point of 121-122° C. The second, with a melting point of 14-15° C. was found to be 3,4' dimethylbiphenyl.

Jacobson and his co-workers (18) found the reduction products of azo compounds to be primary diamines, and through elimination of the amine groups, the hydrocarbon 2,2' dimethylbiphenyl was formed (XIX).



XIX

In their studies of phenanthrenes Short, Stromberg and Wiles (19) found 2-methylcyclohexanone on a Grignard reagent prepared from p-iodotoluene afforded 1-(2-tolyl)-2-methylcyclohexanol in 50% yield. Dehydration and dehydrogenation (XX) with sulfur at 180-250° C. furnished 2,2' dimethylbiphenyl.



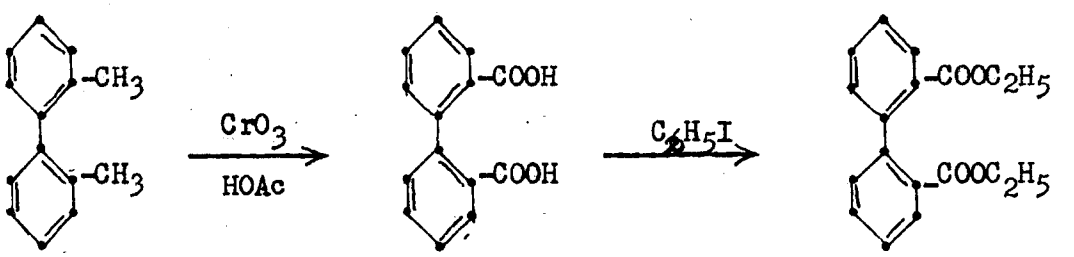
XX

When the last substance is heated more strongly with sulfur phenanthrene is obtained in good yield.

As an intermediate in the preparation of isophthalic acid Schlenk and Brauns (20) prepared 1,3' dimethylbiphenyl. o-Toluidine was dissolved in dilute hydrochloric acid. Through addition of concentrated hydrochloric acid the difficultly soluble o-toluidine chlorohydrate precipitated. This salt was diazotized at room temperature. When the nitrogen evolution subsided and diazotization completed, zinc dust was added and the mixture refluxed. The high boiling distillate contained 1,3' dimethylbiphenyl. Also 3,3' dimethylbiphenyl was prepared in an analogous manner.

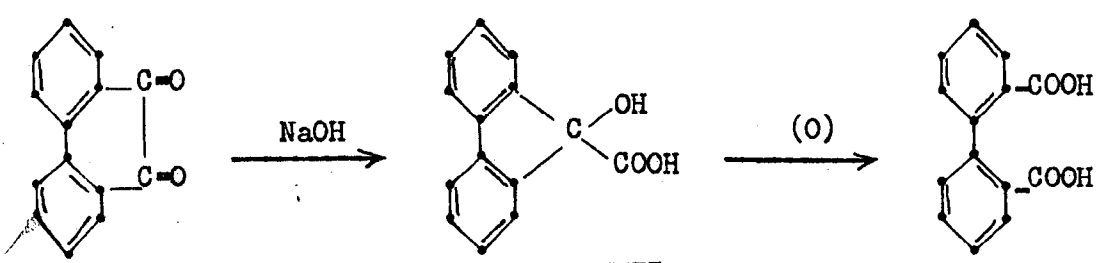
Previous Preparations of the Dicarboxybiphenyls

Doebner (13) found on oxidation of 4,4' ditolyl with acetic acid and chromic acid that he had obtained crystals which were insoluble in any solution he used and did not melt or sublime. Through precipitation in an alkaline solution an amorphous precipitate was formed. The acid formed was transformed (XXI) through treatment of the silver salt with ethyl iodide in diethyl ether. Analysis showed this ester to be identical with the ethyl ester of diphenic acid.



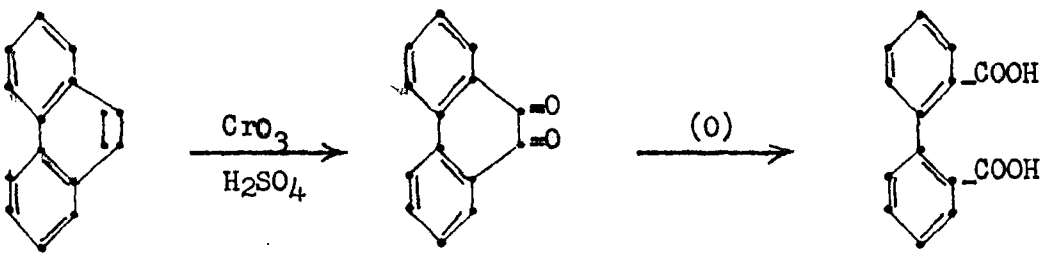
XXI

Thereis a patent by Williams (21) on the preparation of diphenic acid from phenanthrenequinone. He dissolved (XXII) the latter in alkaline solution and oxidized it with sodium peroxide or a current of air.



XXII

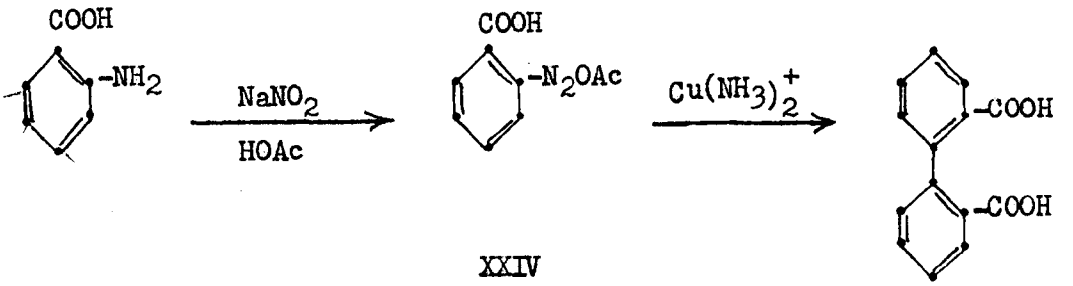
Vorlander (22) stated that the preparation of diphenic acid depends (XXIII) on the oxidation of phenanthrenequinone obtained from phenanthrene by the action of a boiling chromic acid mixture. This method gave a 30% yield.



XXIII

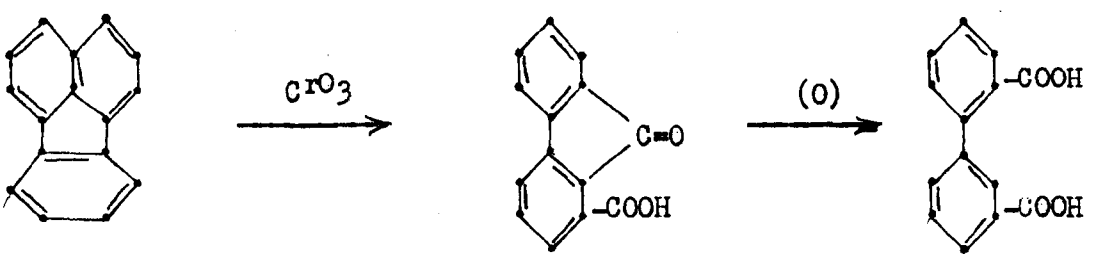
Bischoff and Adkins (23) described a procedure for obtaining 85% yield of diphenic acid from phenanthrenequinone. They suspended the phenanthrenequinone in an alkaline solution of potassium permanganate. After heating and filtering off the manganese dioxide formed, the diphenic acid precipitated when the clear solution was acidified with hydrochloric acid. Phenanthrenequinone treated in the same manner by Charrier (24) but in the absense of sodium hydroxide gave a smaller yield.

Details are given of the diazotization of anthranilic acid with sodium nitrite in hydrochloric acid by Atkinson and Lowler (25) and the reduction with a solution of copper sulfate in ammonium hydroxide and hydroxylamine which gives a 72-84% yield of diphenic acid. Huntress (26) stated a 57% yield of diphenic acid is obtained by diazotizing (XXIV) anthranilic acid in acetic acid and then adding the reaction mixture to a copper hydroxide suspension in dilute ammonium hydroxide.



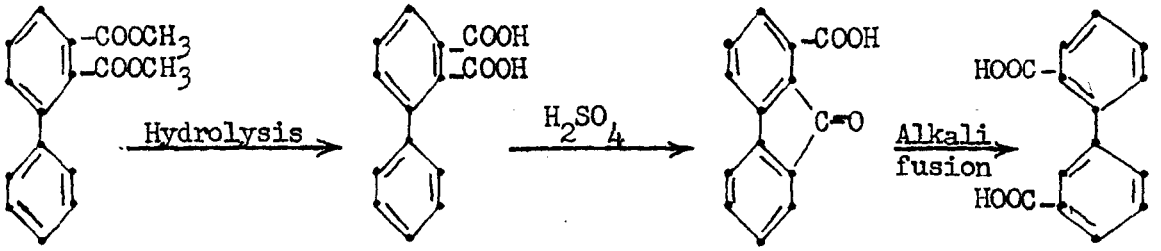
XXIV

Fluoranthene with chromic acid yielded (XXV) fluoranthenequinone and a fluorenonecarboxylic acid. The latter could be converted into a diphenyl dicarboxylic acid by degrading to m-$C_6H_4(COOH)_2$. These facts led Fittig (27) to conclude that the diphenyl carboxylic acid was 2,3' dicarboxybiphenyl.



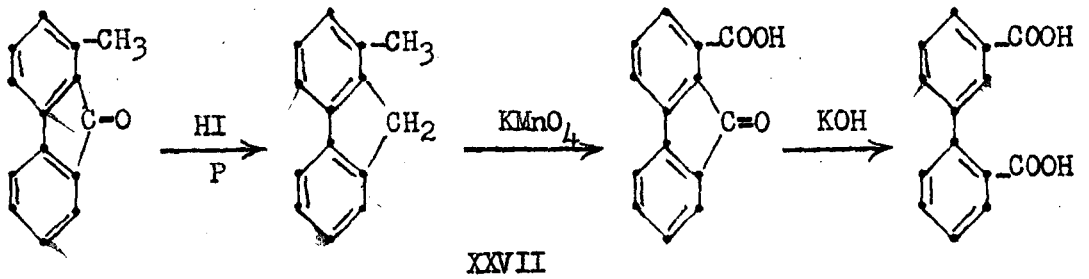
XXV

Butterworth, et al., (28) found the reaction between the diazotized dimethyl ester of 3-aminophthalic acid and benzene gave 3-methyl-3-phenylphthalate in 35% yield, which yielded (XXVI) the 2,3' dicarboxybiphenyl on hydrolysis. The latter was converted by ring closure with sulfuric acid into fluorenone-1-carboxylic acid. 2,3' Dicarboxybiphenyl cannot, however, be regenerated from fluorenone-1-carboxylic acid since the opening of the fluorenone ring by fusion with alkali gives 2,3' dicarboxybiphenyl.



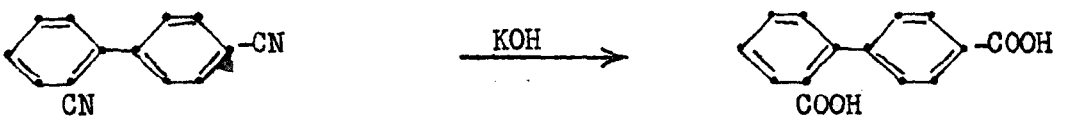
XXVI

From the oxidation of 2,3' dimethylbiphenyl Mayer and Freitag (29) established the structure of isodiphenic acid (2,3' dicarboxybiphenyl). Also, it can be made by the following method of Sieglitz and Schatzkes (30), which though further serving to confirm its structure, is however, of no importance from a preparative point of view. Methyl-3-fluorenone was reduced (XXVII) with 50% hydriodic acid and red phosphorous at 150° C. to a fluorene, which when boiled with 2% potassium permanganate gave fluorenone-3-carboxylic acid. This acid on fusion with potassium hydroxide yielded isodiphenic acid in fine white needles.



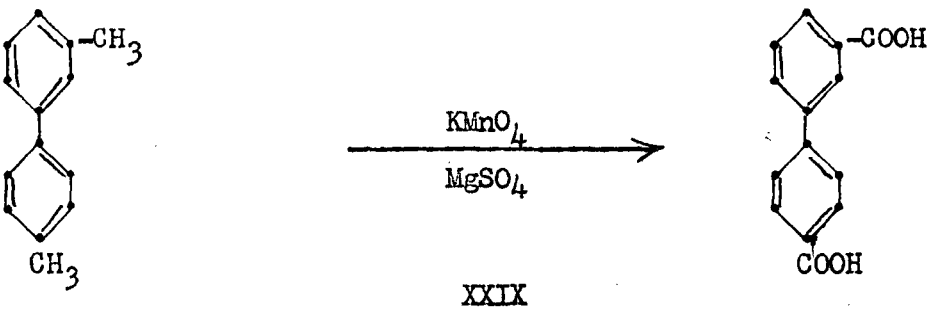
XXVII

Reuland (31) prepared (XXVIII) 2,4'dicarboxybiphenyl by heating the dicyanide with potassium hydroxide. The acid was recrystallized from alcohol.



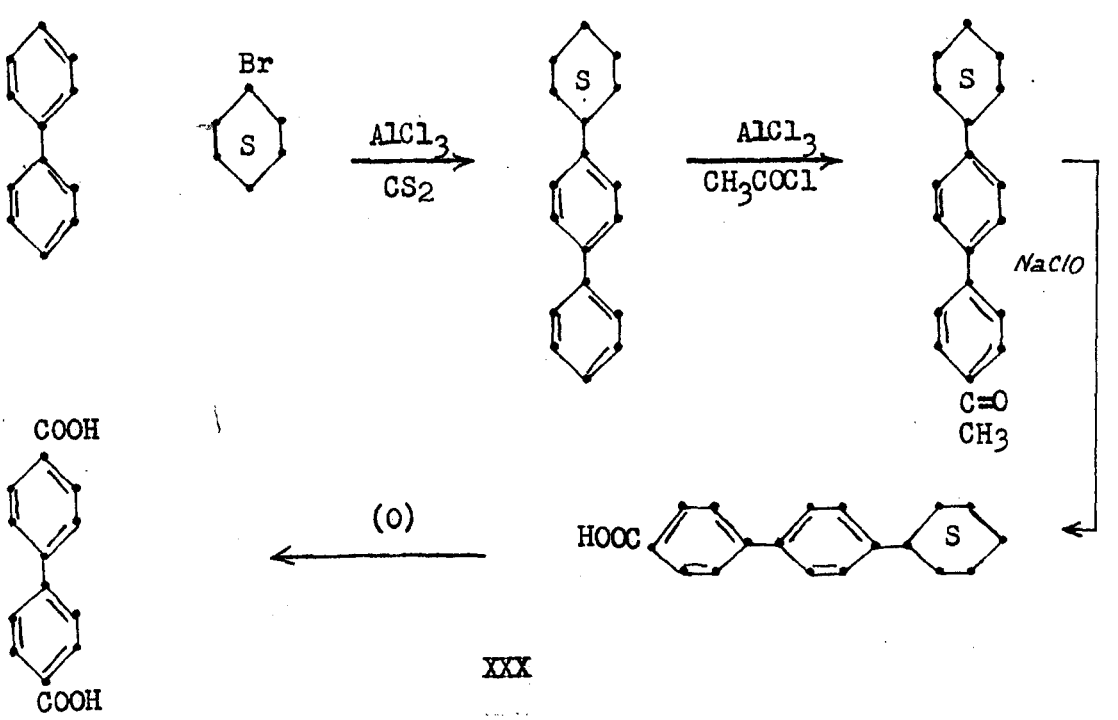
XXVIII

Ghigi (32) found oxidation of 3,4' dimethylbiphenyl with potassium permanganate in the presence of magnesium sulfate gave (XXIX) biphenyl-3,4'-dicarboxylic acid.



XXIX

In a study of 4-cyclohexylbiphenyl derivatives Basford (33) found biphenyl and cyclohexyl bromide with aluminum chloride in carbon disulfide gave (XXX) 4-cyclohexylbiphenyl and 4,4' dicyclohexylbiphenyl. 4-Cyclohexylbiphenyl with acetyl chloride and aluminum chloride gave the 4' acetyl derivatives which on refluxing with sodium hypochlorite gave 4-cyclohexylbiphenyl-4'-carboxylic acid and oxidation of this acid gave biphenyl-4,4'-dicarboxylic acid which melts above 300° C.



XXX

DISCUSSION

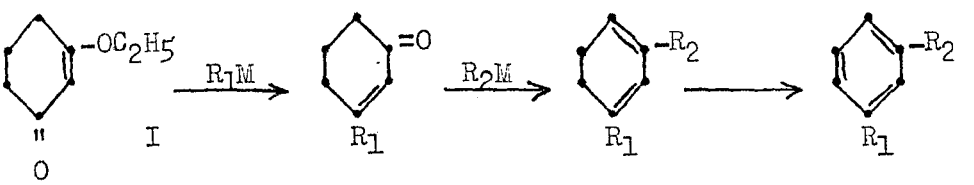
Preparation of Dihydroresorcinol

Dihydroresorcinol was prepared by a new modification of Thompson's method. It was found unnecessary to prepare Raney nickel catalyst preliminary to the synthesis of dihydroresorcinol. The plain nickel aluminum alloy was placed directly into the high pressure bomb without previous treatment. Aqueous sodium hydroxide and resorcinol in the presence of the alloy was a satisfactory reaction mixture for this high pressure hydrogenation. The bomb was filled with hydrogen and the reaction proceeded normally when the bomb was kept from 40° - 60° C. However, when the temperature dropped, no reaction occurred or the reaction was very slow. If the temperature was higher than 60° C., no dihydroresorcinol could be crystallized from the solution which was dark yellow or orange colored.

The preparation of dihydroresorcinol failed when 1 equivalent of aqueous sodium hydroxide to 1 equivalent of resorcinol was mixed with the alloy at atmospheric pressure and room temperature in a shaker. Increased temperature was without effect on the yield. Having the nickel aluminum alloy in an alkaline solution was almost the same condition for the preparation of the Raney nickel. Therefore, it was assumed that during the course of the reaction in the high pressure bomb, the catalyst was formed and used at the same time. It was observed when the alkaline solution of dihydroresorcinol was filtered that the metallic residue was inactive.

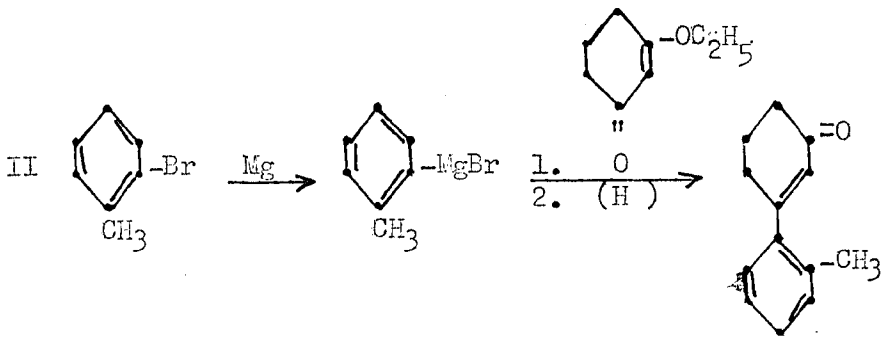
Reactions of 3-Ethoxy-Δ^2-cyclohexenone with Tolylmagnesium Bromides and Methylmagnesium Bromide

It has been reported earlier by Woods, et al. (9, 10, 11, 12) that the reaction of the ethyl enol ether of dihydroresorcinol with organometallic reagents yields 3-substituted-Δ^2-cyclohexenones, and that subsequent reaction of the unsaturated ketone with another organometallic reagent followed by dehydrogenation yields m-disubstituted benzenes. (I)



In this work, reactions of arylmagnesium halides, where the arylmetallic group, R_1M, was ortho, meta, and para tolylmagnesium bromide and the R_2M group was methylmagnesium bromide have been studied.

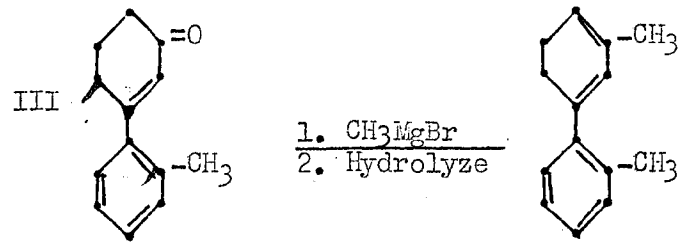
The 3-(2-tolyl)-Δ^2-cyclohexenone was synthesized (II) by adding the mono ethyl enol ether of dihydroresorcinol to an ether solution of 2-tolylmagnesium bromide, which was prepared in approximately 25% excess from magnesium turnings and ortho bromotoluene. The Grignard addition complex was hydrolyzed with sulfuric acid and subjected to steam distillation. In this manner the troublesome impurities of the bromotoluene and biphenyls were readily eliminated, since the 3-(2-tolyl)-Δ^2-cyclohexenone was only slightly volatile with steam.



The analytical and physical data for the tolyl- ^{2}-cyclohexenones are collected in Table II.

3-(2-Tolyl)-Δ^{2}-cyclohexenone, as far as could be determined, has never been reported before in the literature. The carbon-hydrogen values of the ketone and of the 2,4-dinitrophenylhydrazone derivative check well with the calculated values.

An ethereal solution of 3-(2-tolyl)-Δ^{2}-cyclohexenone was added slowly (III) to methylmagnesium bromide in ether. This Grignard complex solution was hydrolyzed with dilute sulfuric acid. The product, 1-(2-tolyl)-3-methylcyclohexadiene-1,3, was collected in 83% yield. Physical data for the three isomeric dienes prepared are collected in Table III.



The dienes tend to polymerize. Therefore, it was advantageous to aromatize as quickly as possible. Aromatization to the 2,3'-dimethylbiphenyl was accomplished (IV) with 5% palladinized carbon. The 2,3'-dimethylbiphenyl was distilled directly from the palladinized carbon residue.

TABLE II

3-Substituted-Δ^2-cyclohexenones and Their Derivatives

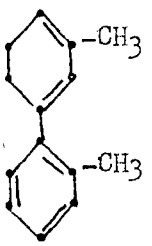
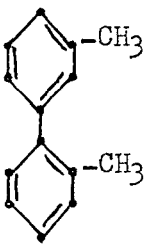
Ketones	Yield %	B.P.° C.	Press. mm.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
o-Tolyl-	41.4	132-132.5	0.2	83.87	7.52	83.88	7.50
m-Tolyl-	43.5	128-128.5	0.2	83.87	7.52	83.90	7.49
p-Tolyl-	51.7	154 (M.P.62-63)	0.5	83.87	7.52	83.85	7.51

2,4-Dinitrophenylhydrazone	M.P.° C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
o-Tolyl-	151-151.5	62.29	4.91	61.93	4.90
m-Tolyl-	127-128	62.29	4.91	62.42	5.10
p-Tolyl-	228-229	62.29	4.91	62.38	5.07

TABLE III

Physical Data for the 3 Dienes

Diene	Yield %	Boiling Point Pressure mm.	n_D^{25}
o-Tolyl	83.3	85° C./0.06	1.5661
m-Tolyl	87.2	100-101° C./0.5	1.5885
p-Tolyl	88.9	115-116° C./0.2	1.5900

IV  Pd-C 

It will be noticed from Table IV that Schultz (34) reported a boiling point of 270° C. at atmospheric pressure for 2,3'-dimethylbiphenyl. In this work, the boiling point found was 81° C. at 0.2 mm. Refractive indices of the 3 dimethylbiphenyls are given in Table IV, and it was observed that the refractive index increased as the methyl group was moved farther from the bond between the rings. This was also noticed with the refractive indices of the 1-tolyl-methylcyclohexadienes-1,3 in Table III.

The 2,3'-dimethylbiphenyl was refluxed (V) with 2% aqueous potassium permanganate with mechanical stirring for 16 to 18 hours. The manganese dioxide was removed by suction filtration and the aqueous solution extracted once with ether to insure removal of any unreacted material. The remaining ether was removed by heating on a steam bath. Concentrated sulfuric acid was added with cooling until the solution was just acid. The white precipitate obtained was recrystallized from hot glacial acetic acid. If the crystals came down slowly, fine white needles were obtained in a 69% yield. Analysis and physical data for the three isomeric dicarboxybiphenyls is found in Table V.

TABLE IV

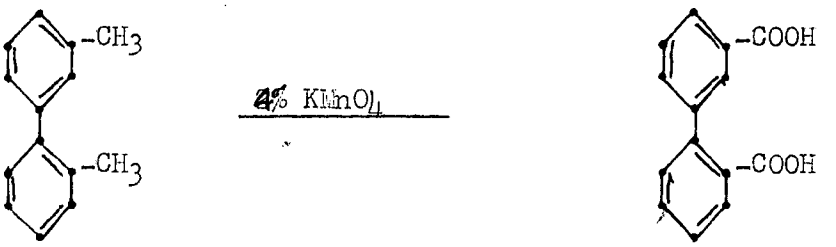
Dimethylbiphenyls

Compd.	Yield, %	B.P.° C.	Press., mm.	n_D^{25}	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2,3'	92.0	81	0.2	1.5490	92.32	7.70	92.89	7.60
3,3'	93.3	108 (M.P. 9)	0.2	1.5922	92.32	7.70	92.41	7.68
3,4'	95.3	99-100 (M.P. 16)	0.5	1.5984	92.32	7.70	92.39	7.71

TABLE V

Dicarboxybiphenyls

Compd.	Yield %	M.P.° C.	Analyses, %			
			Calcd.		Found	
			C	H	C	H
2,3'	68.9%	216-216.5	69.46	4.13	69.60	4.10
3,3'	57.7%	357-358	69.46	4.13	69.52	4.11
3,4'	65.4%	336-337	69.46	4.13	69.53	4.10

V 

Sieglitz and Schatzkes (30) report a melting point of 213-214° C. for 2,3'-dicarboxybiphenyl, while in this work, it was found to be 216-216.5° C.

The preparation of 3-(3-tolyl)-Δ^2-cyclohexenone was accomplished in essentially the same manner as its 3-(2-tolyl) analog. The yield was about 43%.

The conversion of 3-(3-tolyl)-Δ^2-cyclohexenone to 1-(3-tolyl)-3-methylcyclohexadiene-1,3 was accomplished by adding an ether solution of the diene slowly to an ether solution of methyl magnesium bromide. After hydrolyzing the Grignard complex with dilute sulfuric acid, the ether layer was separated and washed with first sodium bicarbonate solution and then water. When dry, the product was distilled under reduced pressure. The yield was approximately 82%.

Immediately following the distillation, the diene was aromatized using 5% palladinized carbon in the absence of a solvent to 3,3' dimethylbiphenyl. The yield was around 93%.

Schlenk and Bruuns (20) report a boiling point of 280° C. at 760 mm. Müller and Töpel (16) report a boiling point of 270-290° C. at 760 mm. Neither reports show a melting point. In this work the boiling point was found to be 108° C. at 0.2 mm. and a melting point of 9° C.

The 3,3' dicarboxybiphenyl was prepared by oxidizing the 3,3' dimethylbiphenyl in aqueous potassium permanganate. A 58% yield of the white crystalline acid was obtained.

Ullmann and Lowenthal (35) report a melting point of 352-354° C. In this work the melting point was found to be 357-358° C.

In the preparation of 3-(4-tolyl)- ^{2}-cyclohexenone, a procedure was followed that was analogous to that given for the aforementioned corresponding compounds. The yield was 52% and the boiling point was 154° C. at 0.5 mm. This compound had a melting point of 64° C. after recrystallization. The 3-substituted- ^{2}-cyclohexenones and their 2,4-dinitrophenylhydrazone derivatives were not found in the literature and the physical data given in Table II is believed to be the first reported on these compounds.

A Grignard reaction was run in a manner similar to those of the previous compounds. 3-(4-Tolyl)- ^{2}-cyclohexenone was added to methylmagnesium bromide yielding 89% of 1-(4-tolyl)-3-methylcyclohexadiene-1,3. Aromatization using palladinized carbon and no solvent was carried out directly. It is interesting to note that these dienes and their aromatized products possess a very pleasing odor; especially 1-(4-tolyl)-3-methylcyclohexadiene-1,3 and the 3,4' dimethylbiphenyl, whose odors are reminiscent of geraniums. The 3,4' dimethylbiphenyl was obtained in a 95% yield. A boiling point of 284-287° C. at 760 mm. is reported by Hey and Jackson (36). Kruber (17) reports a boiling point of 288-289° C. at 752 mm. and a melting point of 14-15° C. The refractive index was reported to be $n_D^{20} = 1.59713$. In the present

investigation the boiling point was found to be 99-100° C. at 0.5 mm, the melting point of 16-16.5° C., and the refractive index at 25° was 1.5984.

Oxidation of 3,4' dimethylbiphenyl with aqueous potassium permanganate using a proceedure exactly similar to those previously described gave 3,4' dicarboxybiphenyl in a 65% yield. The melting point reported in this work was 336-337° C. The melting point found by Weiler (14) was 339-341° C.

By comparing the physical data for these compounds, that is the 3-dimethylbiphenyls and 3-dicarboxybiphenyls, it can readily be seen that the properties reported by this work do not differ markedly from those found earlier.

Ultraviolet Absorption Properties

Figure I shows the ultraviolet curves of the three dimethylbiphenyls, and, from these curves, the following observations can be made: 1. the very slight bathochromic effect of the para and meta methyl groups, and 2. the marked hypsochromic effect of the ortho methyl group. In general, a bathochromic effect results primarily in a small shift of the ~~spectrum~~ CURVE toward the visible region without too great an alteration in the nature of the curve. The hypsochromic effect is defined as a shift of the spectrum toward longer wave lengths and is sometimes the result of a steric factor operative in the molecule. The conjugate effect not only alters the shape of ~~spectra~~ CURVE, (including loss of fine structure), but also causes an extensive shift toward the visible region. Where steric factors seem to repress a conjugate effect, the spectra appears to revert to that of the parent hydrocarbon. The region of absorption in the ultraviolet by a molecule is a consequence of the energy difference between the ground state and some excited state. The greater the energy difference involved the shorter the wave length of the ultraviolet light absorbed by the compound.

Figure II shows the 3 dicarboxybiphenyls in dilute sodium hydroxide solution, Figure III shows the same compounds in distilled water. Figure IV shows the 2,3' dicarboxybiphenyl in very dilute hydrochloric acid solution. The 3,3' and 3,4 ' dicarboxybiphenyls were not soluble in the very dilute hydrochloric acid so that their ultraviolet absorption was not determined. No interpretation could

be made for the curves obtained for these dicarboxybiphenyls. However, since they may be of interest in the future, they are presented here.

FIGURE I ULTRAVIOLET ABSORPTION FOR THE DIMETHYLBIPHENYLS

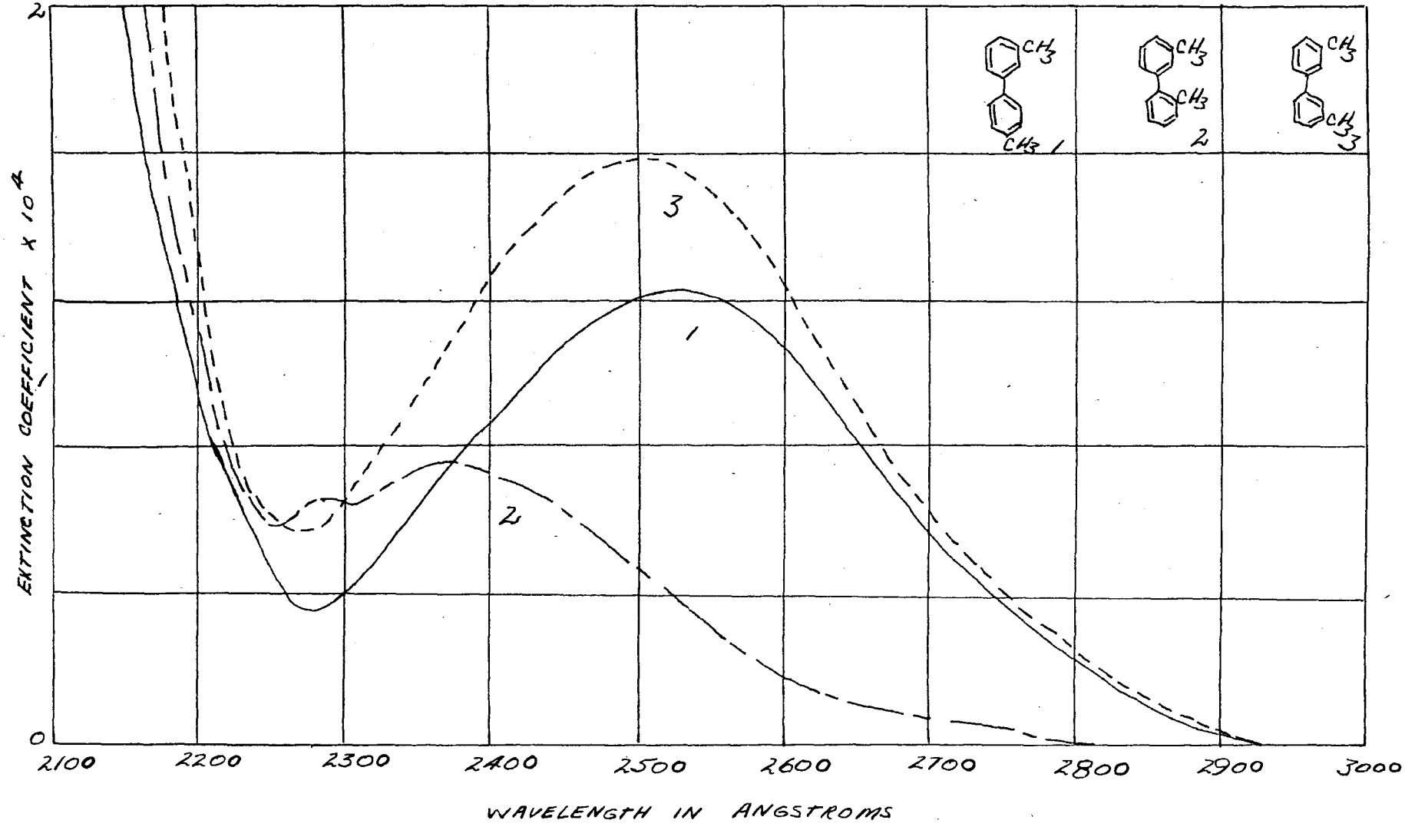


FIGURE II ULTRAVIOLET ABSORPTION FOR THE DICARBOXYBIPHENYLS IN AQUEOUS NaOH

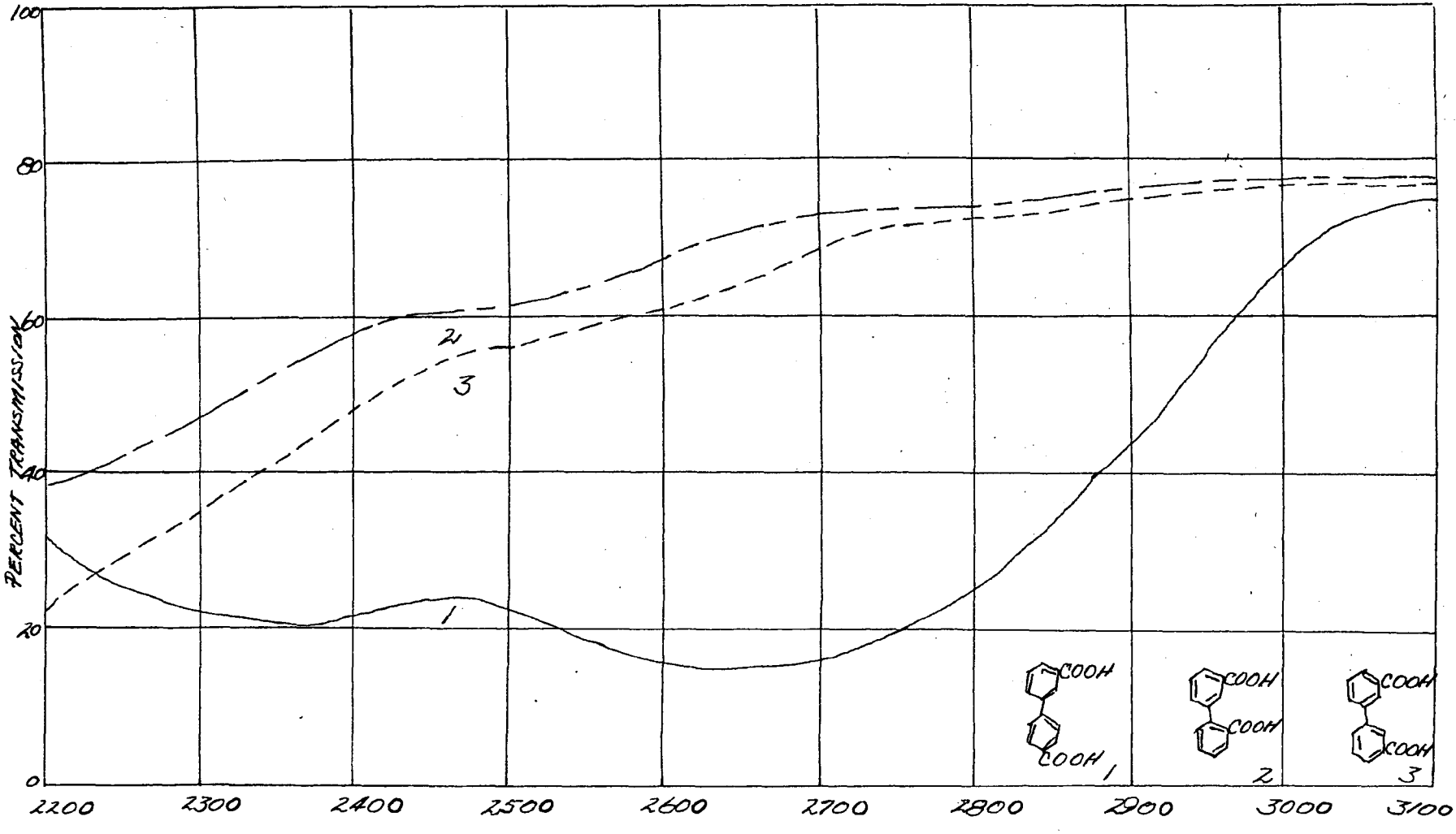


FIGURE III ULTRAVIOLET ABSORPTION FOR THE DICARBOXYBIPHENYLS IN DISTILLED H_2O

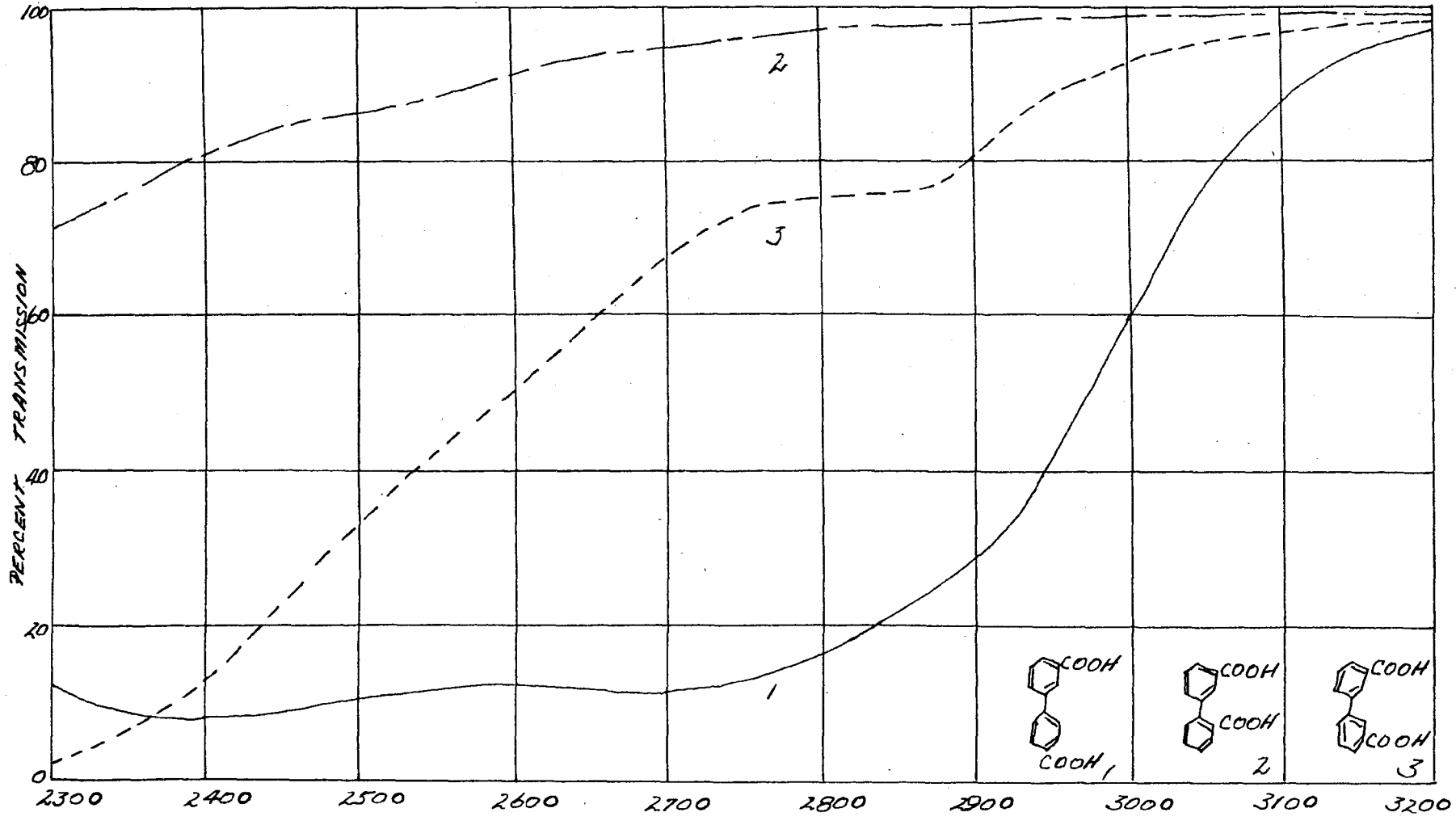
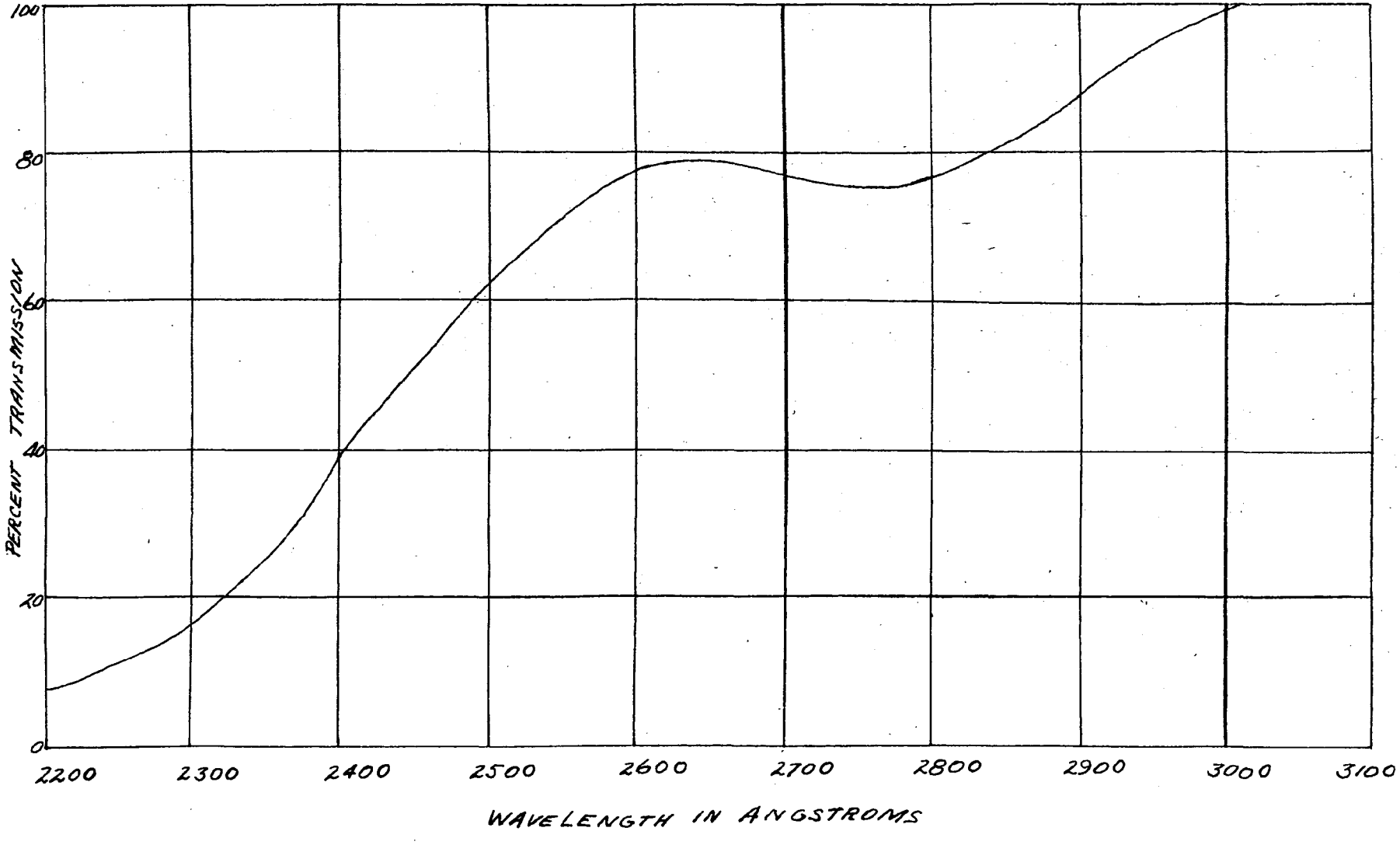
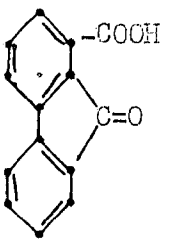


FIGURE II ULTRAVIOLET ABSORPTION OF 2,3' DICARBOXYBIPHENYL IN AQUEOUS HCl

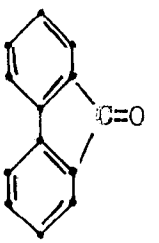


Decarboxylation Studies

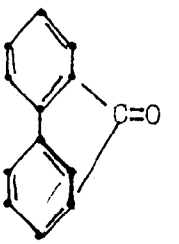
The decarboxylation of 1,3' dicarboxybiphenyl might lead to any of the 3 types of molecules:



I



II



III

Examination of the molecular models of III showed that although considerable strain in bond deformation was present, the molecule might be capable of existance. The models also indicated that the rings would not be coplanar, but rather inclined at an angle in such a manner that the structure would be asymmetric.

In order to study the problem farther, a small amount of 2,3' dicarboxybiphenyl was slurried with a small amount of calcium oxide and water in a suction flask. This mixture was evaporated to dryness. A small test tube was placed in the small suction flask extending to about 2 centimeters from the bottom. Pieces of dry ice were kept in the test tube which acted as a cold finger. By means of a direct flame, the flask was heated slowly to a temperature of about 350° C. and was kept there for approximately 30 minutes. A red material was noticed to form on the cold finger while at the same time a small amount of white material was being formed. The longer the reaction products were heated the more red material was formed. The

white product being quite soluble in benzene was separated from the red, which was very slightly soluble in benzene. This white product was identified as fluorenone with a melting point of 81° C. The p-nitrophenylhydrazone derivative had a melting point corresponding to the one given in the literature and carbon-hydrogen analysis indicated the same empirical formula as the one calculated for the derivative of fluorenone. The red material was easily recrystallized from nitrobenzene. It was identified as rubicene by its melting point and carbon-hydrogen analysis. Rubicene gave a red fluorescence under ~~infrared~~ ULTRAVIOLET light. A small amount of the hydrocarbon in alcohol solution gave a yellow fluorescence. Table VI gives the physical and analytical data for rubicene and for fluorenone and its derivatives.

At the start of the reaction a very minute amount of white crystalline material was formed on the cold finger which disappeared very rapidly. This material had a melting point of 208-209° C, which corresponds to fluorenone-1-carboxylic acid. However, there never was enough isolated on which to run an analysis or from which to make a derivative. It may be assumed that the course of the reaction might be thus:

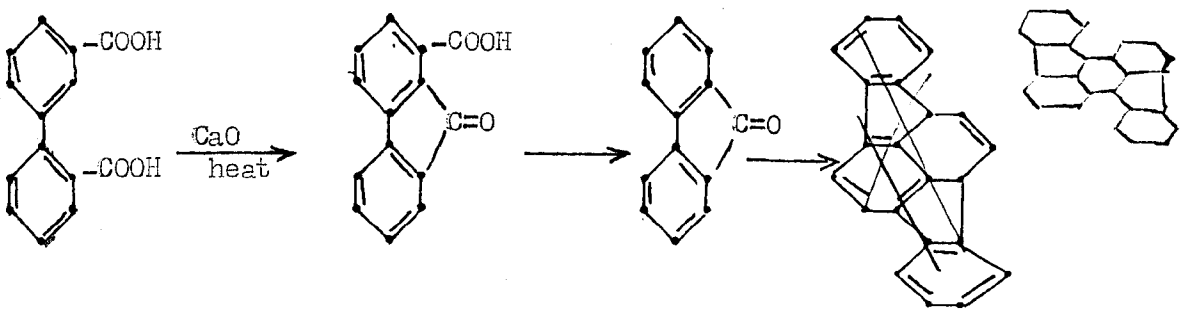


TABLE VI

Fluorenone and Derivatives, and Rubicene

Compd.	Yield %	M.P. °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Fluorenone	45.0	80-2				
P-Nitrophenylhydrazone		267-8	72.38	4.13	72.46	4.18
2,4-Dinitrophenylhydrazone		295-7[d]	63.33	3.33	64.03	3.82
Rubicene	9.9	304-5	95.70	4.29	95.66	4.30

EXPERIMENTAL

The Preparation of Dihydroresorcinol. A solution composed of 100 ml. of water, 55 grams (0.5 mole) of resorcinol and 24 grams (0.5 mole) of sodium hydroxide was placed in a hydrogenation bomb of 306 ml. capacity. Approximately 8 grams of untreated nickel-aluminum alloy (not Raney nickel) was introduced and the bomb charged with hydrogen to about 2500 p.s.i. Hydrogenation was carried out in a thermostated rocker at 40-60° C. until the absorption of hydrogen arrested itself at the theoretical pressure drop corresponding to 0.5 mole of hydrogen (i.e., 1 mole per 1 mole of resorcinol), which in this case was estimated to be 1250 p.s.i. The nickel-aluminum alloy was removed by suction filtration and the filtrate cooled in an ice bath. Concentrated hydrochloric acid was then added until Congo Red paper turned blue. The temperature of the solution was held below 5° C. The precipitate of dihydroresorcinol, which formed after the solution had become chilled in the ice bath, was recovered by suction filtration and pressed as dry as possible with a mushroom stopper. The filter cake was air dried. Autoxidation took place, as indicated by the color becoming dark, but the rate was very slow. After about 12 hours of drying the material was dissolved in approximately 250 ml. boiling benzene and the hot solution filtered with suction through sintered glass, whereby a major contaminant, sodium chloride, was removed.

However, this recrystallization was found to be optional if the dihydroresorcinol was used in the preparation of 3-ethoxy-^{2}-cyclohexenone. The dihydroresorcinol, which crystallized from the benzene on standing in the refrigerator, was filtered and freed from adhering solvent by allowing it to evaporate in the air. The yield* of white, crystalline dihydroresorcinol, of melting point** 102° C. was 88%, which is 49.4 grams or 0.88 mole.

The Preparation of 3-Ethoxy-Δ^{2}-cyclohexenone (Ethyl Enol Ether of Dihydroresorcinol). The details of the preparation of 3-ethoxy-Δ^{2}-cyclohexenone were developed by Mr. Bernard Armbrecht. The method which evolved from his work consisted of treating the silver salt of dihydroresorcinol with ethyl iodide.

Dihydroresorcinol (50 g., 0.45 mole) and 76g. (0.45 mole) of silver nitrate were dissolved in 400 ml. of water in a 1-liter beaker fitted with a mechanical stirrer. The electrodes of a Beckman pH meter were inserted in the solution in order to follow the acidity while 1 N sodium hydroxide was added dropwise to the solution. The addition of sodium hydroxide brought about the precipitation of silver oxide locally, but this disappeared with stirring. It was found that Universal pH paper sufficed as well as the Beckman pH meter if the sodium hydroxide solution was added carefully. When the pH of the solution reached 5.5-6.0, the solid silver salt of dihydroresorcinol, which had precipitated, was

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*All percent yields are based upon the immediate preceding compound.

**All melting points observed were uncorrected.

isolated by suction filtration and pressed reasonably free of adhering solvent. The precipitate (80-85g.) and 300 ml. of benzene were placed in a 1-liter 3-neck flask that was fitted with a trap that would collect the condensed benzene-water azeotrope and allow the upper layer of benzene to overflow back into the flask while the water remained in the trap and could be withdrawn through a stopcock at the bottom. The flask was also equipped with a mechanical stirrer and a dropping funnel. The benzene solution was refluxed until no more water collected in the trap, and then 79 g. (0.5 mole) of ethyl iodide was added through the dropping funnel, while refluxing was continued. Then 15 minutes after the complete addition of the ethyl iodide, refluxing was discontinued and, after cooling, the precipitate of silver iodide was removed by suction filtration. The benzene solution was distilled by means of the water aspirator. After removal of the benzene, 38 g. (0.27 mole or 52 % yield) of 3-ethoxy-Δ^2-cyclohexenone distilled at 82-84° C./0.8 mm. (n_D^{25} = 1.501).

The Preparation of 3-(2-Tolyl)-Δ^2-cyclohexenone from the 3-Ethoxy-Δ^2-cyclohexenone. The o-tolylmagnesium bromide was prepared from 8 g. (0.33 mole) of magnesium turnings and 50 g. (0.34 mole) of o-bromotoluene in 100 ml. of anhydrous ether in a 500 ml. 3-neck flask. The flask was fitted with a condenser, a Hirshberg stirrer and a dropping funnel. Through the dropping funnel a solution of 37 g. (0.27 mole) of 3-ethoxy-Δ^2-cyclohexenone in 150 ml. of anhydrous ether was introduced cautiously at a rate to keep the ether refluxing. After cooling in an ice bath, the Grignard complex hydrolyzed with 250 ml. of ice and water containing 20 ml. of

concentrated sulfuric acid. The apparatus was rearranged for steam distillation and 1.5 liters of distillate removed. The aqueous solution in the reaction flask was extracted twice with a total of 150 ml. of ether. The ether extract was washed with 75 ml. of 10% aqueous sodium carbonate and then once with 50 ml. of water and dried over anhydrous magnesium sulfate. The ether was removed by means of a water aspirator and using a vacuum pump and an electrically heated oil bath the 3-(2-tolyl)- Δ^2-cyclohexenone was collected in 41.4% yield (20.3 g. or 0.12 mole) at 132-132.5° C./0.2 mm. Anal. calcd. for $C_{13}H_{14}O$: C., 83.87%; H., 7.52%. Found: C., 84.24%, 83.88%; H., 7.50%, 7.50%.

In the usual manner 3-(2-tolyl)- Δ^2-cyclohexenone formed a red 2,4-dinitrophenylhydrazone which melted at 151-151.5° C. Anal. calcd. for $C_{19}H_{19}O_4N_4$*: C., 62.29%; H., 4.91%. Found: C., 61.93%, 61.86%; H., 4.90%, 5.31%.

The Preparation of 1-(o-Tolyl)-3-methylcyclohexadiene-1,3 from 3-(2-Tolyl)- Δ^2-cyclohexenone. Methylmagnesium bromide was prepared from 4 g. (0.16 mole) of magnesium turnings and 50 ml. of anhydrous ether, the methyl bromide being bubbled into the solution until all the magnesium disappeared. A solution of 60 ml. of dry ether and 18 g. (0.10 mole) of the 3-(2-tolyl)- Δ^2-cyclohexenone was slowly added to the methylmagnesium bromide. This Grignard complex solution, which set to a solid on cooling, was hydrolyzed with cold aqueous 10% sulfuric acid. The ether layer was washed

*Microanalysis of compounds containing nitrogen was done by Mrs. Mary Aldridge.

once with 30 ml. of water, then with 30 ml. of 10% aqueous sodium carbonate and finally with 30 ml. of water and was dried over anhydrous magnesium sulfate. After the ether was removed, the apparatus was fitted for vacuum distillation and the 1-(2-tolyl)-3-methylcyclohexadiene-1,3 was collected at 85° C./0.06 mm. in 83.3% yield (15 g. or 0.08 mole), (n_D^{25} = 1.5661).

Conversion of 1-(2-tolyl)-3-methylcyclohexadiene-1,3 to 2,3' Dimethylbiphenyl. Palladinized carbon (5%) was added directly to a 50 ml. round bottom flask fitted with a condenser. Then 14 g. (0.07 mole) of 1-(2-tolyl)-3-methylcyclohexadiene-1,3 was added. Heating was accomplished with a small open flame and refluxing continued for 3 hours in order to complete aromatization. The aromatized product was vacuum distilled directly from the palladinized carbon residue at 81° C./0.2 mm. in a 92% yield (12.9 g. or 0.07 moles). Anal. calcd. for $C_{14}H_{14}$: C.,92.32%; H., 7.70%. Found: C., 92.89%, 92.60%; H., 7.60%, 7.62%. (n_D^{25} = 1.5490)

The Preparation of 2,3' Dicarboxybiphenyl from 2,3' Dimethylbiphenyl. The 2,3' dimethylbiphenyl (2 g. or 0.01 moles) was mixed with 250 ml. of aqueous 4% potassium permanganate and refluxed while mechanically stirring for 16 to 18 hours, or until the pink color was no longer detected. The manganese dioxide was removed by suction filtration and the aqueous solution extracted once with 30 ml. of ether to insure removal of any unreacted material. The solution was made just acid with concentrated sulfuric acid, and then cooled slowly. The finely divided white precipitate was

recrystallized from hot glacial acetic acid. If this product was recrystallized slowly fine, white, needle-like crystals were obtained. The yield was 68.9% (1.8 g. or .0070 mole) and the melting point was 216-216.5° C. Anal. calcd. for $C_{14}H_{10}O_4$: C., 69.46%; H., 4.13%. Found: C., 69.60%, 69.54%; H., 4.10%, 4.11%.

The Preparation of 3-(3-Tolyl)-Δ^2-cyclohexenone from the 3-Ethoxy-Δ^2-cyclohexenone. m-Tolylmagnesium bromide was prepared from 8 g. (0.33 mole) of magnesium turnings and 50 g. (0.34 mole) of m-bromotoluene in 100 ml. of anhydrous ether in a 500 ml. 3-neck flask. The flask was fitted with a condenser, a Hirshberg stirrer and a dropping funnel. Through the dropping funnel, a solution of 37 g. (0.27 mole) of 3-ethoxy-Δ^2-cyclohexenone in 150 ml. of anhydrous ether was introduced cautiously at a rate to keep the ether refluxing. After cooling in an ice bath, the Grignard complex hydrolyzed with 250 ml. of ice and water containing 20 ml. of concentrated sulfuric acid. The apparatus was arranged for steam distillation and 1.5 liters of distillate removed. The aqueous solution in the reaction flask was extracted twice with a total of 150 ml. of ether. The ether extract was washed with 50 ml. of 10% aqueous sodium carbonate and then once with 75 ml. of water and dried over anhydrous magnesium sulfate. By means of a water aspirator the ether was removed. Using a vacuum pump and an electrically heated oil bath, the 3-(3-tolyl)-Δ^2-cyclohexenone was collected in a 43.5% yield (21.4 g. or 0.11 mole) at 128-128.5° C./0.2 mm. Anal. calcd. for $C_{13}H_{14}O$: C., 83.87%; H., 7.52%. Found: C., 83.90%, 83.95%; H., 7.49%, 7.41%.

In the usual manner 3-(3-tolyl)- ^{2}-cyclohexenone formed a red 2,4-dinitrophenylhydrazone which melted at 127-128° C. The ketone was added to a methanol solution of 2,4-dinitrophenylhydrazine hydrochloride which had been acidified with concentrated hydrochloric acid. Anal. calcd. for $C_{19}H_{19}O_4N_4$: C., 62.29%; H., 4.91%. Found: C., 62.42%,62.52%; H., 5.10%, 5.17%.

The Preparation of 1-(3-Tolyl)-3-methylcyclohexadiene-1,3 from 3-(3-Tolyl)- Δ^2-cyclohexenone. The methylmagnesium bromide was prepared from 4 g. (0.16 mole) of magnesium turnings and 50 ml. of anhydrous ether, the methyl bromide was bubbled into the solution until all the magnesium disappeared. An etheral solution (60 ml.) of 18 g. (0.10 mole) of the 3-(3-tolyl)- Δ^2-cyclohexenone was slowly added to the methylmagnesium bromide. This Grignard complex solution, which solidified on cooling, was hydrolyzed with cold 10% aqueous sulfuric acid. The ether layer was washed once with 40 ml. of water, then with 30 ml. of 10% aqueous sodium carbonate and finally with 40 ml. of water and was dried over anhydrous magnesium sulfate. After the ether was removed, the apparatus was fitted for vacuum distillation and the 1-(3-tolyl)-3-methylcyclohexadiene-1,3 collected at 100-101° C./0.5 mm in an 87.2% yield (15.7 g. or 0.08 mole), (n_D^{25}- 1.5885).

Conversion of 1-(3-Tolyl)-3-methylcyclohexadiene-1,3 to 3,3' Dimethylbiphenyl. Palladinized carbon (5%) was added directly to a 50 ml. flask containing 15 g. of 1-(3-tolyl)-3-methylcyclohexadiene-1,3. The flask was fitted with a water condenser and heated by means of a small open Bunsen flame. The refluxing was continued

for 3 hours in order to insure complete aromatization. The aromatized product distilled at 108° C./0.08 mm. in a 93.3% yield (14 g. or 0.08 mole). Melting point, 9-10° C. (n_D^{25} = 1.5922). Anal. calcd. for $C_{14}H_{14}$: C., 92.32%; H., 7.70%. Found: C., 92.41%, 92.44%; H., 7.68%, 7.68%.

The Preparation of 3,3' Dicarboxybiphenyl from 3,3' Dimethylbiphenyl. The 3,3' dimethylbiphenyl (2 g. or 0.01 mole) was mixed with 250 ml. of aqueous 4% potassium permanganate and refluxed while mechanically stirring for 16 to 18 hours or until the pink color of the permanganate was not detectable. The manganese dioxide was removed by suction filtration and the aqueous solution extracted once with 30 ml. of ether to remove any of the unreacted compound. The solution was made just acid with concentrated sulfuric acid, then cooled slowly. The white precipitate was recrystallized from hot glacial acetic acid (120 ml.). This was allowed to recrystallize slowly at room temperature and fine white needles were obtained. The yield was found to be 57.7% (1.5 g. or.0057 mole). Melting point, 357-358° C. Anal. calcd. for $C_{14}H_{10}O_4$: C., 69.46%; H., 4.13%. Found: C., 69.52%, 69.44%; H., 4.11%, 4.09%.

The Preparation of 3-(4-Tolyl)-Δ^2-cyclohexenone from the 3-Ethoxy-Δ^2-cyclohexenone. p-Tolylmagnesium bromide was prepared from 8 g. (0.33 mole) of magnesium turnings and 50 g. (0.34 mole) of p-bromotoluene in 100 ml. anhydrous ether in a 500 ml. 3-neck flask. The flask was set up with a condenser, a Hirshberg stirrer and a dropping funnel. Through the dropping funnel, a solution of 37 g. (0.27 mole) of 3-ethoxy-Δ^2-cyclohexenone was introduced cautiously

into 150 ml. of anhydrous ether at a rate to keep the ether refluxing. After cooling in an ice bath, the Grignard complex was hydrolyzed with 250 ml. of ice water containing 20 ml. of concentrated sulfuric acid. The apparatus was rearranged for steam distillation and 1.5 liters of distillate was removed. The aqueous reaction mixture was extracted with ether twice, using 50 ml. portions each time. The ether extract was washed with 25 ml. of 10% aqueous sodium carbonate and with 30 ml. of water and finally dried over anhydrous magnesium sulfate. Evaporation of the ether left a solid residue which was taken up in petroleum ether (30-60° C.), treated with decolorizing carbon, and recrystallized from petroleum ether solution. These crystals were the 3-(4-tolyl)-Δ^2-cyclohexenone with a melting point of 62-63° C. Mixed melting points showed that this material could also be purified by distillation. Distilling for purification did not alter the yield. The yield was 51.7% (25.4 g. or 0.13 mole). Boiling point, 154° C./0.5 mm. Anal. calcd. for $C_{13}H_{14}O$: C., 83.87%; H., 7.52%. Found: C., 83.85%, 83.57%; H., 7.51%, 7.43%.

In the usual manner 3-(4-tolyl)-Δ^2-cyclohexenone formed a red 2,4-dinitrophenylhydrazone which melted at 228-229° C. Anal. calcd. for $C_{19}H_{19}O_4N_4$: C., 62.29%; H.,4.91%. Found: C., 62.40%, 62.38%; H., 5.07%, 5.09%.

<u>The Preparation of 1-(4Tolyl)-3-methylcyclohexadiene-1,3 from 3-(4-Tolyl)-Δ^2-cyclohexenone</u>. Methylmagnesium bromide was prepared from 4 g. (0.16 mole) of magnesium turnings and 50 ml. of dry ether. The methyl bromide was bubbled into the solution until all the magnesium had reacted. Then 60 ml. of ether containing 18 g. (0.10 mole) of the 3-(4-tolyl)-Δ^2-cyclohexenone was slowly added to

the methylmagnesium bromide. This Grignard complex solution, which became solid on standing, was hydrolyzed with cold 10% sulfuric acid. The ether layer was washed once with 30 ml. of water, then with 30 ml. of 10% aqueous sodium carbonate and with 40 ml. of water and finally dried over anhydrous magnesium sulfate. After the ether was removed by means of a water aspirator, the apparatus was fitted for vacuum distillation and the 1-(4-tolyl)-3-methylcyclohexadiene-1,3 collected at 115-116° C./0.2 mm. in 88.9% yield (16.0 g. or 0.08 mole), (n_D^{25}= 1.5900).

Conversion of 1-(4-Tolyl)-3-methylcyclohexadiene-1,3 to 3,4' Dimethylbiphenyl. Directly to a small flask containing 15 g. of 1-(4-tolyl)-3-methylcyclohexadiene-1,3 was added palladinized carbon (5%). The flask was fitted with a water condenser. A small open flame was used to heat the flask. The refluxing was continued for 3 hours in order to accomplish complete aromatization. The aromatized 3,4' dimethylbiphenyl distilled at 99-100° C./0.5 mm. with a yield of 95.3% (14.3 g. or 0.07 mole). Melting point, 16-17° C. (n_D^{25}= 1.5984). Anal. calcd. for $C_{14}H_{14}$: C., 94.32%; H., 7.70%. Found: C., 92.39%, 92.41%; H., 7.71%,7.79%.

The Preparation of 3,4' Dicarboxybiphenyl from 3,4' Dimethylbiphenyl. The 3,4' dimethylbiphenyl (2 g. or 0.01 mole) was mixed with 250 ml. of aqueous 4% potassium permanganate and refluxed while mechanically stirring for 18 hours or until the pink color was no longer detected. The manganese dioxide was removed by suction filtration and the aqueous solution extracted once with 20 ml. of ether to remove any of the unreacted compound.

The solution was made just acid, and then cooled slowly. The white precipitate was recrystallized from hot glacial acetic acid and allowed to crystallize slowly in fine, white crystals. The yield of 3,4' dicarboxybiphenyl was 65.4% (1.7 g. or 0.0065 mole). Melting point, 336-337° C. Anal. calcd. for $C_{14}H_{10}O_4$: C., 69.46%; H., 4.13%. Found: C., 69.53%, 69.50%; H., 4.10%, 4.09%.

Ultraviolet Absorption Spectra. The ultraviolet absorption spectra were determined using a Beckman spectrophotometer. The solvent used for the dimethylbiphenyls was cyclohexane. The concentration of the three dimethylbiphenyls was 4×10^{-5} mole/liter. The cyclohexane was purified by successive extensive treatments with chlorosulfonic acid, concentrated sulfuric acid, alkaline permanganate solution and a final distillation from sodium. The solvent used for the three dicarboxybiphenyls in Figure II was aqueous sodium hydroxide of concentration 4 mg./250 ml. water. The concentration of the dicarboxybiphenyls was 0.8 mg./100 ml. of solvent. Distilled water was the solvent used while making the curve for Figure III, the dicarboxybiphenyl concentration being 0.4 mg./100 ml. The concentration of the hydrochloric acid for Figure IV was 1 drop/100 ml. of distilled water, and the 2,3' dicarboxybiphenyl concentration was 0.5 mg./100 ml. of solvent.

The Decarboxylation of 2,3' Dicarboxybiphenyl to Yield Fluorenone and Rubicene. 2,3' Dicarboxybiphenyl (1.5 g. or 0.0057 mole) was slurried with 2 g. (0.03 mole) of calcium oxide and water in a 50 ml. suction flask. This mixture was evaporated to dryness and then a small test tube was placed in the top of the flask, held

by means of a rubber stopper, extending about 2 cm. from the bottom. Pieces of dry ice were kept in the test tube, which acted as a cold finger. By means of a direct flame from a Bunsen burner the flask was heated slowly to a temperature of about 350° C. and held there for 30 minutes. A mixture of a red material and a white material formed on the cold finger simultaneously. The longer the reaction products were heated the more red material was formed. The 2 materials were separated by the use of benzene, the white product being the more soluble and the red product only slightly soluble in benzene. The white product was fluorenone and recrystallized from 15 ml. of a 1:1 mixture of benzene and petroleum ether (60-80° C.) using decolorizing carbon. Yield, 45.0% (0.5 g. or 0.002 mole). Melting point, 80-82° C.

In the usual manner the orange-red p-nitrophenylhydrazone derivative of fluorenone was made. Melting point, 267-268° C. Anal. calcd. for $C_{19}H_{13}O_2N_3$: C., 72.38%; H., 4.13%. Found: C., 72.48%, 72.46%; H., 4.20%, 4.18%.

Also in the usual manner the orange-red 2,4-dinitrophenylhydrazone of fluorenone was made. Melting point, 295-297° C. Anal. calcd. for $C_{19}H_{12}O_4N_4$: C., 63.33%; H., 3.33%. Found: C., 64.03%, 64.03%; H., 3.82%, 3.91%.

The red substance was recrystallized from 10 ml. of nitrobenzene and identified as rubicene. Melting point, 304-305° C. The yield was 9.9% (0.2 g. or 0.0006 mole). Anal. calcd. for $C_{26}H_{14}$: C., 95.70%; H., 4.29%. Found: C., 95.66%, 95.58%; H., 4.30%, 4.36%.

The rubicene gave a bright red fluorescence under infrared light and a small amount of the hydrocarbon in ethanol gave a yellow

fluorescence.

At the start of the reaction a very minute amount of white, needle-like material was formed on the cold finger, which disappeared quite rapidly. This material had a melting point of 208-209° C. which corresponded to fluorenone-1-carboxylic acid. However there never was enough compound isolated to run an analysis on or to make a derivative.

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