m-DIARYLBENZENES: SYNTHESES AND ULTRAVIOLET SPECTRA

By

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TABLE OF CONTENTS

INTRODUCTION

A method had been developed earlier in this laboratory by Tucker[1] for the preparation of meta substituted diaryl-benzenes from the monoethyl ether of dihydroresorcinol. It seemed pertinent that this synthetic route should be extended and the utility of this enol ether as a starting material for preparing meta disubstituted benzenoid hydrocarbons be exploited. Therefore, a series of polyphenyls was prepared by the general reaction scheme shown below. The nature of the
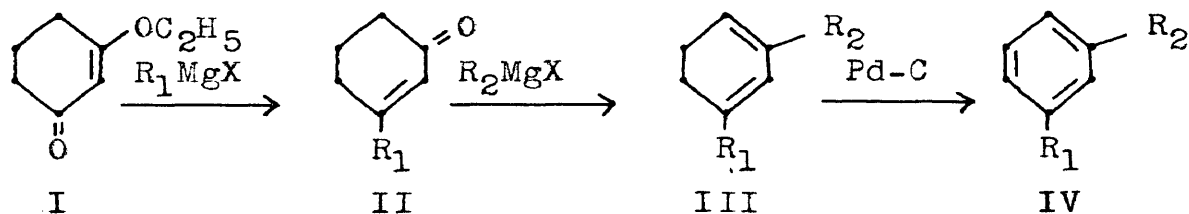
substituents, R_1 and R_2, was varied to include all the possible combinations of phenyl, 2-xenyl, 3-xenyl, and 4-xenyl groups in the final compound (IV).

Since the groups R_1 and R_2 possessed conjugate unsaturation, it was also a purpose of this research to investigate the ultraviolet light absorption of these substances in which the meta substituents cannot jointly enter into a resonant hybrid. This was done by determining the absorption curves in the ultraviolet region of the spectrum for each compound prepared. These absorption curves not only demonstrated the prohibited resonance between meta substituents, but also brought out certain other fundamental facts applicable to

the theory of absorption of ultraviolet light by organic molecules. These are discussed in a later section.

While this work was in progress, it became apparent that certain other avenues of approach were worthy of investigation. To confirm further the interpretation of the ultraviolet spectra, a series of compounds was prepared in which R_1 was the tolyl group (there being three possible isomers) and R_2 was the methyl group, thus resulting in three isomeric dimethylbiphenyls. A still further extension of the problem resulted in the preparation of the three isomeric compounds of type II, in which R_1 was a chlorophenyl group, and also compounds of type II and IV in which the R groups were the α- and β- naphthyls.

HISTORICAL

As has been stated in the Introduction, earlier work in this laboratory[1] has shown the potentiality of dihydro-resorcinol as a starting reagent for the preparation of meta substituted aromatic hydrocarbons. The thesis of Dr. Erwin W. Tucker[1] very thoroughly encompasses the historical background of the efforts of early workers to prepare the few polyphenyls which are known. This historical search will not be repeated here and the reader is referred to Dr. Tucker's thesis.

It should be of interest, however, to review the work which has been done on substituted polyphenyls. Since this thesis concerns itself with meta disubstituted benzenoid compounds, wherein the substituents are either phenyl or xenyl (the accepted nomenclature for the biphenyl radical with one free valence), this historical summary will cover, primarily, compounds of this type. However, in view of some recent and very interesting work on the chemistry of o-terphenyl, this compound will be included in this portion of the thesis.

Schmidt and Schultz[2] appear to be the first workers to have reported the preparation of any derivatives of m-terphenyl. A trinitro compound resulted from the treatment of m-terphenyl with fuming nitric acid. No attempt was made to prove its structure. This compound on reduction with zinc and hydrochloric acid afforded a "288° melting base".

A monobromo and tetrabromo derivative have been re-
ported by Olgiati[3]; the former substance was prepared from
equimolar amounts of m-terphenyl and bromine in carbon
disulfide and the latter from either m-terphenyl or from
monobromo-m-terphenyl by treating with excess bromine.
Oxidation of the monobromo compound with chromic oxide gave
either 4- or 6-bromo-3-carboxydiphenyl which led Olgiati to
conclude that the monobromo derivative would be 4'-bromo-m-
terphenyl*. Oxidation of the tetrabromo compound gave both

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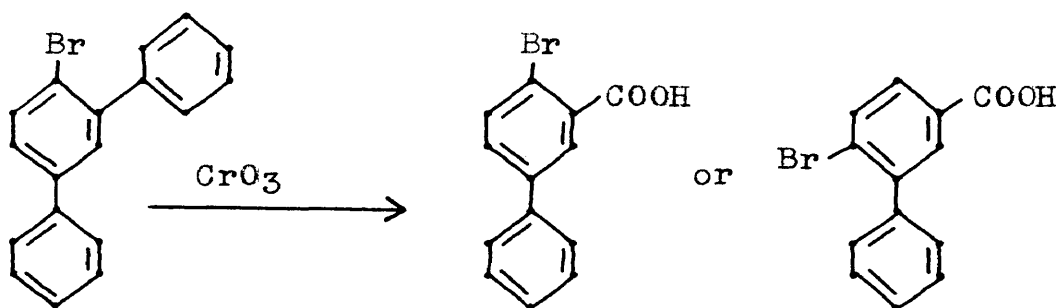
* This nomenclature and that used throughout this thesis is
in accordance with that recommended by Chemical Abstracts.
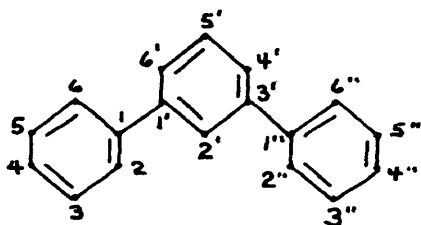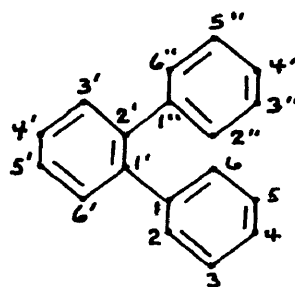
m-Terphenyl   o-Terphenyl

4-bromobenzoic acid and 3,4-dibromobenzoic acid which seemed to conclude an original compound, 3",4,4',4"-tetrabromo-m-terphenyl.
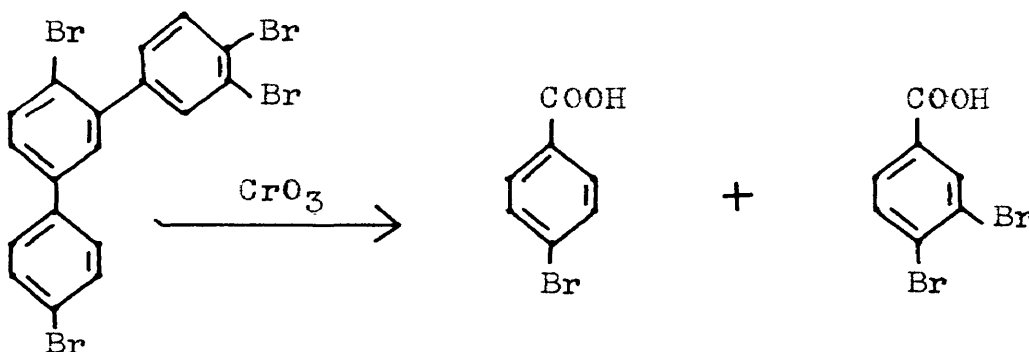
France, Heilborn and Hey[4] have also studied the nitro derivatives of m-terphenyl by preparing a mono-, a di-, and a tri-nitro-m-terphenyl. The mononitro compound was shown to be 4'-nitro-m-terphenyl since on oxidation it gave 2-nitro-5-carboxydiphenyl, the structure of which was proven by an independent synthesis. For the dinitro compound they
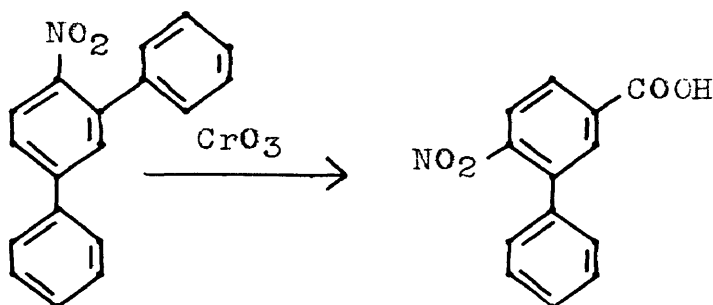
proposed the structure 4,6'-dinitro-m-terphenyl since this compound on oxidation gave 4-nitrobenzoic acid, indicating the second nitro group was in the para position of the termi- nal ring. They proposed the structure 4,4",6'-trinitro-m- terphenyl for the trinitro derivative, basing this on anology but on no chemical evidence. This work was essentially con- firmed by Wardner, and Lowry[5] who synthesized the same nitro

NO2 ... NO2 $\xrightarrow{\text{CrO}_3}$ COOH ... NO2
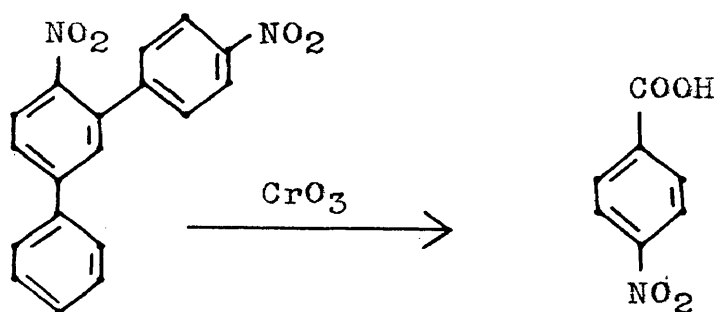
derivatives and came to the same conclusions as to structure. They further reported that the trinitro compound was resistant to oxidation. By catalytic reduction of the mononitro derivative these workers prepared the corresponding monoamine (m.p. 64°). From this they prepared the hydrochloride salt, the acetyl derivative (m.p. 117°) and the benzoyl derivative (m.p. 152°). Diazotization of the amine followed by coupling with various naphthyl residues gave colored compounds possessing dying properties.

The monochloro and monobromo derivatives of m-terphenyl have been synthesized by Cook and Cook[6] through the treatment of m-terphenyl with the corresponding halogen in the presence of iron. In both cases the halogen was shown to be in the 4'-position. The 4'-chloro-m-terphenyl was oxidized to yield the acid, 2-chloro-5-carboxybiphenyl, whose structure was proven by synthesis from 3-nitro-4-aminotoluene. This same oxidative procedure was also employed to prove the structure of 4'-bromo-m-terphenyl. In an attempt to account for the absence of any 4-bromo-3-carboxybiphenyl in the oxidation products, they prepared 3-methyl-4-bromobiphenyl and carried out the same oxidative procedure on it. All attempts failed; the desired product was apparently destroyed during the oxidation.

Cook and Cook[7] have also prepared the 4'-amino-m-terphenyl and 4'-iodo-m-terphenyl. The former was obtained by treating 4'-chloro-m-terphenyl with an excess of 28% hydroxylamine solution, cuprous chloride, calcium oxide, and copper for a period of thirty hours at 190° C. and 800 to 850 p.s.i. The product was isolated as the amine hydrochloride. The free amine was liberated with potassium hydroxide. Transformation of this to the diazonium compound and addition of potassium iodide afforded the 4'-iodo-m-terphenyl

The reaction of cyclohexene oxide with phenol in the presence of boron trifluoride has been shown by Price and Mueller[8] to result in a small amount of 4,4"-dihydroxy-m-terphenyl, although the principle products of the reaction were p-cyclohexylanisole and 1,3-dianisyl cyclohexane. Similarly some 4,4"-dimethoxy-m-terphenyl is obtained when cyclohexene oxide is treated with anisole and aluminum chloride. Substitution of 1,2-dichlorocyclohexane for cyclohexene oxide results in similar reaction products. The 4,4"-dihydroxy-m-terphenyl was reacted at 300° C. with zinc dust to give m-terphenyl.

At the time of this writing, Bradsher and Swerlick[9] are apparently in the process of a more comprehensive investigation of certain reactions of m-terphenyl. A preliminary report has indicated some interesting results. Bradsher implied that his earlier work had shown that monohalogenation and nitration resulted in substitution of the 4'-position

while the Friedel and Crafts reaction resulted in substitution on the 4-position. In preparing the 4'-cyano-m-terphenyl by the reaction of crude monobromo compound with cuprous cyanide, these workers obtained not only the expected 4'-cyano-m-terphenyl, but also a small nitrile fraction which yielded 4-carboxy-m-terphenyl on hydrolysis. Also, in studying the benzoylation of m-terphenyl by the Friedel and Crafts method, they found that their product contained some 4'-benzoyl-m-terphenyl as well as the expected 4-benzoyl isomer. However, when using the Perrier complex of benzoyl chloride-aluminum chloride, only the 4'benzoyl-m-terphenyl was obtained, and this in 69% yield. Perrier complexes with p-tolyl

$$Al_2Cl_6 \cdot 2C_6H_5COCl \; +$$
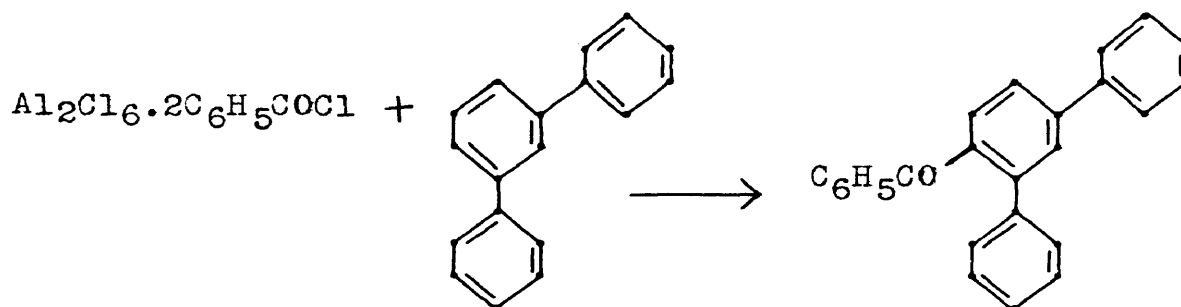
and m-tolyl chlorides also brought about substitution in the 4'-position. These workers also report the preparation of several new m-terphenyl derivatives, but details have not yet been published.

o-Terphenyl Derivatives

An extensive investigation into the chemistry of o-terphenyl has been initiated by Allen and co-workers with the result that a number of its fundamental reactions have been elucidated. As Allen and Pingert[10] have pointed out, the

few known derivatives of o-terphenyl prior to their investigation were compounds resulting from degradative studies on large and complex molecules. Allen and Pingert, after reviewing the earlier attempts to prepare o-terphenyl, found that the most satisfactory method involved a Wurtz-Futtig reaction of chlorobenzene with sodium. From 2.5 kg. of chlorobenzene and 230 g. of sodium they were able to obtain 70 g. of o-terphenyl (m.p. 58°).

The general reactivity of the molecule is described by Allen and Pingert as being along two main chemical axes:
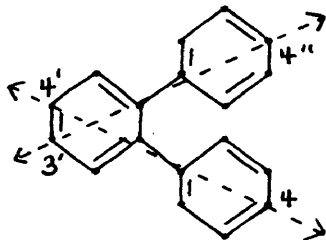
The 4- and 4"-positions have been shown to be the most reactive, while the 3'- and 4'-positions are "secondary in reactivity". This situation was borne out in such reactions as halogenation and nitration.

For some reason it had been speculated that such a molecule as o-terphenyl might permit the isolation of one of the Kekule structures of the middle ring. In an attempt to find any such property, the molecule was ozonized and the hydrolysis fragments studied. As seen below, a preferred Kekule structure would result in different products.

$$C_6H_5COCHO + \begin{array}{c} CHO \\ | \\ CHO \end{array}$$

$$\begin{array}{c} C_6H_5C = O \\ | \\ C_6H_5C = O \end{array} + \begin{array}{c} CHO \\ | \\ CHO \end{array}$$
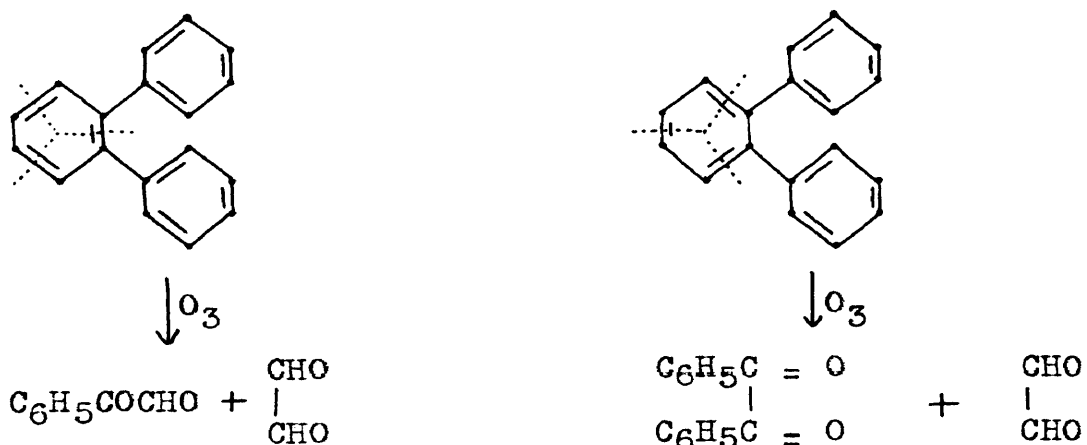
It is not difficult to appreciate the problems involved in such a study when one sees that either or both terminal rings may be attacked by the ozone also. That this did occur was quite obvious to Allen and Pingert since they were unable to identify in appreciable amounts any fragments other than glyoxal. Nor were they able to reproduce these ozonolysis experiments to any satisfaction.

These same workers have shown that o-terphenyl is capable of rearrangement to various isomers under certain conditions. In anhydrous benzene with aluminum chloride, o-terphenyl first rearranges to m-terphenyl and finally to p-terphenyl. If an equivalent amount of aluminum chloride is used, the results are more drastic; among the products formed are p-terphenyl and triphenylene. As the temperature and concentration of aluminum chloride are increased, condensation products predominate.

Allen and Pingert[11] have reported the acetyl, benzoyl, bromo, and nitro derivatives of o-terphenyl. As these workers expected, acetyl chloride or acetic anhydride combined with o-terphenyl in the presence of aluminum chloride

to give 4-acetyl-o-terphenyl. The structure was verified by showing that this compound was identical with substance obtained from a Wurtz reaction of o-iodobiphenyl with p-bromoacetophenone. Using sodium hypochlorite the acetyl
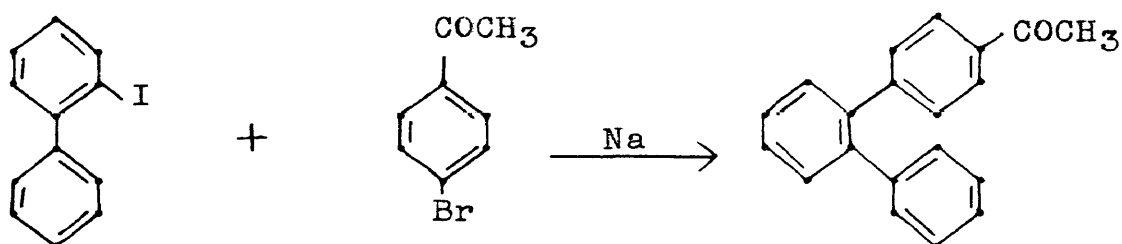
derivative was converted to 4-carboxy-o-terphenyl. In the attempt to prepare the benzoyl derivative by this same method a difficultly separable mixture resulted. However, if a Perrier complex of aluminum chloride-benzoyl chloride was employed, the 4-benzoyl-o-terphenyl was obtained in high yield and purity. A Wurtz synthesis similar to the one mentioned above was used to verify the structure. By modifying their technique Allen and Pingert were able to obtain four products containing more than one bromine atom. Of these, 4,4"-dibromo-o-terphenyl, was verified by oxidation to give p-bromobenzoic acid. The second and third obtained by
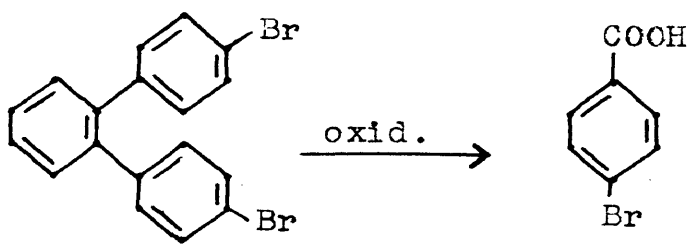
further bromination, 4,4',4"-tribromo-o-terphenyl and 4,4', 4",5'-tetrabromo-o-terphenyl, were also verified by oxidation;

the latter gave large amounts of p-bromobenzoic acid and a
small amount of 4,5-dibromophthalic acid.   The structure of

Br—[ring]—Br with Br's   oxid.   COOH—[ring]—Br   Br,Br—[ring]—COOH,COOH
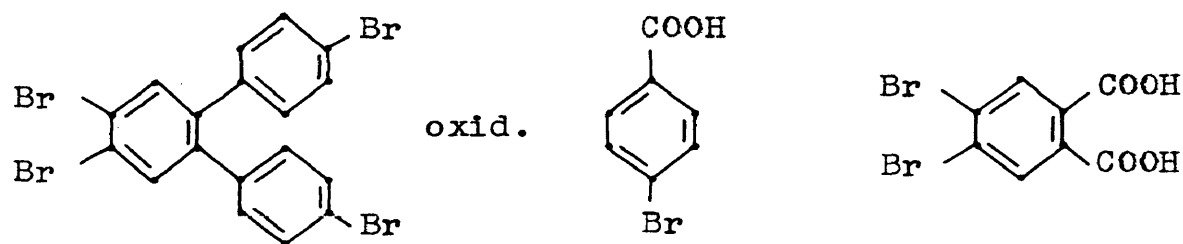
the tribromo derivative was assumed to be that indicated
since it also gave p-bromobenzoic acid on oxidation and on
further bromination gave the 4,4',4",5'-tetrabromo-o-ter-
phenyl.   A fourth substance, obtained as an end-product of
the bromination, was shown to be 3,5,10,11-tetrabromotri-
phenylene, wherein the bromine has acted the role of
condensing agent.   The ring system was shown to be correct
by zinc dust distillation to yield triphenylene.

Nitration of o-terphenyl gave a mononitro compound,
4-nitro-o-terphenyl, and further nitration resulted in a
mixture of 4,4"-dinitro- and 2,4-dinitro-o-terphenyl.
These structures were again confirmed by oxidation giving,
p-nitrobenzoic acid and 2,4-dinitrobenzoic acid respectively.
These nitro compounds were both reduced to the corresponding
amines, which on diazotization and replacement by hydrogen,
yielded o-terphenyl demonstrating retention of the ring
system.   The 4,4"-dinitro-o-terphenyl was also brominated
to give 4,4"-dinitro-4',5'-dibromo-o-terphenyl.   This struc-
ture was assigned by analogy of this compound to the tetra-
bromo derivative since they were similar in physical appear-
ance and gave no mixed melting point depression.

Allen and Pingert[12] have shown that the 4,4"-diamino-o-terphenyl is somewhat similar to 4,4'-diamino-cis-stilbene in its ability to form disazo dyes which are substantive to cotton. They prepared a number of these disazo dyes by coupling with several of the common aromatic reagents used in the preparation of commercial dyes.

Sulfonation studies on o-terphenyl were carried out by Allen and Burness[13]. The monosulfonic acid could not be obtained in appreciable amounts by direct sulfonation, but was readily obtained when chlorosulfonic acid was used as the sulfonating reagent. It was shown to be o-terphenyl-4-sulfonic acid by conversion to 4-hydroxy-o-terphenyl which in turn was synthesized from 4-amino-o-terphenyl. An o-terphenyl-4,4"-disulfonic acid was obtained by direct sulfonation. By slight variations in reaction conditions a di- and tri-sulfonic acid were obtained. The disulfonic acid was shown to be the 4,4"-isomer by alkaline fusion to the known 4,4"-dihydroxy-o-terphenyl. Similarly a trihydroxy compound was obtained from the trisulfonic acid, but its structure was not proven. These workers presumed it to be o-terphenyl-4,4',4"-trisulfonic acid. Sulfonation of the 4-amino-terphenyl gave a 4-amino-o-terphenyl-3-sulfonic acid. Proof of structure was demonstrated by conversion of the amine group to a nitrile, followed by conversion of the sulfonic acid to the sulfonamide, treatment of the nitrile with sodium hydroxide to give a cyclic derivative:
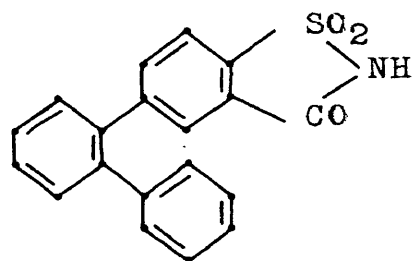
This compound, like saccharin, gave a sweet taste. Sulfonation with chlorosulfonic acid of the 4-carboxy-o-terphenyl gave a monosulfonic derivative of the carboxyterphenyl, but its structure was not elucidated.

In extending the chemistry of o-terphenyl, Allen, Burness, Edens, Kibler and Salminen[14] have prepared a number of amine derivatives. These compounds were prepared by essentially standard procedures. Some examples of the derivatives prepared are: 4-benzoylacetamido-, 4-(2'-methoxy-benzoylacetamido)-, 4-(1'-hydroxy-2'-naphthoylamido)-o-terphenyl. Allen, Burness and VanAllen[15] prepared a 4-vinyl-o-terphenyl from the 4-acetyl derivative by catalytic reduction of the carbonyl to a methyl-4-o-terphenyl carbinol and dehydration over alumina to the vinyl derivative. The 4-vinyl-o-terphenyl slowly polymerized on standing, in the absence of an inhibitor.
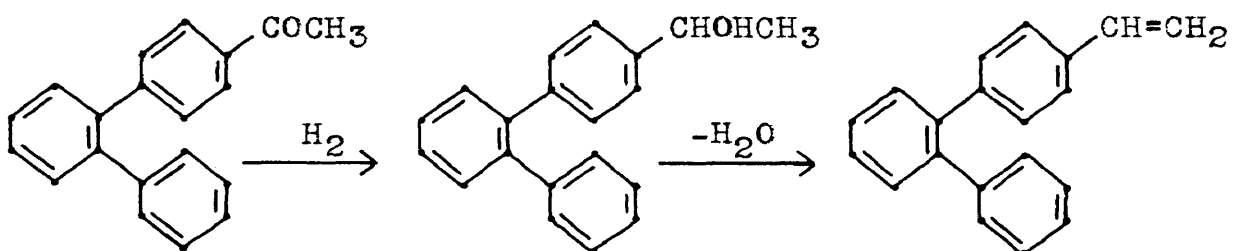
DISCUSSION

The research reported in this thesis was concerned with
two related investigations. First, the method of Woods and
Tucker[16] for preparing meta disubstituted benzene deriva-
tives from dihydroresorcinol was to be extended and its
utility demonstrated by preparing a series of polyphenyls.
That this particular type of series should be chosen was not
without forethought nor motive. These polyphenyls were the
substances needed for the second avenue of investigation
which was planned, namely to demonstrate by a physical
measurement the prohibited resonance between meta substi-
tuents on the benzene ring. That this series of polyphenyls
would demonstrate such a phenomenon was well borne out by
the absorption curves of the ultraviolet spectra of these
compounds, which will be discussed later.

Synthesis

The synthetic scheme developed by Woods and Tucker[16]
for preparing meta disubstituted benzenoid hydrocarbons
started with resorcinol (V). By the method of Thompson,
this compound was readily hydrogenated in good yield to
dihydroresorcinol (VI) using a Raney nickel catalyst and
2500 - 3000 psi pressure of hydrogen. Although the tempera-
ture is not critical, the best results were obtained if the
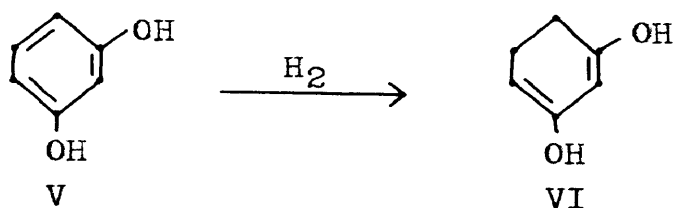
temperature was maintained within a few degrees of 50° C. during the reduction. Higher temperatures tended to cause further reduction, while lower temperatures increased the reaction time. The reaction product was worked up as described by Thompson[17].

This material was then converted into a monosilver salt (VII) by treatment of a water solution of the dihydroresorcinol (VI) with silver nitrate and adjustment of the pH. The pure silver salt, which is only slightly soluble in water, is a white crystalline compound which readily reacts with ethyl iodide in a refluxing benzene medium to give the monoethyl ether of dihydroresorcinol (I) and silver iodide. This enol ether was readily isolated by fractionatal distillation under reduced pressure.
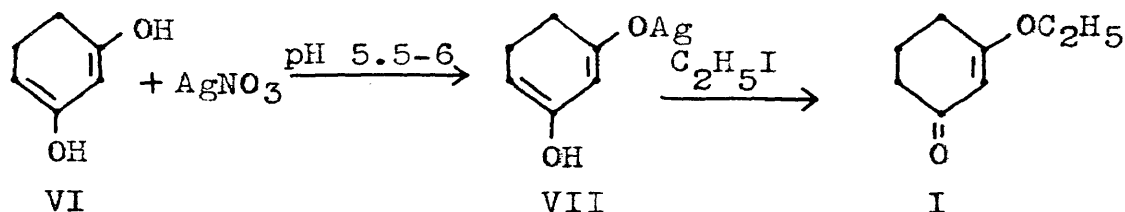
The Grignard reaction of this enol ether (I) was accomplished by essentially standard procedures. After completion of addition of the monoethyl ether of dihydroresorcinol to the Grignard reagent solution, the complex formed was, in most cases, hydrolyzed with 10 percent sulfuric acid solution. This particular reagent accomplished both the hydrolysis and dehydration necessary to obtain the desired 3-substituted-Δ^2-cyclohexenone (II). No attempt was made to isolate the tertiary alcohol formed by the

Grignard reaction. The method of isolation of the cyclo-hexenone derivative varied with the ketone prepared.
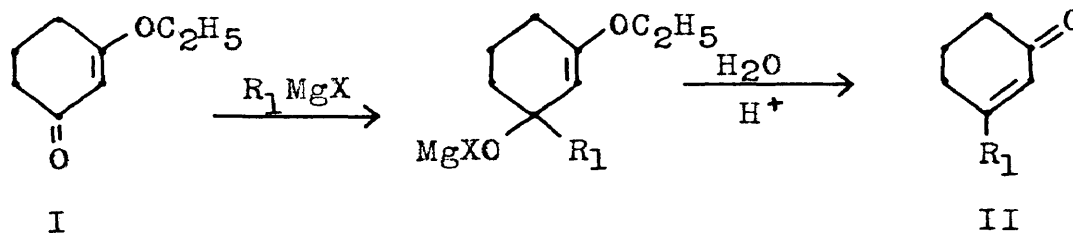
Since this enol ether is in fact an α, β-unsaturated ketone, the Grignard reaction may occur either as a 1,2- or a 1,4- addition. However, either mode of addition would result in the same ketone after the acid hydrolysis of the Grignard complex. For simplicity all the equations shown herein will indicate a 1,2-addition of the Grignard. It should be observed, however, that the second Grignard reaction, that involving the cyclohexenone (II) to give the 1,3-substituted-1,3-cyclohexadiene (III) must necessarily involve only a 1,2-addition if the desired product is to be obtained.

Treatment of the ketone thus obtained with a second Grignard reagent afforded after hydrolysis with ten percent sulfuric acid a 1,3-disubstituted cyclohexadiene-1,3 (III). The method of isolation of this compound also depended upon its nature.
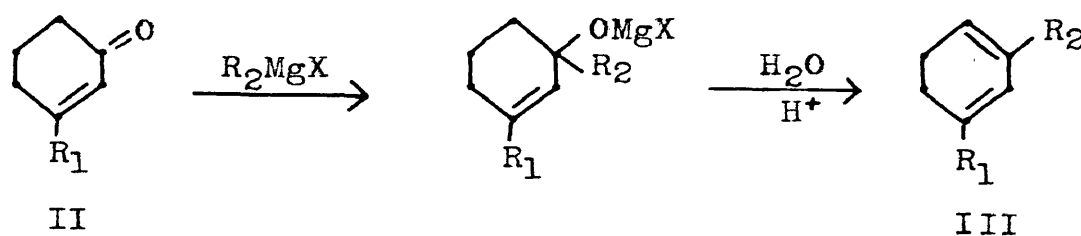
If this diene (III) is now added to a refluxing mixture of 5 per cent or 10 per cent palladium on charcoal catalyst in p-cymene, it is readily dehydrogenated to the aromatic structure, the desired benzene derivative (IV). Isolation of the final compounds generally involved removal of the p-cymene by distillation, followed by addition of benzene to the residue, removal of the catalyst by filtration, and then crystallization of the desired compound from some suitable solvent or mixture of solvents.

$$\text{III} \xrightarrow[\text{Pd-C}]{-H_2} \text{IV}$$
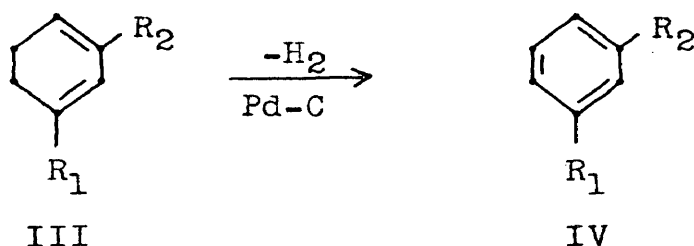
By this procedure the following polyphenyls were prepared: 1-phenyl-3-(2-xenyl)-benzene (XIX); 1-phenyl-3-(3-xenyl)-benzene (XVIII); 1-(4-xenyl)-3-(3-xenyl)-benzene (XXI); 1-(4-xenyl)-3-(2-xenyl)-benzene (XXII); 1,3-di-(3-xenyl)-benzene (XXIII); 1-(3-xenyl)-3-(2-xenyl)-benzene (XXIV); and 1,3-di-(2-xenyl)-benzene (XXV). The other three members of this series: 1,3-diphenylbenzene (XVI); 1,3-di-(4-xenyl)-benzene (XX); and 1-phenyl-3-(4-xenyl)-benzene (XVII) had been prepared by Woods and Tucker[16].

Four aryl halides were required to accomplish the synthesis of the compounds listed above, namely the phenyl and the three isomeric biphenyl halides. Excluding the chlorobiphenyls the choice of halides used was based solely on availability or ease of synthesis. Phenyl bromide (VIII)

being readily available from commercial sources presented no difficulty. The three isomeric xenyl halides, however, were not available and were synthesized.

The para isomer, 4-bromobiphenyl (IX), was prepared by the method described in Organic Syntheses[18]. This synthesis required the diazotization of p-bromoaniline (XXVI) followed by coupling with benzene in an alkaline medium (Figure 1).

The remaining two isomers were readily prepared from o-aminobiphenyl (XXVII), which is a relatively inexpensive chemical. This compound was conveniently purified by distillation under reduced pressure. It may be further purified by recrystallization (m.p. 50° C.) but this was not considered necessary. To prepare the 3-xenyl-bromide (X) the method described by Huber et al.[19], was employed with certain modifications (figure 1). The o-aminobiphenyl (XXVII) was first acetylated and the crystalline acetyl derivative (XXVIII) isolated. Bromination of this material then gave the acetyl derivative of either 3-bromo-2-amino-biphenyl (XXIX) or 5-bromo-2-aminobiphenyl or a mixture of the two. Since these positional isomers lead to the same final product, no attempt was made to determine the exact composition of the bromination product. This solid bromide was isolated and then hydrolyzed to the 3- or 5-bromo-2-aminobiphenyl by refluxing in a hydrochloric acid- alcohol mixture. The reaction mixture on cooling gave the crystalline amine hydrochloride (XXX) which was isolated as such. This then was diazotized and the amino group replaced with

NH$_2$ $\xrightarrow[\text{HCl}]{\text{NaNO}_2}$ N$_2$Cl $\xrightarrow[\text{2. NaOH}]{\text{1.}}$ Pr

XXVI   IX

NH$_2$ $\xrightarrow{\text{CH}_3\text{COCl}}$ NHCOCH$_3$ $\xrightarrow{\text{Br}_2}$ Br NHCOCH$_3$ $\xrightarrow{\text{HCl}}$

XXVII   XXVIII   XXIX

Br NH$_2\cdot$HCl $\xrightarrow[\substack{\text{2. C}_2\text{H}_5\text{OH} \\ \text{Cu}}]{\text{1. HNO}_2}$ Br

XXX   X

NH$_2$ $\xrightarrow[\text{2. KI}]{\text{1. HNO}_2}$ I

XXVII   XI
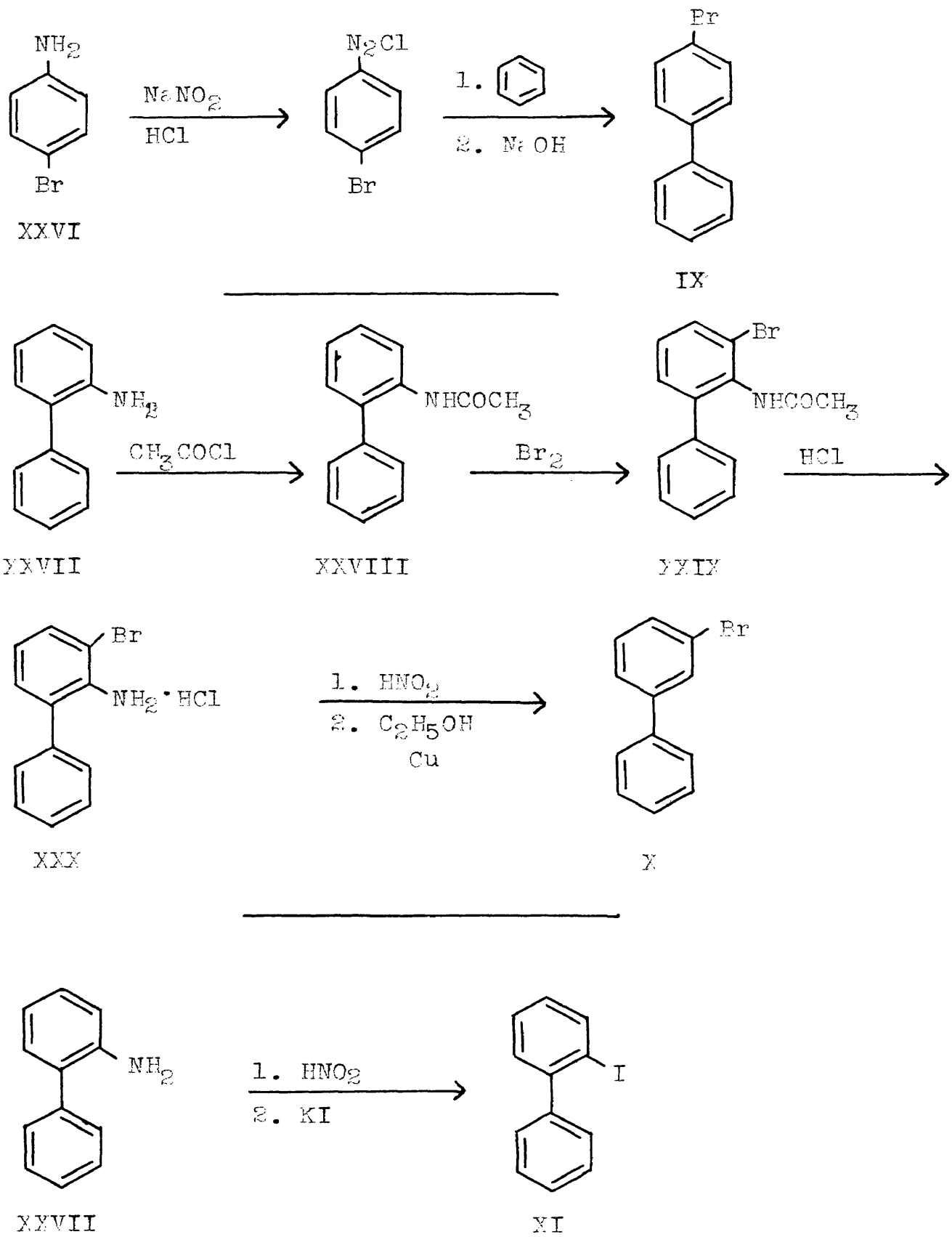
Figure 1

hydrogen by the standard Gatterman procedure. Extraction of the deamination mixture with ether, followed by distillation gave crude 3-xenylbromide (X). It should be mentioned here that whether the bromination took place on the 3- or 5- position is of no consequence, since both positions become the 3- position of the biphenyl system after replacement of the amino group by hydrogen. The crude bromide was then dissolved in petroleum ether and the solution passed through a column of activated alumina. This procedure very effectively removed all colored impurities and on redistillation of the chromatographed material colorless 3-bromobiphenyl (X) was obtained, which was then used without further treatment in the Grignard reactions.

Since this problem deals with positional isomers of the biphenyls it seemed advisable that this method of preparation of the 3-bromobiphenyl (X) be verified. To accomplish this the Grignard compound of 3-bromobiphenyl (X) was prepared and then carbonated with dry ice. The expected 3-xenyl carboxylic acid was obtained in good yield with physical properties in excellent agreement with those recorded in the literature.

As indicated in the last equation of Figure 1, the third biphenyl isomer was also readily prepared from o-aminobiphenyl (XXVII) by a straightforward Sandmeyer reaction using potassium iodide to give 2-xenyl iodide (XI). Extraction of the diazotization reaction mixture with toluene followed by a single distillation afforded a product of sufficient purity to be used directly.

Examination of the reaction equations in Figures 2, 3, 4, 5, and 6, show that those benzene derivatives which are unsymmetrically substituted can be prepared by either of two routes depending upon the order in which the Grignard reactions are carried out. For example, 1-(3-xenyl)-3-(2-xenyl)-benzene (XXIV) may be prepared by the Grignard reaction of 3-xenylmagnesium bromide (Xa) with 3-(2-xenyl)-Δ^2-cyclohexenone (XV) or by reaction of 2-xenylmagnesium iodide (XIa) with 3-(3-xenyl)-Δ^2-cyclohexenone (XIV), followed in either case by aromatization with palladium charcoal. The intermediate 1,3-cyclohexadiene derivatives are presumably not identical since they are positional isomers with respect to the double bonds of the cyclohexadiene rings, but this isomerization disappears on aromatization. In each case where a given compound could be prepared by alternate routes, both routes were employed and the final products obtained compared by mixed melting point procedures. As expected, the compounds were identical in all cases.

On the other hand, those polyphenyls which are symmetrically substituted 1,3-diarylbenzenes are available through only one synthetic route. In addition to m-terphenyl (1,3-diphenylbenzene) (XVI), there are three other such compounds: 1,3-di-(4-xenyl)-benzene (XX); 1,3-di-(3-xenyl)-benzene (XXIII); and 1,3-di-(2-xenyl)-benzene (XXV). Nonetheless, there can be little doubt as to the validity of the structures assigned to these polyphenyls. Not only is the

Figure 2

XII   VIIIa   XVI

XII   IXa   XVII

XII   Xa   XVIII

XII   XIa   XIX
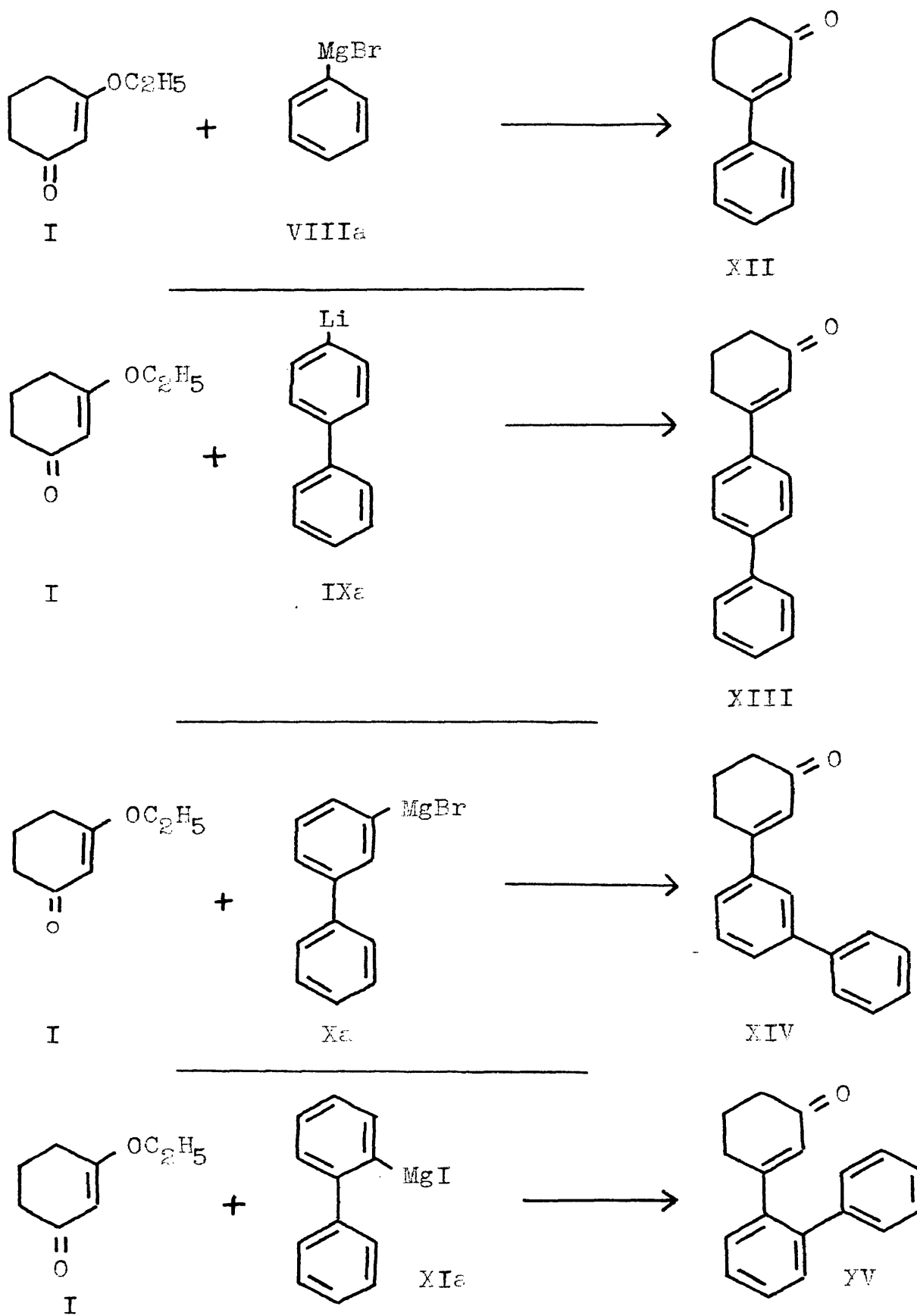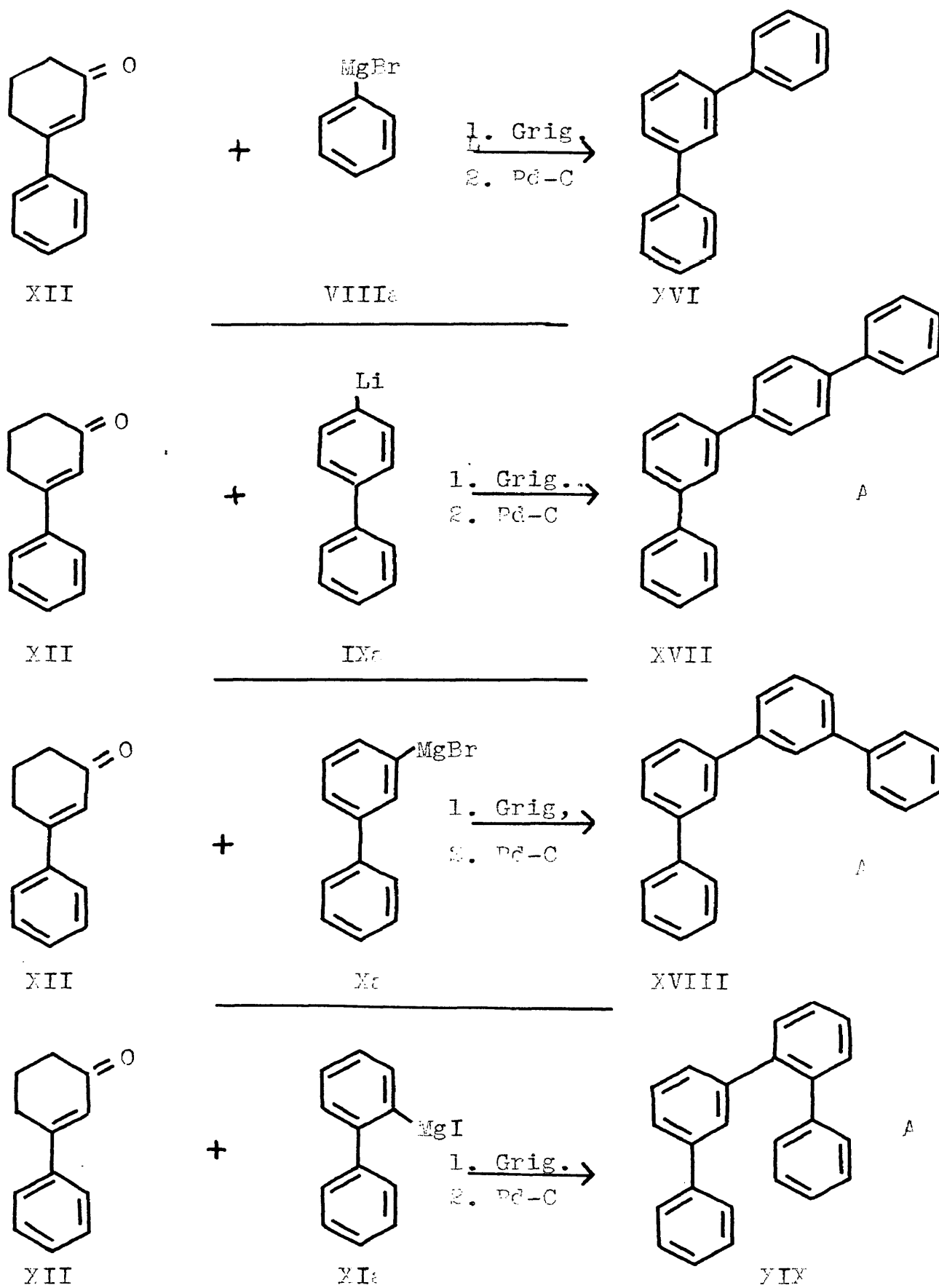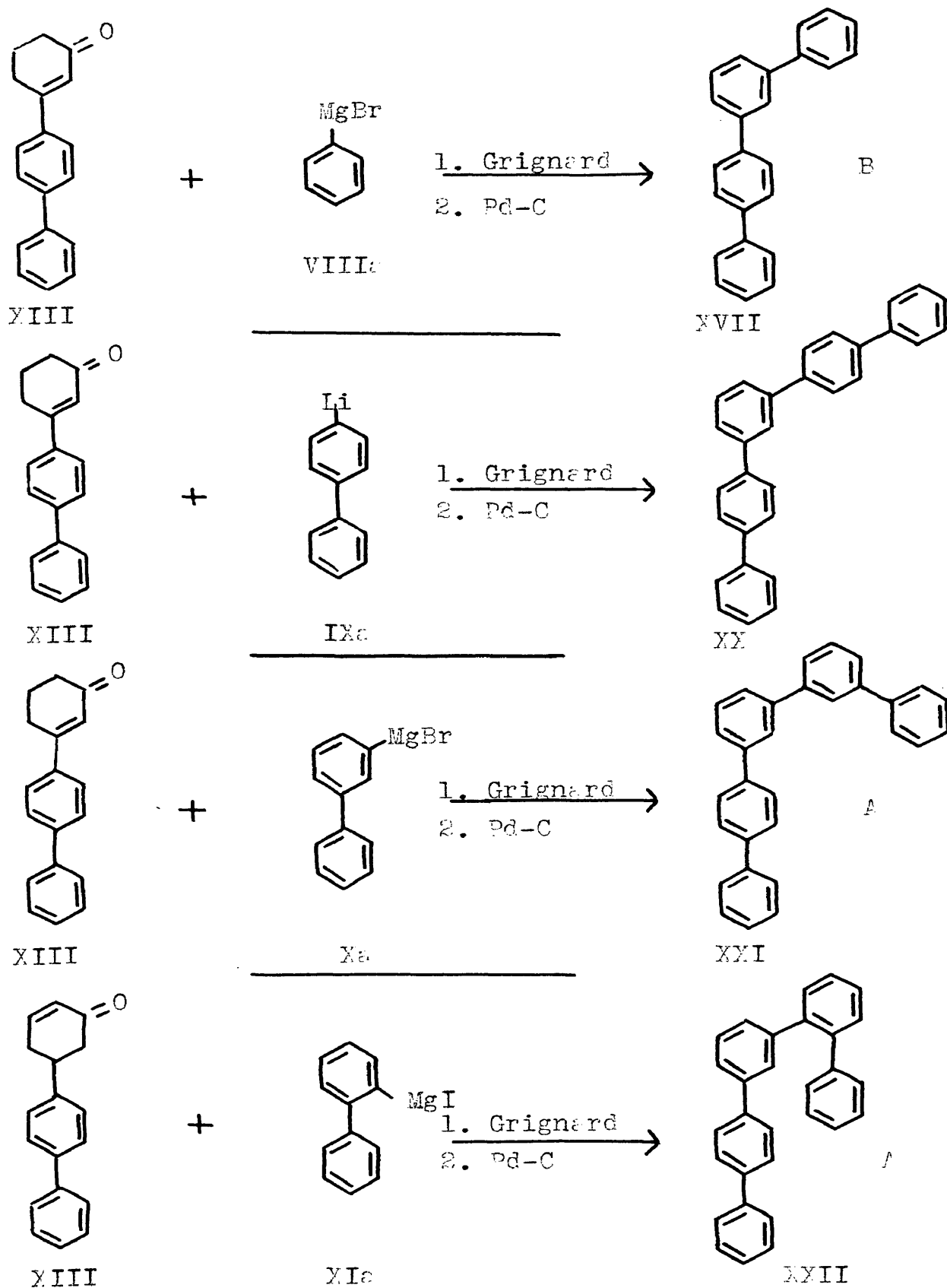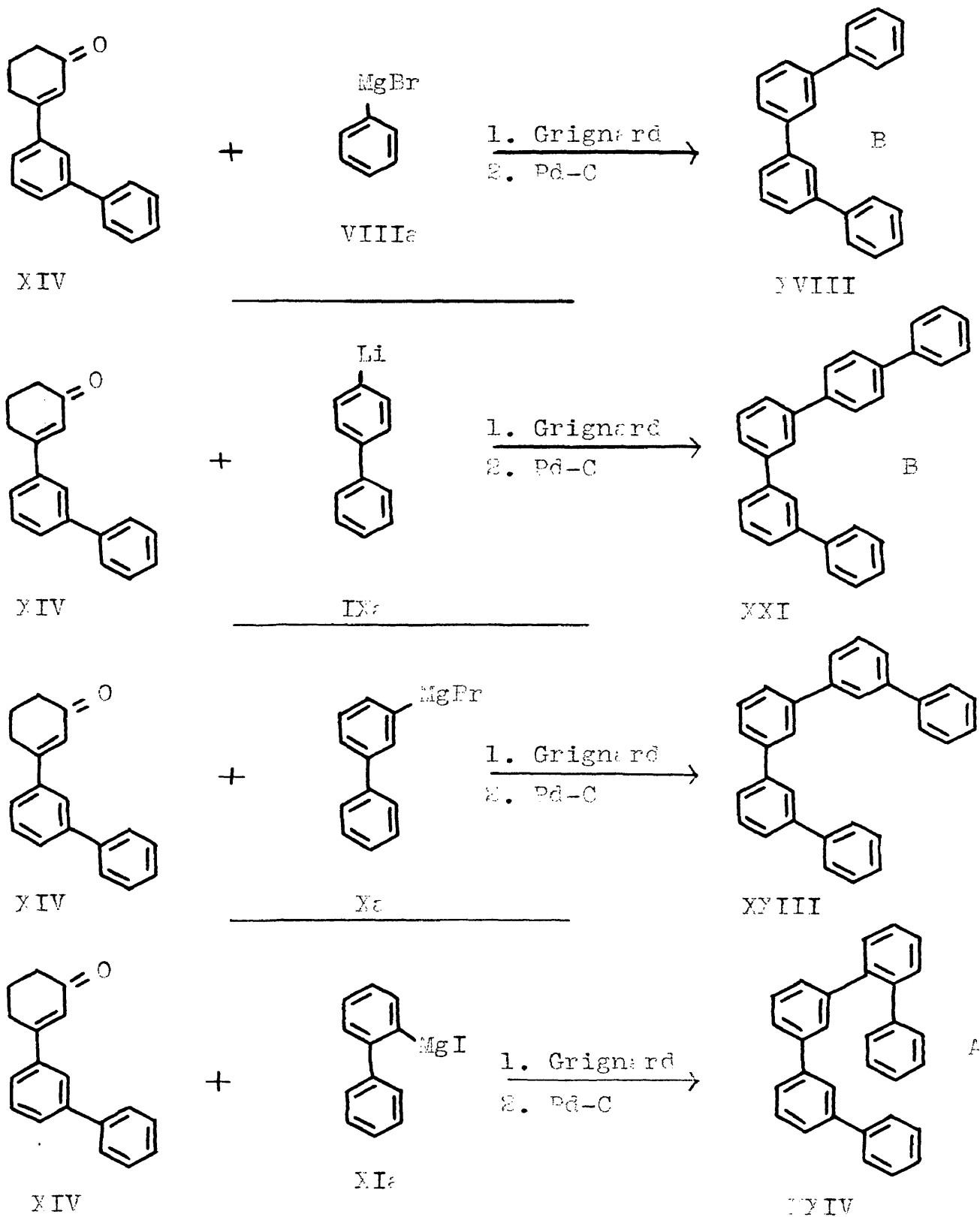
Figure 3

Figure 4

Figure 5
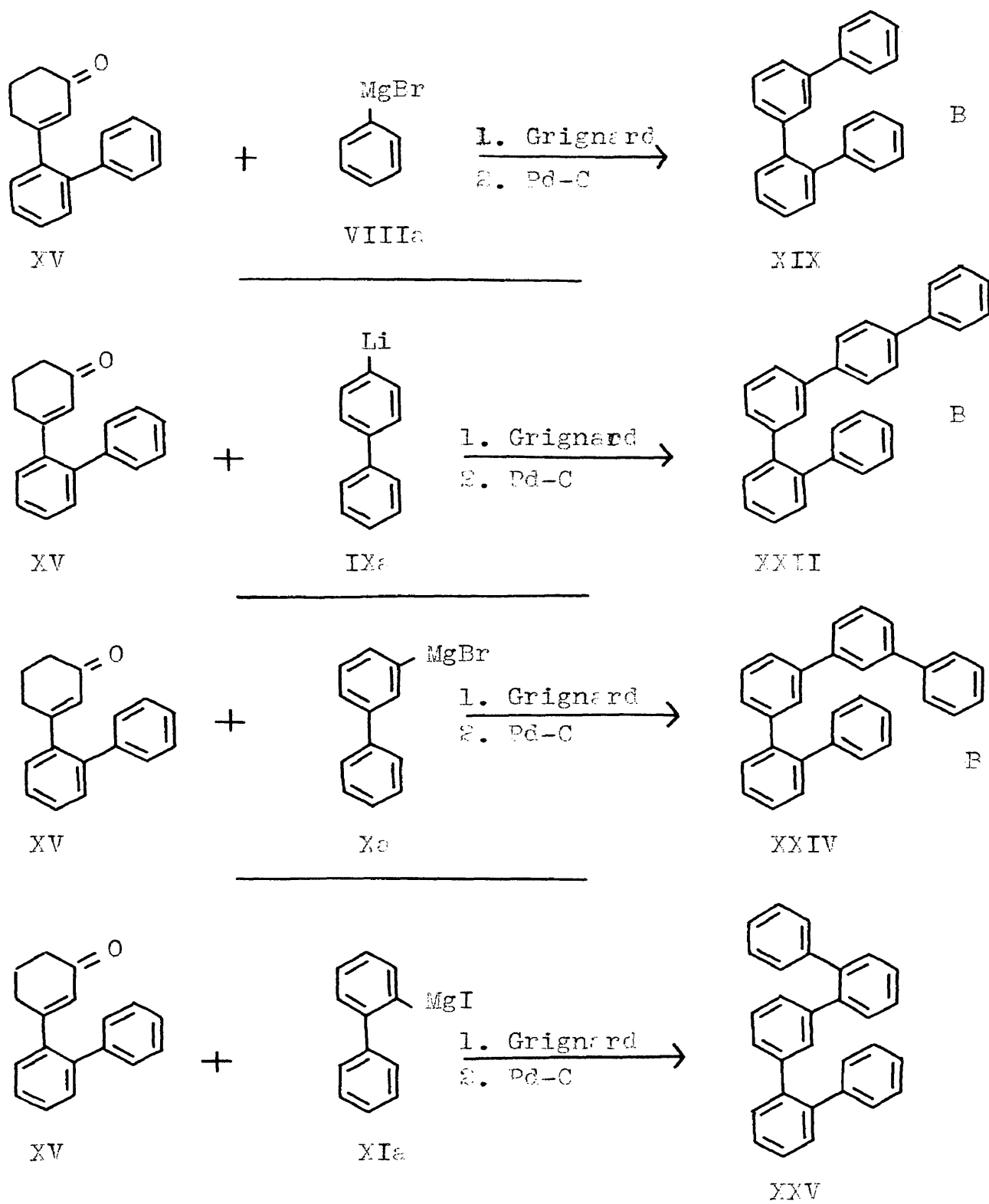
Figure 6

synthetic method straightforward with very slight possi-
bility of obtaining compounds with structures other than
those assigned, but certain ones have been prepared by other
workers against which the physical data could be compared.
One of these, m-terphenyl (XVI), is a well known compound
and the physical data obtained by Woods and Tucker[16] is con-
sistent with that given in the literature. Also, m-quater-
phenyl (1-phenyl-3-(3-xenyl)-benzene) (XVIII) has been
prepared by Bowden[20] and the melting point of his compound
compares very closely to that obtained for the product pre-
pared by either of the synthetic methods described here.

As might be expected in a situation where two routes to
the same product are available, one of the two may be more
favorable from a purely synthetic standpoint as well as from
ease of manipulation. In preparing m-quaterphenyl (XVIII),
route (A) (Figure 3) was preferable because any coupling pro-
duct of the Grignard reagent, 3-xenylmagnesium bromide (Xa),
gave m-quaterphenyl itself --- an unusual case where a side
reaction actually led to the desired final product. In the
case of the two other four-ring compounds (XVII, XIX),
route (B) (Figures 4, 6) was preferable because both ke-
tones (XIII, XV) were solids and could be easily purified
by recrystallization. The advantage was that in the second
Grignard reaction the side reaction products, namely bromo-
benzene, benzene, and biphenyl, were easily removed by steam
distillation, while any unreacted ketone was removed readily
by recrystallization since its properties were quite dif-
ferent from that of the diene obtained.

For the five-ring polyphenyls the choice of routes is not so clear-cut. Compounds XVII, XX, XXI, and XXII, each of which contains the 4-xenyl group, were easier to prepare if the 4-xenyl group was added at the time of the second Grignard reaction. The reason for this was simply one of manipulation. 3-(4-Xenyl)-Δ^2-cyclohexenone (XIII) is fairly insoluble in ether and therefore was, in practice, added to the Grignard reagent as a slurry or by using a Sohxlet extraction procedure. A second difficulty encountered was the inability to obtain 3-(3-xenyl)-Δ^2-cyclohexenone (XIV) in a crystalline form. Although one might qualitatively expect a molecule of this molecular weight to be crystalline, crystallization of this ketone could not be induced by the usual procedures but purification to some extent could be accomplished by the use of molecular distillation in a Hickman apparatus. The material thus obtained was an extremely viscous fluid, essentially a glass. This is by no means a unique case since there are several examples in the literature of high molecular weight, 3-substituted, biphenyl derivatives which could not be crystallized. One might offer the suggestion that this difficulty in crystallization is due to some inherent lack of symmetry or rigidity in these molecules. Thus, from the viewpoint of purity of reagents it is better to prepare those compounds containing the 3-xenyl group by adding this group during the second Grignard reaction, and thereby eliminating the troublesome 3-(3-xenyl)-Δ^2-cyclohexenone (XIV). A further problem of crystallization was met in the

majority of the 1,3-disubstituted-1,3-cyclohexedienes (III), particularly those containing a 3-xenyl group. This type of substance could not be induced to crystallize by the usual methods. This problem was not pursued further, however, and the more stubborn dienes, as glasses, were used directly in the aromatization step.

The difficulty of obtaining crystalline compounds persisted even after the dehydrogenation reaction. All those compounds which contained either a 3-xenyl or 2-xenyl group in the final polyphenyls were very slow to crystallize and in some instances it was exceedingly difficult to induce the initial crystallization. The best procedure for crystallization was found to be dissolution of the compound in a small amount of benzene followed by the addition of alcohol until the solution became definitely cloudy. The resulting mixture was heated, then allowed to cool slowly.

While the preparation of these compounds was in progress, three other synthetic problems were started which were outgrowths of the original dihydroresorcinol problem and also had a direct bearing on the work presented thus far. In the discussion of the ultraviolet spectra of the polyphenyls in a later section of this thesis, it is pointed out that certain structural features of the disubstituted biphenyl molecule show very characteristic absorption curves. To examine this phenomenon more fully it was decided to prepare a series of bitolyls.

In conjunction with Miss Anna Lee VanArtsdale, of this laboratory, the three bitolyls: 2,3'-dimethylbiphenyl (XXXVII); 3,3'-dimethylbiphenyl (XXXVIII); and 3',4-dimethyl-biphenyl (XXXIX), were prepared. An outline of the steps involved are given in Figure 7. These bitolyls were not synthesized by each of the two routes possible, because it had already been found experimentally that the reaction of the enol ether with methylmagnesium halides resulted in very meager yields of the 3-methyl-Δ^2-cyclohexenone, while the corresponding reaction with the tolylmagnesium bromides gave excellent yields. The second Grignard reaction (the 3-tolyl-Δ^2-cyclohexenone with methylmagnesium halide) on the other hand gave very good yields of the diene. It was not consi-dered necessary to check these syntheses by using the alter-nate routes since these bitolyls could be readily oxidized to the known biphenyldicarboxylic acids. This was done in each case and a good yield of the corresponding biphenyl-dicarboxylic acid resulted. A brief inspection of the formulas of these bitolyls shows them to be very similar to the previous polyphenyls discussed, where the methyl group of the lower ring replaces a phenyl group, and the methyl group of the upper ring replaces a phenyl or one of the biphenyl groups.
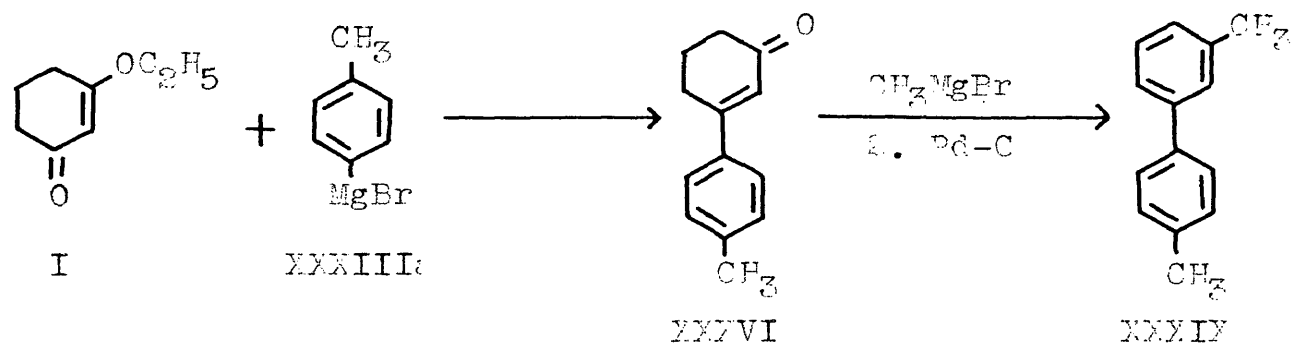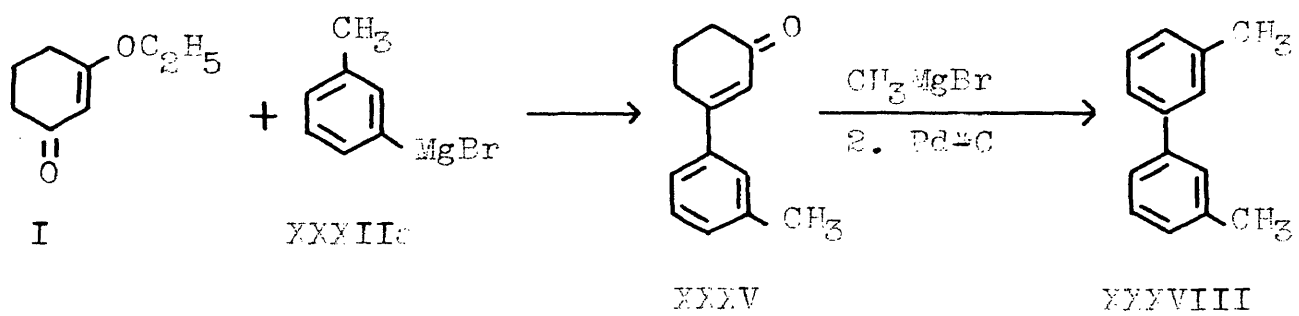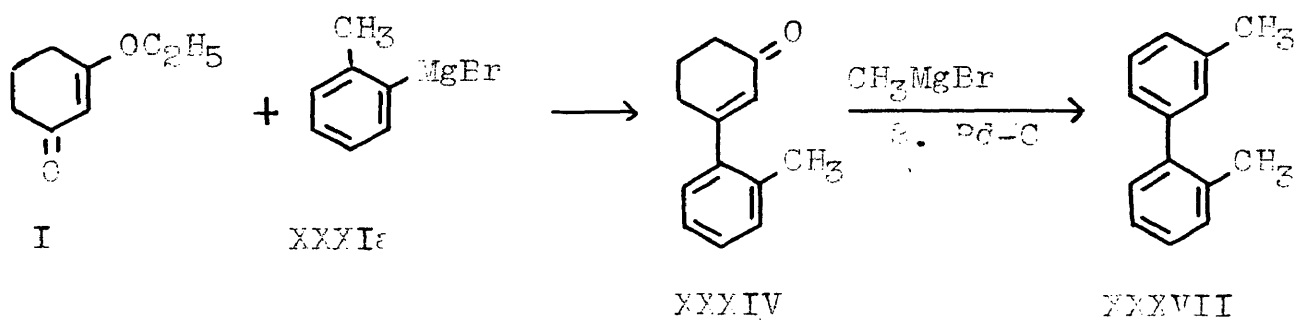
Figure 7

The physical data of these bitolyls is shown in the chart below. Other data and experimental details may be found in the thesis of Miss VanArtsdale[21].

Dimethylbiphenyls

	B.P.	λ max.	ϵ max.
3,2'-dimethyl-	81/0.2 mm	237 mμ	0.8×10^4
3,3'-dimethyl-	108/0.2 mm	251	1.6
3,4'-dimethyl-	100/0.5 mm	254	1.3

The second problem investigated was the preparation of the 1,3-dinaphthyl-benzenes. This work carried out with Mr. Thomas E. Arthur, of this laboratory, proved unexpectedly difficult. These compounds were again desired for investigation of their ultraviolet spectra. The mode of preparation was similar to that of the previous benzene derivatives. The equations are shown in Figure 8. The difficulties involved here were two-fold. First, the very vexing problem of crystallization again appeared, which seemed even more surprising than in the polyphenyls syntheses. Second, the naphthyl halides are very prone to undergo coupling to the binaphthyls during Grignard reactions. This latter difficulty not only cut down on the yields at each step, but made the problem of purification of the desired product more difficult. Since these binaphthyls are non-steam volatile solids they could be separated from reaction mixtures in any reasonable manner only by fractional crystallization. This in itself would not have been a serious handicap if it were not for the reluctance of the desired products to crystallize,
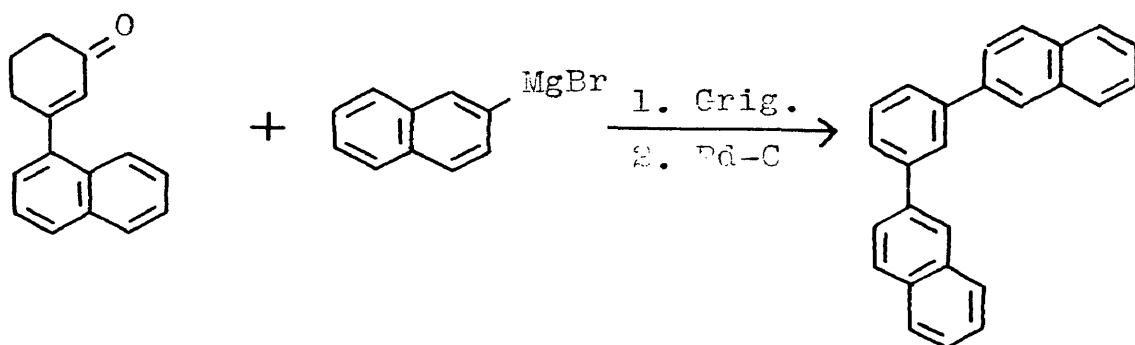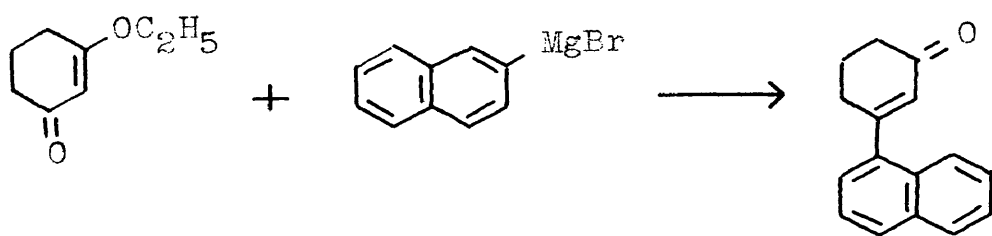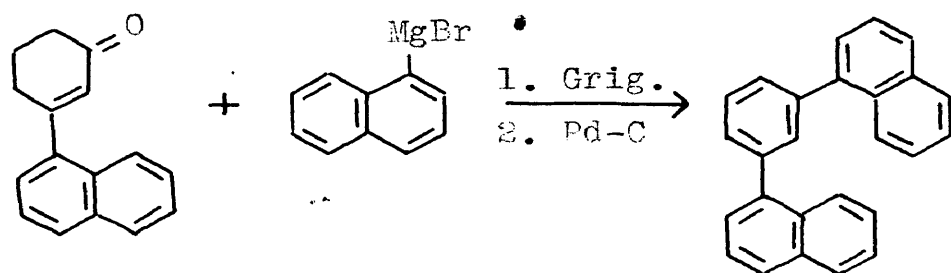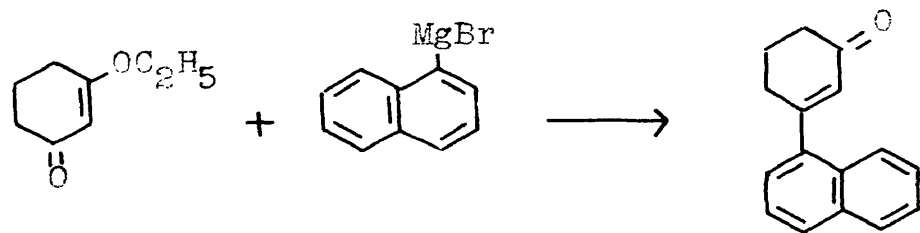
Figure 8

these being more insoluble in ordinary solvents than the binaphthyls. The more complete physical and chemical data will be reported in the thesis of Mr. Thomas E. Arthur.

The third problem, conducted in conjunction with Mr. Herbert Ezekiel of this laboratory, was to prepare the isomeric 3-chlorophenyl-Δ^2-cyclohexenones. The preparation of these compounds further extended the utility of the enol ether of dihydroresorcinol in preparing new organic compounds. The equations for the reactions involved are shown in Figure 9. This material will be presented in a thesis by Mr. Herbert Ezekiel.

The success attained in preparing the polyphenyls lead to the idea that this synthetic method might be the means of preparing a very unique type of compound which might best be described as a closed ring of benzene rings. The only known compounds of this type are biphenylene, triphenylene, and tetrabenzocylooctatetraene which may be looked upon as closed rings of two, three, and four benzene rings respectively. Triphenylene, however, also falls into the common class of condensed nuclear aromatic hydrocarbons of which there are a host. It was decided that if a compound of the m-quinquephenyl structure could be prepared with a halogen atom in the 3-position of each terminal benzene ring, it might be possible to perform an intramolecular coupling through these two halogens. The synthetic method was available and it only remained to find a practical synthesis of the halide to be used in the two Grignard reactions. The method, of course, required that the halide
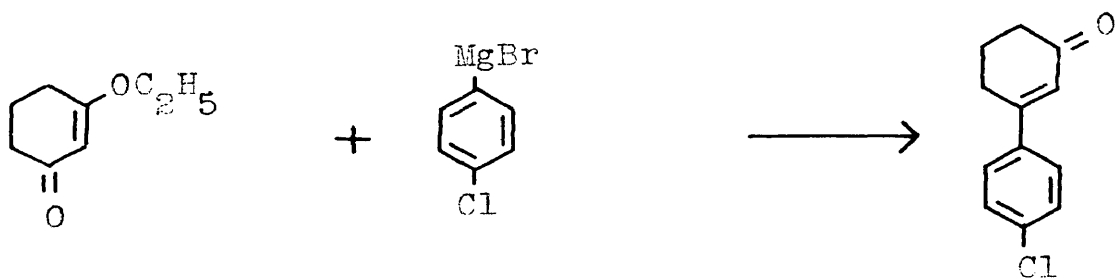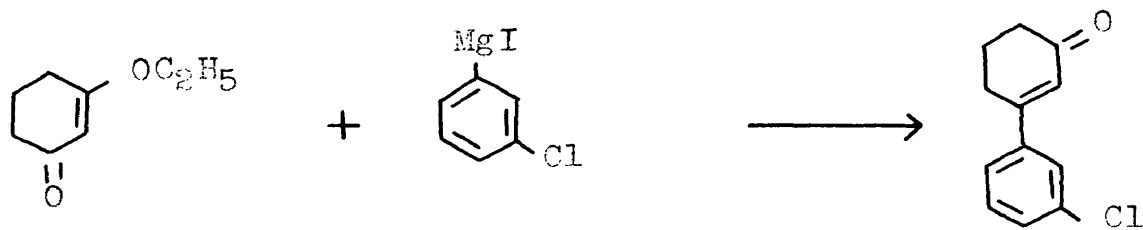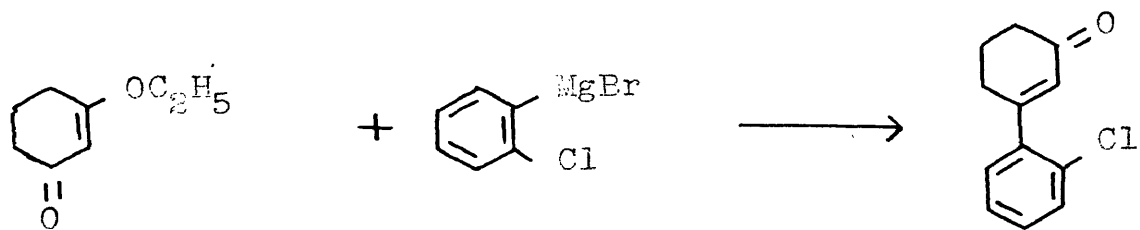
Figure 9

be either 3-iodo or 3-bromo-3'-chlorobiphenyl. After
abandoning several ideas and actual experimental attempts
to prepare this dihalide, an Ullman reaction was employed.
Involved was the coupling of m-iodochlorobenzene (XL) with
m-iodonitrobenzene (XLI). Since this was an unsymmetrical
type of coupling, three reaction products resulted. For-
tunately, the three products, 3,3'-dichlorobiphenyl (m.p.
23° C.), 3-chloro-3'-nitrobiphenyl (XLII) (m.p. 89° C.),
and 3,3'-dinitrobiphenyl (m.p. 198° C.), had sufficiently
different physical properties that a good separation of the
reaction mixture was readily effected. The best procedure
was found to be the removal by crystallization of as much
of the 3,3'-dinitrobiphenyl from the reaction mixture as
possible using benzene as a solvent; fractional distilla-
tion of the remaining material after removal of the solvent
yielded a solid distillate of the desired 3-nitro-3'-chloro-
biphenyl (XLII). This substance was obtained in a state of
sufficient purity after one recrystallization. This com-
pound was reduced to the amine (XLIII) by stannous chloride,
and the amine converted to 3-iodo-3'-chlorobiphenyl (XLIV) by
the Gatterman method. The subsequent steps to the 3,3'''''-
dichloro-m-quinquephenyl (XLVI) are shown in Figure 10. In
no case could any of the intermediate or even the final com-
pounds be induced to crystallize. The only questionable
step in the synthesis was the final aromatization step in-
volving treatment of the diene derivative with palladium-
charcoal catalyst, the question being whether dehydrohalo-
genation would occur. The possibility that this occurred
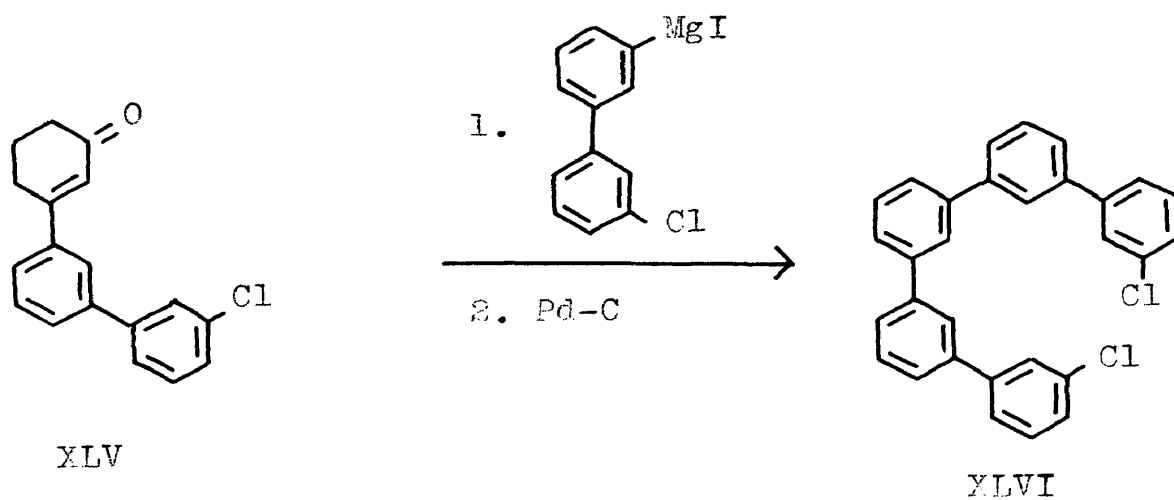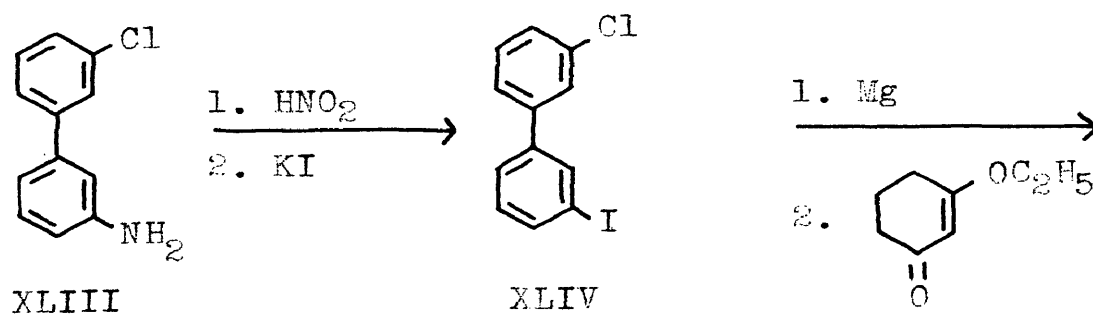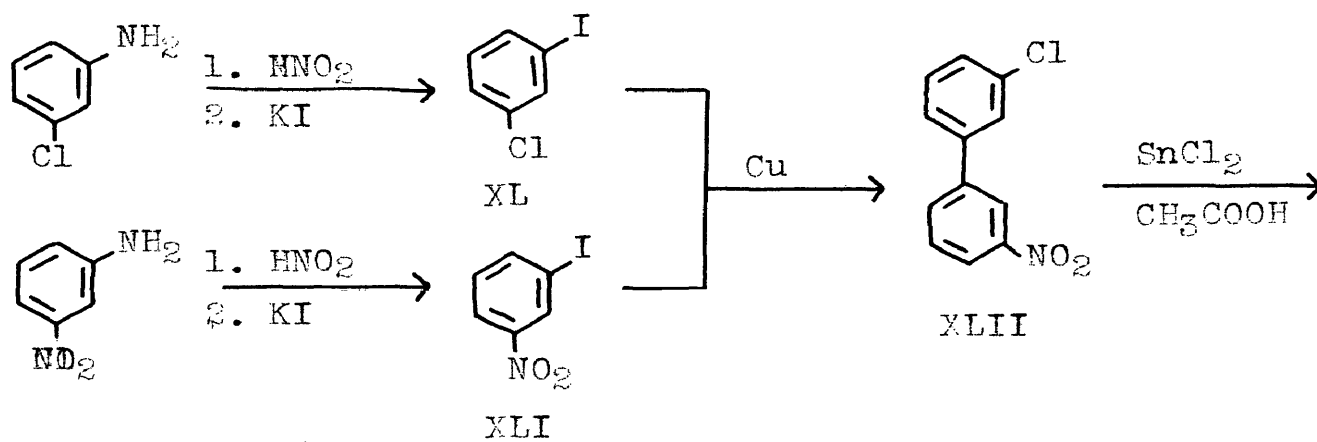
Figure 10

was ruled out for several reasons. To test this point the
synthesis of 3,3''-dichloro-m-terphenyl was carried out
using m-chloroiodobenzene as the Grignard reagent and in the
dehydrogenation step no hydrogen chloride could be detected
by reliable methods. The same was found to be true when the
dehydrogenation step was performed in the 3,3'''' -dichloro-
m-quinquephenyl synthesis. Further, the results of quanti-
tative elementary analysis for chlorine on the crude product
of the quinquephenyl synthesis were of the right order of
magnitude for two chlorine atoms. Due to the number of
steps involved and certain low yields, only sufficient di-
chloro compound (XLVI) was obtained to permit one coupling
reaction. This was done using the standard Wurtz reaction
method. The dichloro compound, dissolved in a large volume
of xylene, was added very slowly to a well stirred mixture
of molten sodium and xylene. Unfortunately, after working
up the reaction mixture, no product was detected which might
have resulted from the desired ring closure. The three
products found were some unreacted dichloro compound, some
m-quinquephenyl (XXIII) (resulting from dehalogenation), and
a fair amount of resinous, practically infusible material
which was assumed to be the result of intermolecular coup-
ling to give a chain type of polymer.

Ultraviolet Spectra

It is a well known postulate of the theory of resonance that in an ortho or para disubstituted benzene molecule it is possible for the whole molecule to resonate in a hybrid structure. Such a condition is generally written as the quinonoid structure:

and
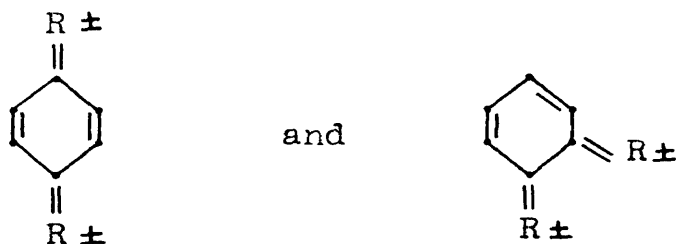
The ground state of such molecules is generally accepted to be some state involving resonance between the two Kekule type structures:

and
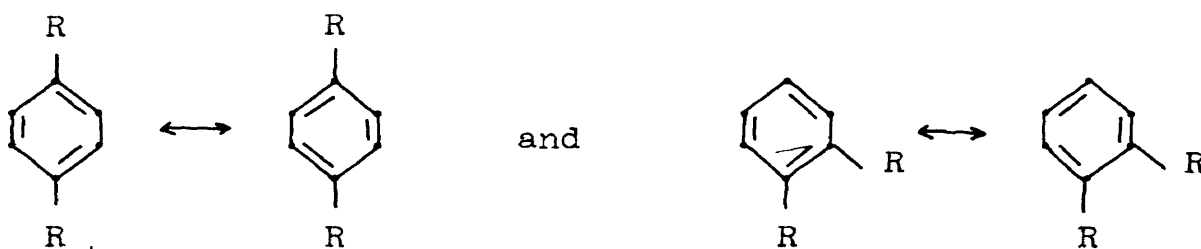
Thus if a molecule of either type shown above can in some manner acquire a sufficient amount of energy, it will attain a quinonoid type of structure, designated as the first, or some other, excited state. Since a separation of charges is involved, obviously the polar form will be of higher energy content. This hybrid ionic state is not actually intended to mean a complete separation of charges into a molecule containing unit negative and unit positive charges at each end, but rather a redistribution of the electron density within the molecule.

If one now examines a meta substituted benzene molecule, it is evident that a resonating unit involving the whole molecule is not possible. Representing the resonance possible in the quinonoid form again, one can only write structures which involve alternately one substituent and then the other in resonance with the ring, but not both:
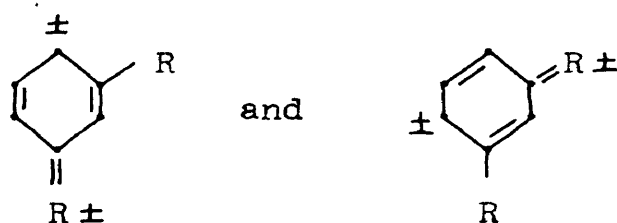
The m-diarylbenzenes discussed in the previous section are molecules of this type, where a resonance unit involving the whole molecule is not possible. These molecules, however, present an additional interesting feature, namely that there is complete conjugation of the double bonds throughout each molecule. Thus there is the interesting situation where complete conjugation exists, but resonance as a unit is prohibited.

It was for this reason that the ultraviolet absorption spectra of these m-diarylbenzenes were determined. Certain ones (e.g., 1,3-di-(4-xenyl)-benzene) (XX) contain p-terphenyl units, others (e.g., 1,3-di-(2-xenyl)-benzene) (XXV) contain o-terphenyl units, either of which are presumably capable of resonating as a unit, while others (e.g., 1,3-di-(3-xenyl)-benzene)(XXIII) contain no group larger than a biphenyl group capable of resonating as a unit. Since a molecule is capable of being elevated from its ground state to an excited

state by absorption of photons (or the energy therein)
provided it is of the right frequency, the spectral curves
of these molecules should show certain features which can
be attributed to the various structural features.

Previous work on molecules of this nature has shown
that the prohibited resonance in the m-polyphenyls is indeed
real and can be demonstrated by the ultraviolet absorption
curves. Gillam and Hey[22] have measured the absorption of a
series of m-polyphenyls and their results are tabulated
below:

Compound	Formula	λ max.	ϵ max.
Diphenyl	$C_{12}H_{10}$	2515 A	18×10^3
m-Terphenyl	$C_{18}H_{14}$	2515	44
m-Noviphenyl	$C_{54}H_{38}$	2530	184
m-Deciphenyl	$C_{60}H_{42}$	2530	213
m-Undeciphenyl	$C_{66}H_{46}$	2530	215
m-Duodeciphenyl	$C_{72}H_{50}$	2530	233
m-Tredeciphenyl	$C_{78}H_{54}$	2530	252
m-Quattuordeciphenyl	$C_{84}H_{58}$	2530	283
m-Quindeciphenyl	$C_{90}H_{62}$	2540	309
m-Sedeciphenyl	$C_{96}H_{66}$	2550	320

A series of values for the p-polyphenyls was also
obtained by these investigators, and is tabulated below:

Compound	Formula	λ max.	ϵ max.
Diphenyl	$C_{12}H_{10}$	2515 A	18×10^3
p-Terphenyl	$C_{18}H_{14}$	2800	25
p-Quaterphenyl	$C_{24}H_{18}$	3000	39
p-Quinquephenyl	$C_{30}H_{22}$	3100	62
p-Sexiphenyl	$C_{36}H_{26}$	3175	56

Using Planck's equation for the energy of light, $E = h\nu$, it can be seen that in the meta series the ΔE required to reach the first excited state has remained essentially constant even though the number of rings has constantly increased. In the para series, however, there has been a definite decrease in ΔE (i.e., λ has increased, therefore ν has decreased) in going to higher members of the series. Thus it is seen that in the meta series, where there is no resonating unit larger than a biphenyl unit, the levels of both ground and excited state have remained essentially constant. More exactly it is the difference between these levels which has remained constant, since no statement concerning the absolute values of the ground and excited states can be made from spectral data. Conversely, in the para series, the energy between the two levels has steadily decreased. If one assumes the ground state to remain at a constant level from one member of the series to the next, the spectral curves must be interpreted as a steady lowering of the first excited state as the number of rings involved increses. From this it would follow that the resonance energy in an excited p-polyphenyl molecule is a function of the number of

rings involved in the resonating unit of the first excited state, this resonance energy increases as the number of rings increases.

The ultraviolet absorption curves for the series of polyphenyls reported in this thesis are shown in Figures 11, 12, 13, and 14. The experimental conditions used in determining these curves were the standard conditions for this type of instrumentation. The more complete details are outlined in the Experimental section.

Figure 11 shows the curves of the three completely meta polyphenyls. Although the m-quater and m-quinque-phenyls were not included in the series of Gillam and Hey[22], the curves in this figure are essentially confirmation of their results. In each of the three compounds the absorption maximum lies just below 250 mμ and does not shift appreciably as the number of rings increases, while the value of the extinction coefficient shows a steady increase. This latter phenomenon was also observed by Gillam and Hey and they were able to show a semi-quantitative relationship between the extinction coefficient and the number of rings, assigning a relative value of extinction per ring. The results shown in the curves of Figure 11 are in excellent accord with this observation.

The curves shown in Figure 12 are those of the compounds containing a 4-xenyl group, with the exception of the molecule which also contains the 2-xenyl group. Each of these substances contains a p-terphenyl unit and a very definite bathochromic shift has resulted. One would expect

Figure 11

Wave Length mμ
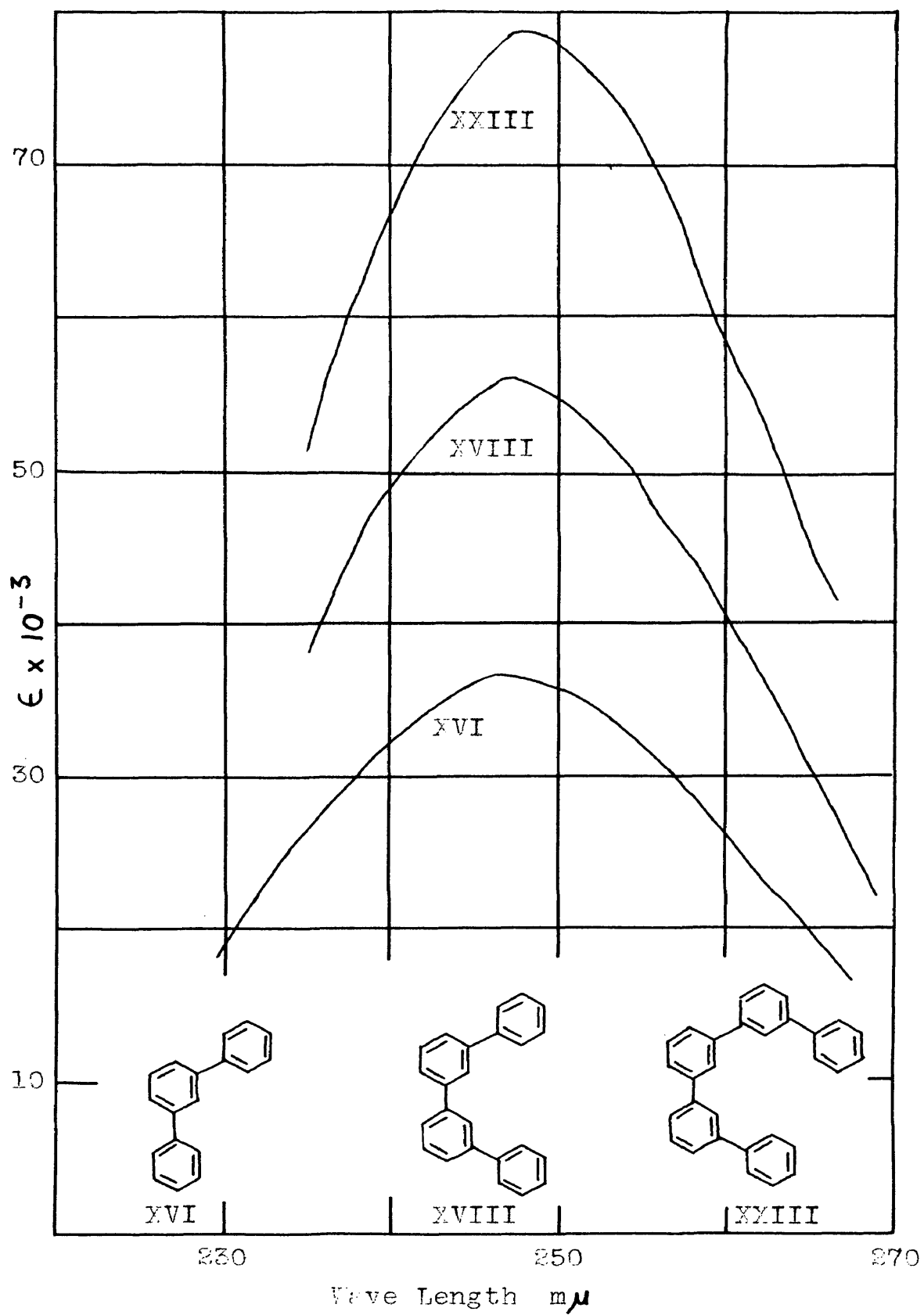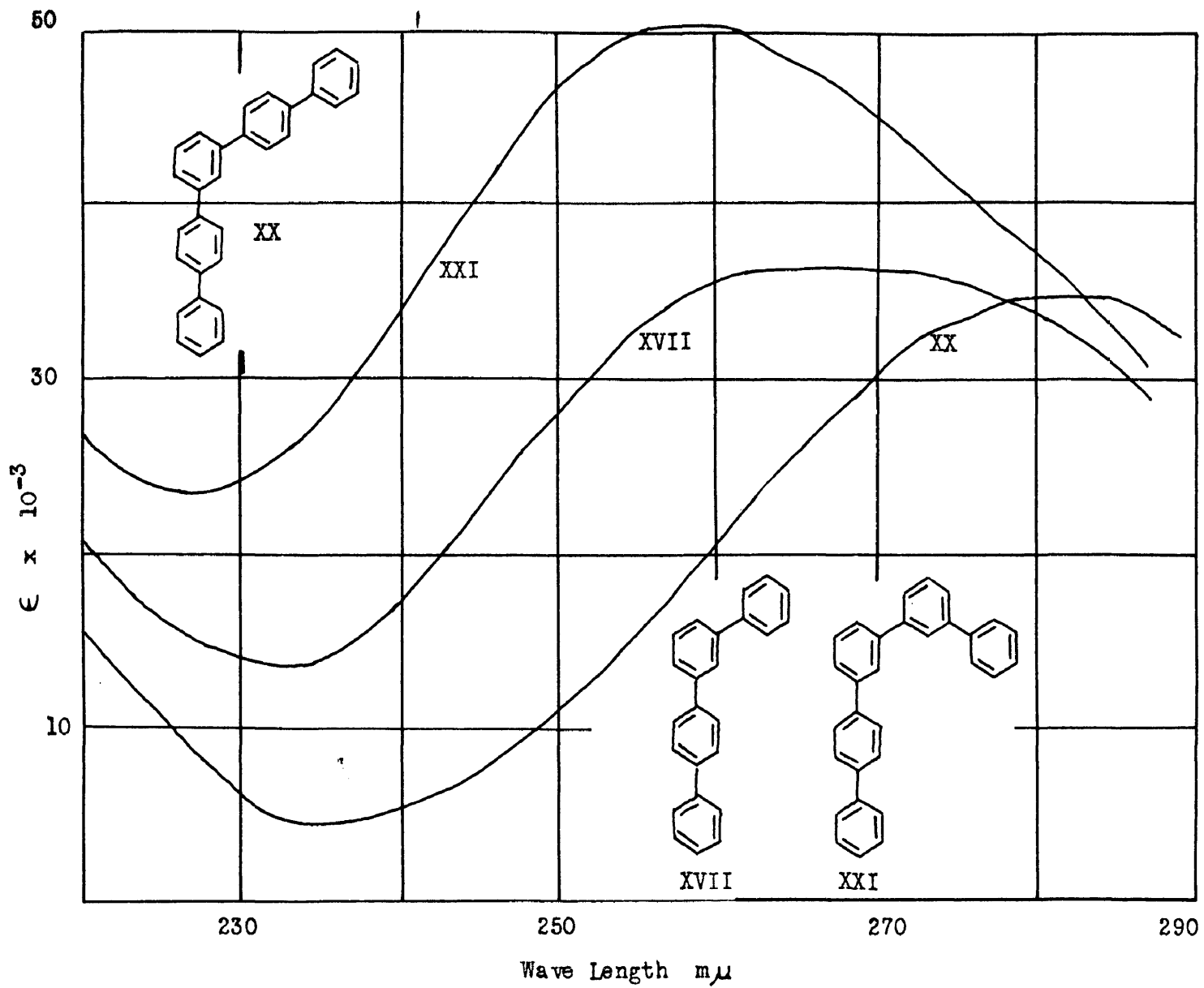
Figure 12

that 1,3-di-(4-xenyl)-benzene (XX) which, in effect, con-
tains two p-terphenyl units, would show a maximum at app-
roximately that of p-terphenyl. Gillam and Hey[22] reported
the Λmax. of p-terphenyl at 276 mμ in hexane solution,
while that observed for 1,3-di-(4-xenyl)-benzene (XX) is at
282 mμ . On the other hand, the compounds, 1-phenyl-3-
(4-xenyl)-benzene (XVII) and 1-(3-xenyl)-3-(4-xenyl)-benzene
(XXI) with Λmax. at 267 mμ and 258 mμ , respectively,
both show shifts toward the shorter wave lengths in spite of
the p-terphenyl unit present in each. The explanation for
this probably lies in the fact that both of these molecules
also contain the m-terphenyl unit and that these two indivi-
dual absorbing units are masked under a single envelope,
intermediate between the absorption of either alone.

The third set of curves shown in Figure 13 gives the
absorption spectra for those molecules containing the ortho
structure. A very marked hypsochromic effect is evident.
Thus it is seen that the introduction of two more benzene
rings onto the m-terphenyl group has actually resulted in a
shift of the wave length of maximum absorption toward the
shorter wave lengths even though these rings are in the
ortho position where a degree of resonance is theoretically
permissible and should cause a shift toward the longer wave
lengths. This apparent anomaly can be readily explained on
the basis of steric hindrance preventing the molecule from
attaining a coplanar structure. An examination of the models
shows that an ortho terphenyl unit is very seriously hindered
in becoming coplanar due to the overlapping of the ortho
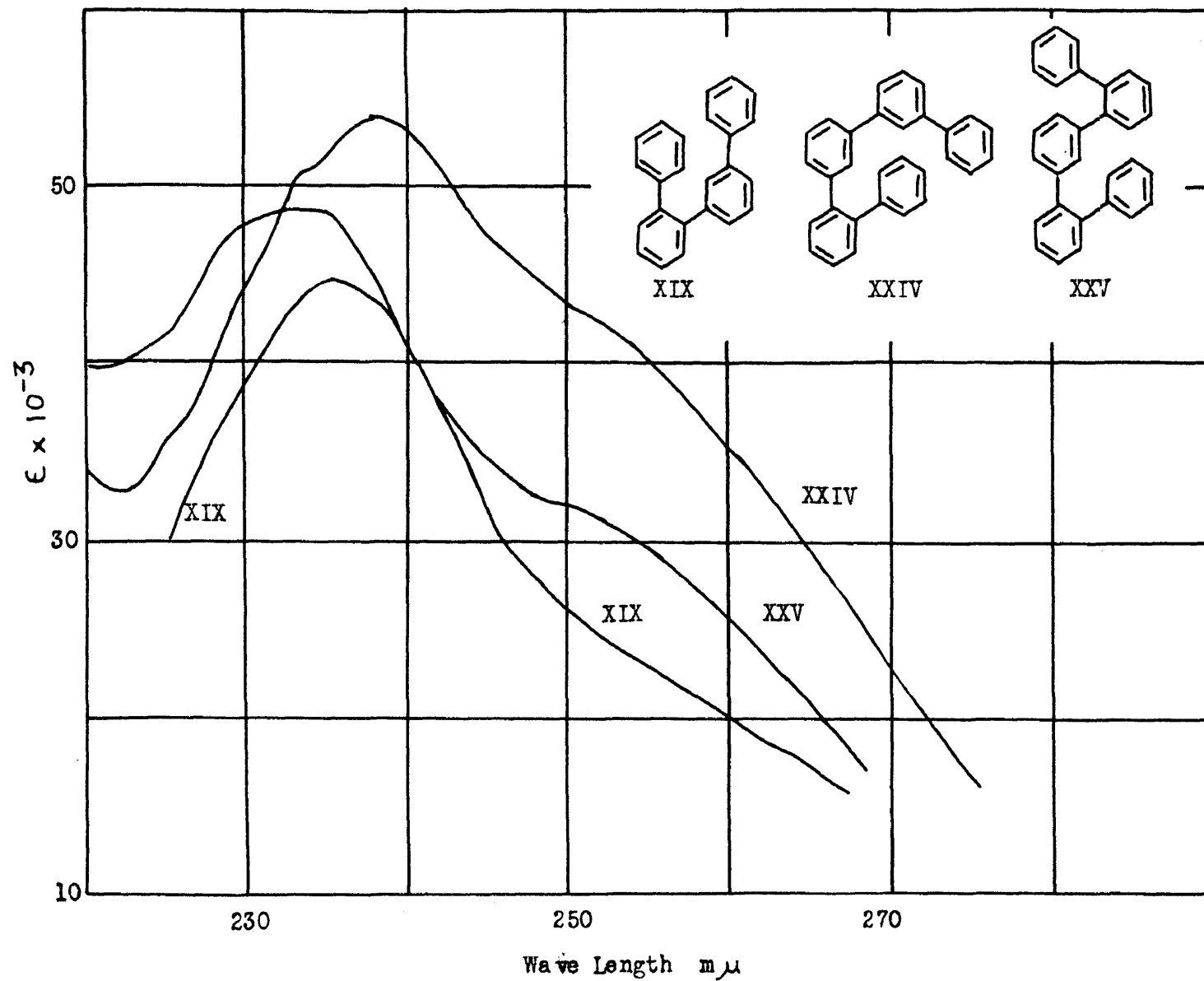
Figure 13

protons of the terminal rings. This steric interference
has been observed by Friedel, Orchin and Reggel[23] who also
found it to cause a hypsochromic shift.

The next set of curves shown in Figure 14, contrasts
the absorption spectrum of 1-(2-xenyl)-3-(4-xenyl)-benzene
(XXII) with the two symmetrically substituted compounds
containing the ortho and the para terphenyl units. It is
interesting to note that compound XXII shows peaks in the
region of the characteristic ortho terphenyl spectrum and
the para terphenyl spectrum, this being the only case where
the entire absorption region is not enclosed in a single
envelope.

In view of the above results, it becomes apparent that
o-terphenyl itself should show an absorption curve in the
ultraviolet region very similar to these compounds, with a
λmax. in the region of 235 mμ . It was surprising then to
find that the results of Pickett, Walter and France[24] indi-
cated no absorption peak in this region for o-terphenyl.
In order to verify this work, the absorption curve was re-
determined with a sample of o-terphenyl very kindly fur-
nished by Dr. C. F. H. Allen of the Eastman Kodak Co. The
results were indeed gratifying in that a curve very similar
to those in Figure 13 was obtained with a maximum extinction
at 233 mμ (2.9 x 10^4) and thus the values reported by the
above mentioned workers are in error.

The absorption curves of the bitolyls were also obtained
and were in excellent accord with what might be predicted

Wave Length mμ
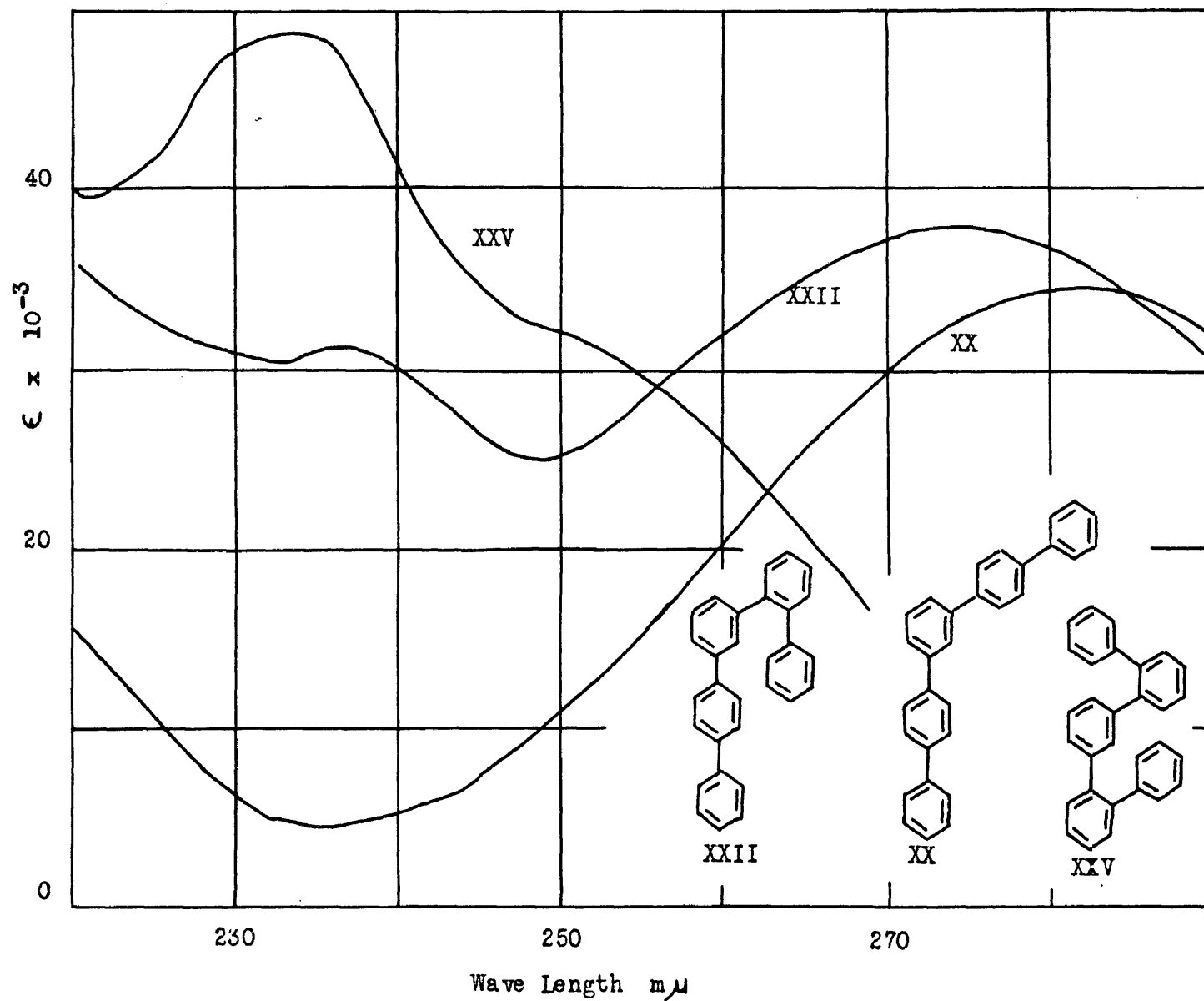
Figure 14

from the results of the polyphenyl curves. The 3,3'-dimethyl biphenyl (XXXVIII) gave a curve very characteristic of the m-polyphenyls; the 3,4'-dimethylbiphenyl (XXXIX) showed a slight bathochromic shift as would be expected; and the 2,3'-dimethylbiphenyl (XXXVII) gave a pronounced hypsochromic shift showing the hindered rotation of the biphenyl group caused by the single ortho methyl group.

In an attempt to correlate these results with the principles and theories developed by other workers in this field, certain inconsistancies were found. It is true that ultraviolet spectroscopy at the present time is still very much an empirical science. However, some generalizations have been made which have proved helpful in systematizing the information that has been reported.

Jones[25] has made a very comprehensive study of the ultraviolet absorption of a large number of compounds. Combining his observations with those of other investigators, he has suggested that the changes in the spectra of parent hydrocarbons, produced by substitution, can be classified under four headings:

(1) The bathochromic effect, which results in a shift of the whole absorption curve to longer wave lengths with little change of shape. Certain groups such as alkyl, most alicyclic groups, amino, carbonyl, and hydroxy are recognized in this effect.

(2) The fine-structure effect, caused by the introduction of methylene or dimethylene bridges in some molecules,

results in an increase in the fine-structure resolution of the absorption curve.

(3) The conjugation effect, which is observed in those molecules having unsaturated groups in a position of conjugation with an aromatic system. Examples of this are the ethylenic and carbonyl groups, but it is also noticed with certain groups such as the amino, hydroxyl, and hydroxylate ion which possess a donatable pair of electrons so situated that they are in conjugation with the aromatic ring. This effect generally results in a radical change in the appearance of the curve, where certain bands may be eliminated or shifted several hundred Angstrom units. The field of dye-stuff chemistry recognizes these as the auxochromes.

(4) The steric effect, which appears in certain compounds where a conjugated system is present but is unable to enter into some resonant hybrid due to steric interference. This is recognized by the fact that there is no basic change in the appearance of the curve, i.e., the curve is the same as that of the parent compound without the conjugated group present.

By these generalizations Jones was able to classify a host of spectral curves of aromatic hydrocarbons, phenols, and amines. Although a few isolated cases could not be satisfactorily correlated, these four effects did as Jones stated, "afford a basis in terms of which a somewhat heterogeneous mass of data might be organized into a form suitable for discussion."

The data in this thesis certainly fall under at least
two of these headings proposed by Jones. The conjugation
effect is apparent in comparing the curve of m-terphenyl
(XVI) with the curve of 1,3-di-(4-xenyl)-benzene (XX) or
with the curve of 1-phenyl-3-(4-xenyl)-benzene (XVII) where
the conjugating group is the phenyl system. A second effect,
the steric, no doubt accounts for the hypsochromic shift
involved when the curve of m-terphenyl (XVI) is compared
with that of 1,3-di-(2-xenyl)-benzene (XXV) or with other
curves of compounds containing the ortho biphenyl group.
On the basis of Jones steric effect alone, however, this
does not seem to be a satisfactory explanation, since the
steric effect does not predict the large hypsochromic shift
which is exhibited here. Perhaps the best means of resol-
ving this difficulty is to assume the o-terphenyl unit as
the parent hydrocarbon for those compounds containing this
structure, rather than attempting to correlate them with the
biphenyl curves. This, however, does not adequately account
for the strong hypsochromic effect noted in the 2,3'-di-
methylbiphenyl (XXXVII) curve, since this molecule must
certainly be considered as a derivative of the parent bi-
phenyl hydrocarbon. Nor is it easy to rationalize the
peculiarities of the 1-(2-xenyl)-3-(4-xenyl)-benzene (XXII)
curve by these effects alone. This is the only case where
a curve possesses two separate maxima in the wave length
range investigated. It is quite apparent that the right-
hand portion of this curve is related to the p-terphenyl
unit while the left-hand portion can be correlated to the

o-terphenyl unit. The minimum between these two peaks actually occurs at the wave length of maximum absorption of biphenyl and the m-polyphenyls (Figure 11). Therefore, it is difficult to picture either biphenyl or m-terphenyl as the parent hydrocarbon to which this curve can be correlated by Jones' generalized effects.

The present idea, held by several investigators in this field, that wherever there is repression of resonance, the absorption curve tends to revert to that of the parent hydrocarbon, does not seem adequate. Yet, it should be possible to correlate resonance with this hypsochromic effect. When one attempts to compare the spectra of molecules like styrene, the methyl styrenes, and biphenyl with the parent hydrocarbon, benzene, it is quite apparent that the present concepts are not adequate. Nor can these concepts be applied satisfactorily to the comparison of o-terphenyl with biphenyl. We recognize that in the o-terphenyl molecule steric interference prevents coplanarity, which is a necessary requirement for resonance to occur, yet the spectra does not revert to the parent hydrocarbon, but indeed undergoes a hypsochromic shift of 15 mμ .

It is generally accepted that absorption of light in the ultraviolet region is a consequence of the energy difference between some ground state and some excited state. From Planck's equation, we recognize that the greater this ΔE value, the further into the ultraviolet region a molecule will absorb. Any effect which will raise the energy level of

the first excited state, without effecting the ground state, will increase ΔE, and thus cause a hypsochromic shift of the absorption curve. Conversely, a lowering of the energy level of the first excited state will have the opposite effect. The lowering of ΔE is generally a consequence of increasing the resonance energy. This, in turn, should result from the presence of a conjugating group added to a given molecule. These foregoing statements would imply then that biphenyl will absorb further toward the visible region of the spectrum than benzene, since the presence of an additional phenyl group on benzene should give rise to a conjugate effect. This is not true, however, for the main peak of the benzene spectrum occurs at 255 mμ and the principle peak of biphenyl at 248 mμ.

If we picture the ground state of benzene as being some hybrid structure involving the two Kekule forms, then the excited state can be represented by the ionic forms as shown below:
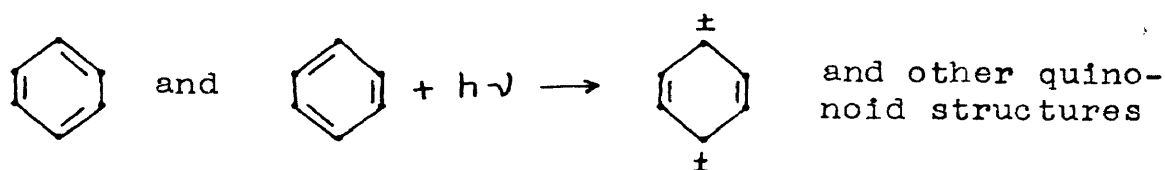
This is generally agreed to be the situation for benzene in its ground and excited states. Applying the same ideas to the biphenyl molecule, the ground and excited states may be written as:
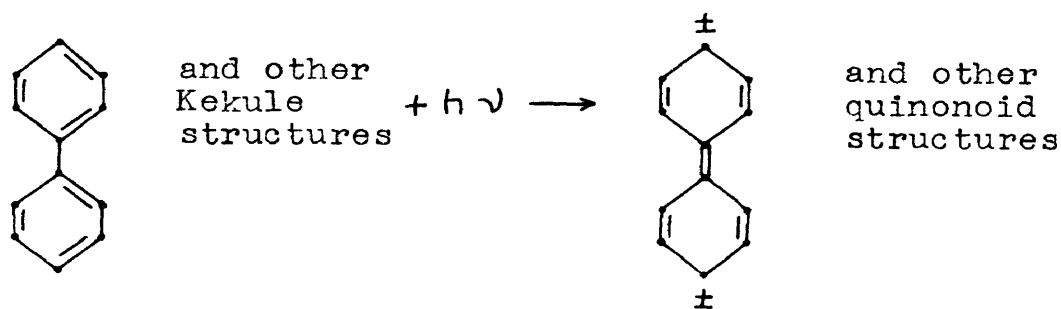
It should be mentioned that of the possible quinonoid structures of biphenyl, several will involve quinonoid forms of each benzene ring separately and that the one shown above would probably contribute least to the resonance of the excited state since it involves the greatest separation of charges.

To the extent that there is any repulsion between the ortho protons, the energy of the excited state of biphenyl will be somewhat higher than without this repulsion (which is exactly the situation in benzene). Thus, the absorption of biphenyl at shorter wave lengths than that of benzene can be explained.

This argument, of course, leads to the conclusion that restricted rotation exists in the biphenyl molecule. We must further conclude that biphenyl is not a coplanar molecule in the ground state. On the basis of electron diffraction studies, Karle and Brockway[26] have actually come to this same conclusion. Extending the argument, it would be concluded that o-methyl, o-phenyl, or any ortho substituted biphenyl will absorb further into the ultraviolet than biphenyl. The same reasoning can be applied to the styrenes, where interference of the α-protons of the ethylene group with the ortho protons of the ring raise the energy level of the excited state by hindering coplanarity. Further extension of the argument leads to the conclusion that the optically active biphenyls will absorb still further toward the ultraviolet region than biphenyl or else some other form than that represented above becomes effective.

By this reasoning, one should be able to calculate an energy of activation for the biphenyl molecule in going from a non-planar to a planar configuration. If the assumption is correct that the 250 mμ band of biphenyl represents the energy absorbed in reaching a planar ionic hybrid state, then we can calculate the energy of activation from the equation, $\Delta E = h\nu$. This gives a value of 11.4 kcal. for the biphenyl molecule. This same calculation for 2,3'-dimethyl biphenyl (λ max. = 235 mμ), a more hindered molecule, gives 12.1 kcal. Thus, the greater the steric hindrance toward becoming coplanar, the greater should be this energy of activation. Gilman[27] shows that 2,2'-diamino-6,6'-dimethyl biphenyl, which is stable toward racemization requires an activation energy of 22.5 kcal. to effect racemization. He further deduces that any biphenyl compound with an activation energy for racemization of less than 20.0 kcal. would racemize too rapidly to be resolved.

A further application of this correlation of activation energies to ultraviolet spectra might be made to the work of Berliner and Bondhus[28]. In studying competitive bromination reactions of benzene, toluene, and t-butyl benzene, they found the following relative order of reaction rates: benzene < t-butyl benzene < toluene. This anomalous order was explained on the basis of hyperconjugation and no bond resonance. This order is also predicted from the ultraviolet absorption curves of these molecules. It seems reasonable to assume that the activated molecules in both ultraviolet absorption and in the bromination reaction

would be of the ionic hybrid type. Thus a correlation between absorption peaks and consequently activation energy should predict the relative order of reaction rates. The following maxima have been observed

Benzene	243	249[b]	255[a]	262	
t-Butyl benzene		252[b]	257[a]	264	267
Toluene		255	262[a]	269[b]	

a: peak of highest extinction

b: peak of next highest extinction

Thus the shift of these maxima (and thus the energies of activation) would predict the results found by Berliner and Bondhus in competitive bromination reactions.

This argument on the relationship between the biphenyl and benzene absorption spectra is based on the rather fundamental assumption that the 248 mμ band of the biphenyl curve is related to the 255 mμ band of benzene. It should be mentioned that there have also been other theories presented to explain this seeming anomalous behavior. Gillam and Hey[22] first suggested the idea that the intense 248 mμ band of biphenyl is not related to the weak 255 mμ band of benzene, but rather it is the strong band of benzene in the region of 197 mμ (log ϵ = 3.9) shifted toward the visible. This has been further extended by Doub and Vandenbelt[29], who have surveyed a large number of benzene derivatives and attempted to show how the principle peak in the absorption curve of each of these derivatives is related to the 197 mμ band of benzene. Unfortunately, their data covers the

region above 220 mμ while the real answer to this argument lies in the region below 220 mμ . Carr and Stucklen[30] have investigated the absorption of a few benzenoid compounds in this difficultly accessible Shuman region and, contrary to the ideas of Doub and Vandenbelt, they report a strong band in the 200 mμ region for these compounds. This band is not shifted toward the visible (or disappeared), but actually a new band is appearing at the expense of the 255 mμ band of benzene.

By far the most progress which has been made in ultra-violet spectroscopy has been in the correlation of wave lengths of maximum absorption to such phenomena as structure, resonance, conjugation, etc. The problem of correlating extinction coefficient to these or other phenomena in organic molecules has not been so successful. Mulliken[31] has attempted the correlation of extinction coefficients by the methods of wave mechanics, as have other workers, but this is at present limited to very simple molecules. A more specific example of investigation along this line is that of Calvin[32], who assumes that if a biphenyl molecule has a hindrance to becoming coplanar, the absorption of the biphenyl will be double (in ϵ max.) that of two independent benzenes, appropriately substituted.

Braude[33] in a recent publication proposes a new theory of absorption intensities based solely on considerations of molecular geometry. The only assumption in Braude's theory is that the light must fall within the space of the molecule in order to be absorbed. His basic equation is reached by

assuming that light of intensity, I, falls on a slice of thickness, dl, of a cell of unit area filled with the vapor or solution of the absorbent at a concentration, c moles/ liter. If the average cross-section area of the molecule in the plane perpendicular to the direction of the incident light be (a) and there is no superposition of molecules in the direction of the propagation of light, the relationship below should hold.

$$\text{Illumination falling on molecules} = \frac{\text{Area of molecules}}{\text{Total area}} \cdot$$

$$\text{Total illumination} =$$

c N (a) dl I . 10^{-3}

where N is Avogadro's number.

If all the illumination is absorbed,

Illumination absorbed = -dl = c N (a) dl $\cdot$ I $\cdot$ 10^{-3}

Integrating this equation between the limits, l = 0 amd l = 1

$$-\int_{I=0}^{I=I} \frac{dI}{I} = c\ N\ (a)\ \cdot\ 10^{-3} \int_{l=0}^{l=1} dl$$

$$-2.303\ \log \frac{I}{I_o} = c\ N\ (a)\ l\ \cdot\ 10^{-3}$$

From Beer's law: $[\epsilon] = -\frac{1}{cl} \log \frac{I}{I_o}$ where $[\epsilon]$ is the extinction coefficient

From Braude's equation: $-\frac{1}{cl} \log \frac{I}{I_o} = \frac{1}{2.303} \cdot N\ (a)\ \cdot\ 10^{-3}$

By combining:

$$[\epsilon] = \frac{1}{2.303} \cdot N(a) \cdot 10^{-3} = 2.62 \cdot 10^{20} \ (a)$$

For simple molecules, (a) will be of the order of 10^{+2} A $(10^{-15} cm^2)$ so that ϵ will be approximately 10^5.

In the actual application of the equation, Braude states that four other factors must be taken into consideration, each of which will reduce this calculated value of $[\epsilon]$. First, the effective chromophore area, a, of a polyatomic molecule will generally be smaller than the maximum cross-sectional area, (a), because a given electronic or vibrational transition will be confined to a particular atom or group of atoms and only light falling in this area will be absorbed. Second, vibrational and electronic transitions are polarized along a particular axis and only the electric vector of the light in that axis will be effective. If the molecules are then randomly oriented, the statistical factor is 1/3 for the effective incident intensity. Third, since the ground state of the molecule will be distributed over several transitional and some electronic vibrational states, and if the transition takes place from only one particular sub-level or -levels, the extinction coefficient will be further reduced by a factor, x, which will depend upon the fraction of the molecules occupying the levels concerned. Fourth, there will be an interaction probability, k, which may be less than unity. Therefore the equation now becomes.

$$[\epsilon] = k \cdot x \cdot 1/3 \cdot 2.62 \cdot 10^{20} \ a = 0.87 \cdot 10^{20} \ k \ x \ a$$

For purposes of simplication, Braude lets k and x be unity, so that

$$\epsilon = 0.87 \cdot 10^{20} a$$

By applying straightforward geometric principles, Braude made several calculations of ϵ by this method for polyene and polycyclic hydrocarbons. Some assumptions as to the actual structure of the effective chromophore area were necessary, but these were not unreasonable. Below are listed a few random results which he obtained.

$$H \cdot (CH=CH)_n \cdot H$$

	ϵ observed	ϵ calculated
n = 1	15,000	17,400
3	79,000	81,000
5	51,000	87,000

$$C_6H_5(CH=CH)_n C_6H_5$$

	ϵ observed	ϵ calculated
n = 1	27,000	34,800
3	65,000	69,600
5	94,000	104,000
Benzene	46,000	52,200
Naphthalene	133,000	104,000
Anthracene	180,000	122,000

The comparison of ϵ calc'd. with ϵ obs. for benzene is made on the strong 180 mμ band of benzene. For the polyphenyls discussed in this thesis, it is not apparent

just how the effective chromophore area is determined.
Further, no information for comparison was obtained on the
spectra below 220 mμ , where presumably the absorption
band of the effective chromophore area in Braude's theory
would be located.

EXPERIMENTAL

Preparation of Dihydroresorcinol. During the course of this investigation, dihydroresorcinol was prepared several times. In each case the procedure described by Thompson[17] was used and the yields obtained were favorable with those reported by Thompson. A typical run involved the solution of 55 g. (0.5 moles) of resorcinol (duPont Technical Grade) and 24 g. (0.6 moles) of sodium hydroxide in 125 ml. of water. This solution was poured into a graduated cylinder to measure its volume and then poured into a 270 ml. hydrogenation bomb with a minimum of washing. Raney nickel (prepared by the method of Pivalic and Adams[34]), in the amount of ca. 5 g. was added, the bomb closed and charged to a pressure of 2500 p.s.i. of hydrogen. The bomb was placed in a rocker, heated to 50° C. and held at this temperature with rocking for a period of 8 hours. The calculated pressure drop was 1550 p.s.i. and approximately this pressure drop was reached in 2 hours. The bomb was recharged to 2500 p.s.i. of hydrogen and the heating and rocking continued for the remaining 6 hours with only a slight pressure drop at the end of this time. After cooling, the bomb was vented, opened, and the contents filtered. It was found in later runs that this filtration could be hastened if about 75% of the required amount of concentrated hydrochloric acid to neutralize the sodium hydroxide was added before filtering.

In either case, the filtrate was chilled to 5 - 10° C. and
concentrated hydrochloric acid added until the solution re-
acted acid to Congo Red paper. After precipitation of dihy-
droresorcinol was complete (ca. 30 minutes), the cold mixture
was filtered and the filter cake pressed as dry as possible.
The crude dihydroresorcinol thus obtained was dried in a
vacuum desiccator overnight or in the air and recrystallized
from benzene to remove sodium chloride and other contami-
nants. The product thus obtained was a white crystalline
material, quite stable for short periods of time. The yield
was 42 g. (75%).

Silver Salt of Dihydroresorcinol. This conversion was
accomplished by the method of Woods and Tucker[16]. To a solu-
tion of 252 g. (2.27 moles) of dihydroresorcinol and 425 g.
(2.3 moles) of silver nitrate in 200 ml. of water was added
a solution of 10% sodium hydroxide in water (ca. 800 ml.
required) slowly until a pH of 6 was reached. The slightly
brown precipitate of the silver salt of dihydroresorcinol
was isolated by filtration, pressed as dry as possible on
the funnel, and dried in air between sheets of filter paper.
This material was used without further drying or purification.

Preparation of Monoethyl Ether of Dihydroresorcinol.
The silver salt obtained from the 252 g. (2.27 moles) of di-
hydroresorcinol was placed in a 3 l. flask equipped with a
mechanical stirrer, dropping funnel and water separator (to
which was attached a reflux condenser). To this was added
1.5 l. of benzene and the whole mixture heated to refluxing

by means of a "Glascol" heater until no more water was collected in the separator. Ethyl iodide (360 g., 2.3 moles) was added as rapidly as possible and the refluxing continued for 15 minutes. While still warm, this mixture was filtered to remove silver iodide and the filtrate distilled under reduced pressure after removal of the benzene. The monoethyl ether was collected at 90 - 110° C. at ca. 1 mm., yielding 148 g. (47% from dihydroresorcinol).

Preparation of 3-Xenyl Bromide.* A solution of 340 g. (2.0 moles) of o-aminobiphenyl (redistilled technical grade) in 750 ml. of pyridine was placed in a 3.1 beaker. The solution was surrounded with an ice-bath and, with mechanical stirring, 236 g. (3.0 moles) of acetyl chloride was added slowly, maintaining the temperature between 10 - 15° C. This solution was stirred for 1 hour after the addition was complete and then poured into a 4 l. beaker containing one liter of concentrated hydrochloric acid and approximately 1 kg. of ice. The acetyl derivative precipitated immediately and, after stirring for a few minutes, was collected on a Buchner funnel and washed with water. A small sample was dried on a porous plate and its melting point found to be 115 - 116° C. (Huber et al.[19] report 118 - 119° C.).

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* This procedure is essentially that of Huber et al.[19] except for the method of isolation and purification of the final product.

The main portion of this material was not dried further, but divided into three equal portions by weight. Each portion was dissolved in 1000 ml. of glacial acetic acid in a 2 l. flask and to each was added a solution of 34 ml. of bromine in 600 ml. of glacial acetic acid. (Total amount of bromine used: 300 g. (1.85 moles)). These flasks were loosely stoppered and allowed to stand 24 hours. The contents of each flask was then diluted with an equal volume of water and the precipitated bromo compound collected on a Buchner funnel. The filtrates in each case were diluted further with water and any additional material which precipitated was also collected. After pressing as dry as possible on the funnel, the precipitates were combined. A small sample, dried as before, was found to melt at 126 - 127° C. (Huber et al.[19] report 127° C.).

The material thus obtained was placed in a 5 l., round bottom flask equipped with a reflux condenser. Ethanol (900 ml.) and concentrated hydrochloric acid (600 ml.) were added and the resulting solution refluxed for 4 hours. The solution, after cooling and standing 18 hours, afforded a heavy crystalline precipitate of the amine hydrochloride, which was removed by filtration, pressed reasonably dry and washed with ether. Weight: 434 g. (1.53 moles, 76% yield from o-aminobiphenyl).

The amine hydrochloride (256 g., 0.9 moles) was added to 450 ml. of ethanol and 85 g. of concentrated sulfuric acid in a 4 l. beaker. The mixture was heated to approximately 50° C. with stirring and then chilled in a salt-ice

bath to 5° C. Maintaining the temperature between 5 - 10° C., a solution of 65 g. (0.94 moles) of sodium nitrite in 100 ml. of water was slowly added. After this addition was finished, 22 g. of freshly precipitated copper was added. The entire mixture was allowed to warm to room temperature during which time a vigorous evolution of nitrogen took place. It was then heated to approximately 60° C. on a steam bath, allowed to cool, and filtered. The material on the filter was washed with ether and the filtrate was heated on a steam bath to remove as much ether and alcohol as possible. The residue was extracted with ether, washed with water in a separatory funnel and the ether solution dried over anhydrous magnesium sulfate. After removing the magnesium sulfate by filtration and the volatile solvent by evaporation, the residue was distilled at a pressure of approximately 0.7 mm. Crude 3-bromobiphenyl was collected between 110 and 120° C. This material was dissolved in a sufficient amount of 30 - 60° petroleum ether to effect solution and the solution passed through a column of activated alumina. The resulting solution was clear and colorless. The column was washed with a small amount of the 30 - 60° petroleum ether and the washings combined with the original solution. After removing the petroleum ether, the remaining liquid was distilled at 0.1 mm. and the desired 3-bromobiphenyl collected at 113 - 114° C. A yield of 180 g. was obtained representing an 86% yield on the deamination reaction and an overall yield of 65% from o-aminobiphenyl.

Conversion to 3-Carboxybiphenyl. A Grignard reagent was prepared in the usual manner by the addition of an ethereal solution of 15 g. (0.064 moles) of 3-bromobiphenyl to 1.6 g. (0.066 moles) of magnesium in 35 ml. of dry ether. This was poured into a mixture of dry ice and ether and acidified with 150 ml. of 10% sulfuric acid. After washing the resulting ether solution with 20% sulfuric acid solution in a separatory funnel, it was extracted with a 25% solution of potassium hydroxide. Acidification of the alkaline extract yielded 9 g. (0.045 moles) of 3-carboxybiphenyl, melting at 150-153° C., a 70% yield.

Preparation of 2-xenyl iodide. The diazotization reaction was conducted in a 4 l. beaker equipped with an efficient mechanical stirrer, a thermometer, and a dropping funnel. After adding 300 ml. of concentrated hydrochloric acid and 500 ml. of water into this beaker, 127 g. (0.75 moles) of molten o-aminobiphenyl was poured in slowly with vigorous stirring. This resulted in a slurry of fine crystals of the amine hydrochloride. Ice was then added directly to the mixture, and while keeping the temperature between 5°-10° C., a solution of 52 g. (0.75 moles) of sodium nitrite in a minimum of water was added slowly. After the addition was complete, a solution of 350 g. (2.1 moles) of potassium iodide in a minimum of water was added to the diazotization solution. It was found that the initial reaction of the potassium iodide was quite vigorous and if the potassium iodide solution was added too rapidly

at the start, the evolution of nitrogen was so rapid that considerable loss of material by frothing out of the beaker resulted. This, however, was easily prevented if approximately the first 1/3 of the potassium iodide solution was added cautiously. The reaction mixture thus obtained was allowed to warm to room temperature and was then heated to 70° C. During this process, a heavy oily layer separated at the bottom of the beaker. The upper, water layer was decanted and the lower layer dissolved in toluene. The toluene extract was washed several times with water and then with a sodium bisulfite solution to remove any free iodine present. This latter treatment considerably lightened the color of the toluene layer. The organic layer was then separated, dried over anhydrous magnesium sulfate, and after removal of the magnesium sulfate, the volatile solvents were removed. The residue was distilled at a pressure of 0.2 mm. and 142 g. of slightly yellow distillate collected between $113-114^\circ$ C. This represented a yield of 67% of crude o-iodobiphenyl.

4-Xenyl bromide. The 4-xenyl bromide used throughout this investigation was student prepared material, synthesized by the procedure of Gomberg and Bachmann[18].

3-Phenyl-Δ^2-cyclohexenone. This material was prepared by Dr. I.W. Tucker[1] in sufficient quantity that it was not necessary to synthesize additional amounts for this investigation.

3-(4-Xenyl)-Δ^2-cyclohexenone. This compound was also synthesized by Dr. I.W. Tucker[1] and it was not necessary to repeat the preparation during the course of this research.

3-(3-Xenyl)-Δ^2-cyclohexenone. A 1 l., three neck, round bottom flask, equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser and containing 14.8 g. (0.612 moles) of magnesium turnings was flushed with dry nitrogen while all glass walls were being gently heated with a Bunsen flame. The nitrogen sweep was continued until the apparatus was cool, then discontinued. Calcium chloride drying tubes were placed at the top of the condenser and dropping funnel. Dry ether (250 ml.) was introduced and the addition of 142.6 g. (0.612 moles) of 3-xenyl bromide in 100 ml. of dry ether started. The initial reaction of the magnesium with the halide was very slow, it being necessary to reflux the ether mixture to induce the initial reaction. After the reaction was initiated the bromide was added at such a rate as to maintain a mild reflux. When the addition was complete, the mixture was refluxed with stirring for another hour. Following this, a solution of 92 g. (0.658 moles) of monoethyl ether of dihydroresorcinol in 100 ml. of dry ether was added, and again the mixture was heated under reflux for a short period. The Grignard complex separated out of the ether solution during the reaction, and had the appearance of a semi-crystalline solid. This slurry was hydrolyzed by the dropwise addition of about 50 ml. of 10% sulfuric acid solution. The resulting mixture was steam distilled for a period

of 4 to 5 hours or until there was no further appearance of organic material in the steam distillate. The residue in the distillation flask was taken up in ether and the water layer withdrawn in a separatory funnel. The ether solution was washed successively with water, sodium bicarbonate solution, again with water, and then dried over anhydrous magnesium sulfate. After removal of the magnesium sulfate and evaporation of the ether solvent, the residue was distilled in a Hickmann apparatus with a high vacuum diffusion pump. The product was collected at an indicated pressure of 9μ and an oil bath temperature of 160 to 175° C. A yield of 70 g. (46%) of 3-(3-xenyl)-Δ^2-cyclohexenone was obtained. This product was slightly colored and very viscous. Numerous attempts were made to obtain this compound in a crystalline state. Various solvents were employed using the standard techniques for inducing crystallization, but in none of these attempts could crystals be obtained. Seeding with similar type compounds was also unsuccessful.

A solution of this compound in a mixture of 30-60° petroleum ether and benzene was passed through a column of activated alumina. Without washing or eluting, the alumina in the column was carefully pushed out onto clean paper keeping the structure of the column relatively undisturbed. Small sample portions of the column were removed and by testing each portion with 2,4-dinitrophenylhydrazine reagent, that section of the column on which the ketone had been absorbed was determined. The section indicated was separated from the balance of the alumina and heated with a quantity of ethanol to

displace the ketone from the alumina. This mixture was then filtered while hot. On cooling the ketone separated as a viscous oil. The oil was recovered by removal of the alcohol by evaporation. Again, this oil could not be induced to crystallize from common solvents. A similar chromatographic absorption technique was carried out in which the ketone was absorbed on the alumina, but then eluted from the column with ethanol while the column was still intact. A glassy material was again obtained which could not be crystallized. No further attempts were made to obtain this glass as a crystalline solid, and it was used in subsequent reactions as the glass.

The red 2,4-dinitrophenylhydrazone of this compound was prepared, m.p. 210-211°. Anal. Calc'd. for $C_{24}H_{20}O_4N_4$: C, 67.28; H,4.71. Found: C,67.81; H, 4.68.

Preparation of 3-(2-xenyl)-Δ^2-cyclohexenone. Employing apparatus of the type described in the previous synthesis of 3-(3-xenyl)-Δ^2-cyclohexenone, the Grignard reagent of 2-xenyl iodide was prepared by the dropwise addition of a solution of 42 g. (0.15 moles) of 2-xenyl iodide in 30 ml. of dry ether onto a stirred mixture of 3.3 g. (0.14 moles) of magnesium and 20 ml. of dry ether. The reaction started quickly and proceeded smoothly. After the halide was added, stirring was continued an additional hour until practically all the magnesium had disappeared. A solution of 20.7 g. (0.148 moles) of enol ether of dihydroresorcinol in 20 ml. of dry ether was added slowly. The complex thus formed was decomposed with 50 ml. of 10% sulfuric acid and the resulting

mixture extracted with ether. The ether layer was washed with water and with a dilute sodium hydroxide solution and finally with water. The ether layer was separated and steam distilled. The distillation was continued until there was no appreciable amount of organic material appearing in the distillate. The residue in the distillation flask was extracted with ether and washed as before, followed by separation of the ether layer which was dried over anhydrous magnesium sulfate. After removal of the drying agent, the ether solution was reduced to an approximate volume of 150 ml. and set in the ice box.

Crystals were obtained on standing and these were removed by filtration. A further crop was obtained upon reduction of the volume of the filtrate. The combined yield was 13.3 g. (38%). A single recrystallization from 80-100° petroleum ether gave a satisfactory compound for the subsequent reactions.

A small sample of recrystallized 3-(2-xenyl)-Δ^2-cyclohexenone was prepared for analysis by sublimation followed by recrystallization from 80-100° petroleum ether. This yielded a white crystalline product melting at 104.5-105.5° C. Anal. Calc'd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.56, 86.86; H, 6.66, 6.83.

A red 2,4-dinitrophenylhydrazone was prepared by standard methods. M.P. 220.5 - 221.5. Anal. Calc'd. for $C_{24}H_{20}O_4N_4$: C, 67.28; H, 4.71. Found: C, 67.17, 67.19; H, 4.90, 4.94.

Preparation of 1-Phenyl-3-(3-xenyl)-benzene (B). Into a previously dried and nitrogen flushed 500 ml., three neck flask equipped with stirrer, reflux condenser and dropping funnel was introduced 3.3 g. (0.14 moles) of magnesium and 20 ml. of dry ether. A solution of 25 g. (0.16 moles) of phenyl bromide in 20 ml. of dry ether was then added dropwise to obtain the Grignard reagent. To this was added 25 g. (0.10 moles) of 3-(3-xenyl)-Δ^2-cyclohexenone in 20 ml. of dry ether and the reaction mixture stirred an additional hour after the addition was complete. Hydrolysis of the Grignard complex was effected with 10% sulfuric acid and the entire mixture steam distilled directly (about 500 ml. of distillate was collected). The residue was cooled and extracted with ether. The ether extract was washed with water and with sodium bicarbonate solution. The ether layer was dried over magnesium sulfate. After removal of the magnesium sulfate by filtration and the ether by evaporation, the residue was distilled in a Hickman apparatus. A middle fraction of 18.1 g. (1-phenyl-3-(3-xenyl)-1,3-cyclohexadiene) was collected at a bath temperature of 160-170° and an indicated pressure of 9 μ . This represented a yield of 59%. A combined fore and after fraction of 4.64 g. was discarded. The material thus obtained was a slightly colored "glass", which, after a few unsuccessful attempts to obtain it crystalline, was used in subsequent reactions in this state.

To a 100 ml., round bottom flask with a short air condenser was added 25 ml. of p-cymene and 4 g. of 5% palladium

on charcoal catalyst. The flask was immersed in an oil bath
and the bath heated to that temperature at which the p-cymene
refluxed. At this point, 7.7 g. (0.025 moles) of 1-phenyl-
3-(3-xenyl)-1,3-cyclohexadiene was added dropwise onto the
refluxing mixture through the air condenser. The resulting
mixture was refluxed for two hours at which time the dehy-
drogenation was assumed to be completed. The air condenser
was replaced by a "goose-neck" tube, the temperature of the
bath raised, and as much p-cymene as possible removed by
distillation. The flask and its contents were cooled and
50 ml. of absolute ethanol added. This mixture was heated
and filtered while hot to remove the catalyst. The filtrate
was chilled, resulting in the precipitation of the desired
1-phenyl-3-(3-xenyl)-benzene. The precipitate was removed
by filtration and dried to yield 3.43 g. (45%) of the m-
quaterphenyl. No attempt was made to recover any additional
compound from the filtrate. A pure sample of this material
was prepared by two recrystallizations from absolute ethanol.
M.P. 84-85° C. Anal. Calc'd. for $C_{24}H_{18}$: C, 94.07; H, 5.92.
Found: C, 93.62; H, 6.05.

Preparation of 1-Phenyl-3-(3-xenyl)-benzene (A). In
the same manner as described in the previous preparation, a
Grignard complex was prepared from 1.58 g. (0.065 moles) of
magnesium, 16.3 g. (0.07 moles) of 3-xenyl bromide and 9.7 g.
(0.056 moles) of 3-phenyl $-\Delta^2$-cyclohexenone. The reaction
mixture was steam distilled, extracted with ether, washed,
and dried over anhydrous magnesium sulfate as before.

After removing the magnesium sulfate by filtration, the ether solution was allowed to evaporate slowly. A viscous, glassy residue resulted which was not purified further.

Approximately 2 g. of this viscous material was aromatized by using 5% palladium on charcoal catalyst in p-cymene as in the previous preparation. Crystals were also obtained from absolute alcohol, which after two recrystallizations melted at 84.5-85.0° C. Equal portions of this 1-phenyl-3-(3-xenyl)-benzene and the same compound prepared by the alternate method were thoroughly mixed. This mixture showed no melting point depression, melting at 84-85° C.

Preparation of 1-Phenyl-3-(2-xenyl)-benzene (B). A 500 ml., two neck flask was equipped with a magnetic stirrer, reflux condenser, and dropping funnel. After addition of 2.43 g. (0.1 moles) of magnesium, the flask was flamed dry while flushing with nitrogen. Calcium chloride tubes were attached to the condenser and dropping funnel and 30 ml. of dry ether added. The Grignard reagent of phenylmagnesium bromide was then prepared by dropwise addition of an ether solution of 24 g. (0.15 moles) of bromobenzene. After completion of this reaction, 15 g. (0.06 moles) of 3-(2-xenyl)-Δ^2-cyclohexenone in dry ether was added and stirring continued for one hour. This was followed by hydrolysis with 10% sulfuric acid and steam distillation of the resulting mixture. When no further organic material appeared in the distillate, the residue in the flask was cooled, extracted with ether, and the extract washed with water and sodium

bicarbonate solution. The ether solution was then dried over magnesium sulfate and after filtration and reduction of the volume of ether, crystals were obtained on chilling. These crystals were removed by filtration. After recrystallization from ethanol, 4 g. of the 1-phenyl-3-(2-xenyl)-1,3-cyclohexadiene was obtained. No attempt was made to recover additional material from the filtrates.

This compound (1.5 g.) was added in small portions to a refluxing mixture of 0.5 g. of palladium on charcoal catalyst and 25 ml. of p-cymene in a 100 ml. flask equipped with an air condenser. After addition, the mixture was heated for two hours and then the bath temperature raised and most of the p-cymene was removed by distillation through a bent tube replacing the air condenser. After cooling, the residue was dissolved in benzene and the catalyst removed by filtration. Alcohol was added to the filtrate until it became cloudy. It was then heated and allowed to cool slowly. Crystals of 1-phenyl-3-(2-xenyl)-benzene were thus obtained on standing. These were filtered from the solution and after recrystallizing from ethanol melted at 90.5-91.0° C. Anal. Calc'd. for $C_{24}H_{18}$: C, 94.07; H, 5.92. Found: C, 94.22, 94.10; H, 6.06, 6.03.

Preparation of 1-Phenyl-3-(2-xenyl)-benzene (A).
Employing essentially the same experimental procedure, 1-phenyl-3-(2-xenyl)-1,3-cyclohexadiene was prepared from 2.0 g. (0.085 moles) of magnesium, 28 g. (0.1 moles) of 2-xenyliodide, and 11 g. (0.065 moles) of 3-phenyl-$\triangle^2$-cyclohexenone. A yield of 9.2 g. was obtained (46%).

Dehydrogenation of 3 g. of this diene was accomplished by the same method as described before; 1.56 g. of l-phenyl-3-(2-xenyl)-benzene was obtained from the first crop of crystals. On recrystallization from a benzene ethanol mixture a melting point of 91-91.5° C. was obtained. Anal. Calc'd. for $C_{24}H_{18}$: C, 94.07; H, 5.92. Found: C, 94.08; H, 5.92.

A mixed melting point determination of the compounds obtained by each route showed no depression.

Preparation of 1-(3-Xenyl)-3-(4-Xenyl)-Benzene (A).

The Grignard reagent of 3-xenyl bromide was prepared from 25 g. (0.11 moles) of 3-xenyl bromide and 2 g. (0.08 moles) of magnesium in the manner described in the preparation of l-phenyl-3-(3-xenyl)-benzene. To the ether solution of this reagent, 15 g. (0.064 moles) of 3-(4-xenyl)-Δ^2-cyclohexenone as a slurry in 50 ml. of dry ether was added through the dropping funnel. The reaction proceeded smoothly and after completion, the reaction flask was placed in a salt-ice bath and the Grignard complex precipitated in fine crystals. This precipitate was filtered on a cintered glass funnel and then transferred to a beaker. The complex was hydrolyzed in the beaker with 10% sulfuric acid solution and the resulting mixture extracted with benzene in a separatory funnel. The water layer was withdrawn and the benzene layer washed successively with water, sodium bicarbonate solution, and again with water, and finally dried over magnesium sulfate. The drying agent was removed and the benzene solution remaining

reduced in volume by volatilization of the benzene until crystals were obtained when the solution was chilled. The crude 1-(4-xenyl)-3-(3-xenyl)-1,3-cyclohexadiene (9.6 g.) was separated by filtration and recrystallized from ethanol. A small sample was recrystallized a second time to give a white crystalline material melting at 148-149° C. Anal. Calc'd. for $C_{30}H_{24}$: C, 93.70; H, 6.29. Found: C, 93.35; H, 6.48.

A small portion of this diene (2.4 g.) was added to a refluxing p-cymene and 5% palladium on charcoal catalyst as described in previous aromatization reactions. After heating for two hours, most of the cymene was distilled over and the residue cooled and taken up in benzene. The catalyst was filtered from this hot benzene solution and the filtrate diluted with an equal volume of ethanol. This solution on cooling yielded crystals of 1-(4-xenyl)-3-(3-xenyl)-benzene. Recrystallization from a benzene ethanol mixture gave a product melting at 155-155.5° C. Anal. Calc'd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.57; H, 5.67.

Preparation of 1-(3-Xenyl)-3-(4-xenyl)-benzene (B).
The lithium complex of 4-xenyl bromide was prepared in a dry, nitrogen flushed, 500 ml., 3 neck flask to which were attached a stirrer, reflux condenser and dropping funnel. The lithium (0.764 g., 0.11 moles) was placed in the flask with 20 ml. of dry ether and a solution of 35.0 g. (0.15 moles) of p-bromobiphenyl in 20 ml. of dry ether added dropwise through the funnel. After all the halide solution had been added, the mixture was stirred until all the lithium was consumed. An ether solution of 17.6 g. (0.071 moles) of 3-(3-xenyl)-$\triangle^2$-

cyclohexenone was then added to the 4-xenyllithium solution at a rate which caused the ether to reflux mildly. The reaction mixture was then hydrolyzed with 10% sulfuric acid and steam distilled. Approximately 4 l. of distillate was collected and discarded. The residue was extracted with benzene, washed and dried over anhydrous magnesium sulfate as before. After removing the magnesium sulfate, the volume of benzene was reduced, but the desired 1-(3-xenyl)-3-(4-xenyl)-1,3-cyclohexadiene could not be induced to crystallize. The remainder of the benzene was removed by evaporation and the residue remaining was used without further purification.

This crude material (3.60 g.) was dehydrogenated in the same manner as in the alternate method just described. Crystals of the aromatized compound were obtained when the benzene solution was diluted with four times its volume of ethanol. These were removed by filtration and recrystallized from an ethanol benzene mixture. The resulting crystals of 1-(3-xenyl)-3-(4-xenyl)-benzene melted at 153-154° C.

A mixture of these crystals with an equal amount of those obtained by the alternate method showed no depression in melting point.

Preparation of 1,3-Di-(3-Xenyl)-Benzene. A dry, 500 ml., 3 neck flask was equipped with a stirrer, reflux condenser, and dropping funnel. In this was placed 3.2 g. (0.13 moles) of magnesium and the entire apparatus flushed with dry nitrogen and heated with a Bunsen flame. After adding 20 ml. of dry ether to the flask, a solution of 30.3 g. (0.13 moles)

of 3-xenyl bromide in 20 ml. of dry ether was added dropwise
to obtain the 3-xenylmagnesium bromide. After this reaction
was complete, an ether solution of 24.8 g. (0.1 moles) of
3-(3-xenyl)-Δ^2-cyclohexenone was added at a rate which main-
tained a mild reflux. The refluxing and stirring were con-
tinued for a short period after all the ketone was added.
The flask was then chilled in an ice-bath resulting in the
precipitation of the Grignard complex. The cold mixture was
rapidly filtered on a cintered glass funnel in an atmosphere
of nitrogen. The solid complex was then transferred to a
beaker and decomposed with 10% sulfuric acid. This mixture
was extracted with ether, washed with water and sodium bi-
carbonate solution. The ether layer was then dried over
anhydrous magnesium sulfate. After removing the drying agent
by filtration and evaporating the solvent, the viscous resi-
due was distilled in the Hickman apparatus. A glassy, yellow
distillate (11.4 g.) was thus obtained which was not purified
further since it could not be obtained crystalline by the
usual methods.

The crude 1,3-di-(3-xenyl)-1,3-cyclohexadiene was aroma-
tized by the method described in the previous preparation,
using 7.55 g. of the diene, 4 g. of 5% palladium on charcoal
catalyst and 25 ml. of p-cymene. After the removal of as
much p-cymene as possible by distillation, the residue was
taken up in ethanol and filtered while hot to remove the
catalyst. A satisfactory crystalline material could not be
obtained from this solution. Although a solid precipitate

could be obtained on chilling, it persistently oiled on warming to room temperature. This oil was separated from the alcohol and dissolved in 30 - 60° petroleum ether. This solution was then passed through a column of activated alumina and the column washed with a mixture of 30 - 60° petroleum ether and benzene. The solution resulting from the chromatographic treatment was reduced in volume by evaporation and a crystalline precipitate of 1,3-di-(3-xenyl)-benzene was obtained on cooling. These crystals, after four recrystallizations from ethanol, gave a constant melting point of 109 - 110° C. Anal. Calc'd. for: $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.60; H, 5.89.

Preparation of 1-(4-Xenyl)-3-(2-xenyl)-benzene (A). The Grignard reagent of 2-xenyl iodide was prepared in the standard manner from 0.97 g. (0.04 moles) of magnesium and 11.3 g. (0.04 moles) of 2-xenyl iodide. To the ether solution of the 2-xenylmagnesium iodide was added 7.0 g. (0.028 moles) of 3-(4-xenyl)-$\triangle^2$-cyclohexenone in small amounts as the dry powder. The reaction mixture was refluxed for about 1 hour after all the ketone had been added. Hydrolysis was effected as before with 10% sulfuric acid and the resulting mixture steam distilled. A distillate of approximately 1 l. was collected. The aqueous layer in the distillation flask was separated from the insoluble, viscous organic material by decantation and benzene added to dissolve the organic material. This benzene solution was washed with water and sodium bicarbonate solution and dried over anhydrous magnesium sulfate. After removal of the magnesium sulfate by filtration,

the benzene was distilled off and the residue taken up in a small amount of ether. This ether solution on standing in the ice box yielded crystals of the 1-(4-xenyl)-3-(2-xenyl)-1,3-cyclohexadiene (6.0 g.) which were separated by filtration. This material melting at 118 - 120° C. was not purified further.

Dehydrogenation of this diene was accomplished by adding in small portions 1.5 g. of the diene to a boiling mixture of 0.5 g. of 5% palladium on charcoal catalyst and 25 ml. of p-cymene. After heating for 2 hours, the p-cymene was partially removed as before and the residue taken up in benzene. Filtration of this hot benzene solution effected removal of the catalyst. The filtrate was diluted with ethanol until the resulting mixture turned cloudy. This on standing in the ice box gave 1.1 g. of 1-(4-xenyl)-3-(2-xenyl)-benzene after filtration. This material after three recrystallizations from a benzene alcohol mixture gave a constant melting point of 142 - 143° C. Anal. Calc'd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.27, 94.16; H, 6.09, 6.01.

Preparation of 1-(4-Xenyl)-3-(2-xenyl)-benzene (B).

The alternate procedure for synthesis of this compound was accomplished by preparing the organolithium derivative of 4-xenyl bromide by the procedure described in the preparation of 1-(4-xenyl)-3-(3-xenyl)-benzene and reacting it with 3-(2-xenyl)-$\triangle^2$-cyclohexenone. The 4-xenyllithium was prepared from 0.5 g. (0.07 moles) of lithium and 18.5 g. (0.08 moles) of 4-xenyl bromide. Ten grams (0.04 moles) of the ketone in

ether was added to the ether solution of the 4-xenyllithium.
After hydrolysis with 10% sulfuric acid, the mixture was
steam distilled and the residue, after cooling, taken up in
ether. After washing and drying the ether solution in the
usual manner, the volume was reduced and a precipitate of
1-(2-xenyl)-3-(4-xenyl)-1,3-cyclohexadiene resulted.

This diene (2 g.) was aromatized by the exact procedure
used in the alterate synthesis and a crystalline precipitate
of the 1-(2-xenyl)-3-(4-xenyl)-benzene obtained from an
ethanol benzene mixture. After recrystallization a melting
point of 144.5 - 145.5° C. was obtained. Anal. Calc'd. for
$C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.35, 94.45; H, 5.94,
5.96.

A mixed melting point determination of the products
obtained by the two routes showed no depression.

Preparation of 1-(3-Xenyl)-3-(2-xenyl)-benzene (B). A
500 ml., 2 neck flask with an attached reflux condenser and
dropping funnel was charged with 3.5 g. (0.15 moles) of mag-
nesium and flamed dry in a stream of dry nitrogen. A portion
(20 ml.) of dry ether was added and the addition of 28 g.
(0.12 moles) of 3-xenyl bromide in 20 ml. of dry ether com-
mensed. After the addition was complete, the reaction was
stirred and mildly refluxed for 1 hour. A slurry of 13.3 g.
(0.054 moles) of 3-(2-xenyl)-Δ^2-cyclohexenone in 40 ml. of
ether was then added. This addition was followed by hydroly-
sis with 10% sulfuric acid, extraction with ether, and
washing the extract with dilute sodium hydroxide solution and
with water. The ether solution was dried with magnesium

sulfate and after removal of the drying agent and reduction of the volume of ether solution by evaporation, crystals of the desired 1-(2-xenyl)-3-(3-xenyl)-1,3-cyclohexadiene were obtained on cooling. The first crop of crystals yielded 3.38 g. which was then recrystallized from a mixed benzene ethanol solvent. M.p. 111.5 - 112.5° C.

Aromatization of 2 g. of this compound was carried out by addition of the solid in small portions to a refluxing p-cymene (25 ml.) and 5% palladium on charcoal (0.5 g.) mixture. The entire mixture was refluxed for 2.5 hours and, at the end of this period, the greater portion of the p-cymene removed by distillation. The residue was taken up in 25 ml. of benzene, heated and filtered. The filtrate on dilution with an equal volume of ethanol yielded crystals of 1-(2-xenyl)-3-(3-xenyl)-benzene which were separated by filtration and recrystallized from 60 - 80° petroleum ether. M.p. 113 - 114° C. Anal. Calc'd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 93.86, 94.71; H, 5.86, 5.79.

Preparation of 1-(3-Xenyl)-3-(2-xenyl)-benzene (A).
The alternate procedure for preparing this compound was carried out by essentially those methods described in the previous preparations. The Grignard complex was obtained from 1.0 g. (0.041 moles) of magnesium, 14.0 g. (0.05 moles) of 2-xenyl iodide, and 5.35 g. (0.022 moles) of 3-(3-xenyl)-Δ^2-cyclohexenone. Isolation of the 1-(3-xenyl)-3-(2-xenyl)-1,3-cyclohexadiene was effected by similar methods as have been described.

Aromatization of the compound gave 1-(3-xenyl)-3-(2-xenyl)-benzene by the usual method and this compound showed no mixed melting point depression with the compound prepared by the alternate route.

Preparation of 1,3-di-(2-xenyl)-benzene. This compound, being available through only one synthetic route, was prepared by aromatization of the diene obtained from the reaction of 2-xenylmagnesium iodide with 3-(2-xenyl)-Δ^2-cyclohexenone. The Grignard reagent was prepared by the foregoing methods from 2.43 g. (0.1 moles) of magnesium and 34.0 g. (0.12 moles) of 2-xenyl iodide. To this reagent in ether solution was added 19.2 g. (0.077 moles) of 3-(2-xenyl)-Δ^2-cyclohexenone. After hydrolysis with 10% sulfuric acid, the reaction mixture was steam distilled, followed by extraction of the residue with ether. This extract was washed and dried as before and on reduction in volume of the solution, crystals of the 1,3-di-(2-xenyl)-1,3-cyclohexadiene were obtained from the cooled solution.

This compound was aromatized directly by treatment with 5% palladium on charcoal catalyst in a refluxing p-cymene medium. After removal of p-cymene and catalyst, the desired 1,3-di-(2-xenyl)-benzene was obtained from a benzene ethanol mixture. This, after two recrystallizations from the same solvent mixture, gave a melting point of 155.5 - 156.5° C. Anal. Calc'd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.05, 93.97; H, 6.21, 6.17.

Preparation of m-Chloroiodobenzene. The synthesis of m-chloroiodobenzene from m-chloroaniline was accomplished by

the Sandmeyer reaction. The reaction was carried out in a 3 gal. Pyrex battery jar equipped with a large efficient stirrer, a thermometer, and a dropping funnel. Concentrated hydrochloric acid (885 ml.), water (885 ml.) and 355 g. (2.0 moles) of m-chloroaniline were added in the jar and the mixture stirred to effect solution of the m-chloroaniline. Approximately 2 kg. of ice were added and when the temperature had dropped to 5° C., the addition of a solution of 145 g. (2.1 moles) of sodium nitrite in approximately 500 ml. of water was started. The addition was continued, while the temperature remained between 5 - 10° C., until the solution showed a positive reaction to potassium iodide starch paper. While the solution was still cold, 334 g. (2.0 moles) of potassium iodide in a minimum of water was added. The solution was stirred for 1 hour, during which time it slowly came to room temperature. The temperature was then raised to approximately 70° C. by introducing a steam line directly into the reaction jar. During this period, a heavy organic layer settled to the bottom of the battery jar.. The upper aqueous layer was separated and discarded. The residue was transferred to a 2 l., round bottom flask and steam distilled. The organic layer which appeared in the distillate was isolated and shaken in a separatory funnel with sodium thiosulfate solution to destroy the iodine which had also collected in the steam distillate. The organic layer was separated and dried over magnesium sulfate. After removal of the drying agent, the material was distilled at 35 mm. and the fraction distilling at 118 - 120° C. collected. A yield of 337 g. (79%) of m-chloroiodobenzene was obtained.

Preparation of m-Nitroiodobenzene. Using the same procedure and the same apparatus, 258 g. (52% yield) of crude m-nitroiodobenzene was prepared from 276 g. (2.0 moles) of m-nitroaniline, 138 g. (2.0 moles) of sodium nitrite, and 322 g. (2.0 moles) of potassium iodide. The crude material was isolated by distillation, the fraction boiling at 100 - 110° C. and 1 mm. being collected. The m-nitroiodobenzene obtained in this manner was dissolved in approximately an equal volume of benzene and passed through a column of activated alumina. This process removed a considerable amount of colored impurities and on redistillation, 244 g. of very slightly colored material was obtained.

Preparation of 3-Nitro-3'-chlorobiphenyl. The Ullmann reaction was carried out in a 1 l., 3 neck, round bottom flask to which were attached a thermometer, a short air condenser, a very efficient mechanical stirrer, and a "Glascol" heating mantel. In the flask were placed 330 g. (1.34 moles) of m-nitroiodobenzene and 320 g. (1.34 moles) of m-chloro-iodobenzene. Heat was applied until the temperature reached 200° C. whence the addition of 250 g. (ca. 4 moles) of copper bronze with stirring was begun. The temperature rose rapidly to 235° C. The heat was removed and the addition of copper halted until the temperature returned to 200° C. The addition was then continued slowly while the temperature was maintained between 200 - 210° C. When all the copper had been added, the temperature was held at 200° C. with stirring for 1.5 hours. The reaction mixture was then cooled and approximately 500 ml. of benzene added. Filtration of this

mixture while hot accomplished the removal of the solid in-
organic materials. The inorganic sludge was washed on the
funnel with 500 ml. of hot benzene. The washings were com-
bined with the original filtrate. The filtrate was heated
until the volume was reduced about one-half. The dark solu-
tion remaining was chilled to precipitate as much 3,3'-
dinitrobiphenyl as possible. The solid obtained was removed
by filtration and set aside. The filtrate was further con-
centrated to remove all the volatile solvent. The residue
was distilled at approximately 0.1 mm. Due to the high
boiling point of the desired 3-nitro-3'-chlorobiphenyl it
was very difficult to accomplish the distillation without
serious superheating of the column. Therefore, accurate
temperature readings could not be obtained. The fractions
were actually taken on the basis of the physical appearance
of the distillate. This method was actually very effective.
With water running through the condenser, a forerun of
liquid material was collected which consisted of a mixture
of the two original organic reactants and 3,3'-dichloro-
biphenyl. At the first appearance of solid material in the
condenser, the receiver was changed, water in the condenser
jacket replaced by steam, and the distillation continued.
This fraction was collected as the desired 3-nitro-3'-
chlorobiphenyl. An infrared heating lamp was very effective
in preventing this solid fraction from clogging the condenser
beyond the steam jacket and the neck of the receiver. The
end of this fraction was indicated by the appearance of a
second solid material (3,3'-dinitrobiphenyl) which did not

melt in the steam jacketed condenser. The distillation was
discontinued at this point. The 3-nitro-3'-chlorobiphenyl
fraction was recrystallized from ethanol to yield 71 g.
(23%) of a white crystalline material, melting at 89° C.
Anal. Calc'd. for $C_{12}H_8O_2NCl$: C, 61.69; H, 3.43; N, 6.00.
Found: C, 61.26; H, 3.56; N, 5.92.

The Ullmann reaction described here was one of several
carried out under varying conditions. This procedure was
found to give the best results, but duplication of these
results was difficult. Apparently the nature of the copper
or copper bronze used has an important bearing on the course
of the reaction. Not only was this found to be the situation
in this investigation, but the same comment was found in the
literature where the Ullmann reaction was discussed. Various
types of commercial copper bronzes as well as freshly preci-
pitated copper were used in this investigation, each of which
gave somewhat different results in terms of the yield ob-
tained. Since no exhaustive investigation of this particular
reaction was made in the course of this research, it is felt
that no statement is justified concerning the relative merits
of the various copper alloys used.

Preparation of 3-Chloro-3'-aminobiphenyl. The reduction was
carried out in a 1 l., three neck, round bottom flask equipped
with a thermometer, dropping funnel, stirrer and air condenser,
and heated with a "Glascol" heating mantel. One hundred and
ten g. (0.47 moles) of 3-chloro-3'-nitrobiphenyl was dissolved
in 300 ml. of glacial acetic acid in this flask. After the

temperature had been raised to 105° C., a solution of 320 g.
(1.41 moles) of stannous chloride dihydrate in 350 ml. of
concentrated hydrochloric acid was added slowly through the
dropping funnel with stirring. The temperature was held at
110° C. and the stirring continued for 1 hour. During this
time, a heavy white precipitate of the stannic chloride-
amine hydrochloride complex separated in the flask. The
flask was then chilled and the complex separated by filtra-
tion on a sintered glass funnel. The solid material was
transferred to a beaker and the complex decomposed by the
addition of a solution of potassium hydroxide. The clear
liquid layers separated, were placed in a separatory funnel,
and extracted with ether. The aqueous layer was removed and
the ether layer washed with water. The ether layer was sepa-
rated and allowed to evaporate slowly. A viscous residue of
crude 3-amino-3'-chlorobiphenyl remained after all the ether
had evaporated. The material was not purified further and
was used directly in the subsequent Sandmeyer reaction. A
small sample of the amine was treated with a solution of
hydrochloric acid and a precipitate of the amine hydrochlo-
ride immediately formed. This was isolated by filtration and
after a single recrystallization from water, gave a white
material which melted with decomposition at about 227° C.
Anal. Calc'd. for $C_{12}H_{11}NCl_2$:   C, 60.02; H, 4.62. Found:
C, 59.89, 60.03; H, 4.83, 4.94.

Preparation of 3-Iodo-3'-chlorobiphenyl. To a 4 l.
beaker containing 500 ml. of concentrated sulfuric acid and
1000 ml. of water was added the crude 3-amino-3'-chlorobiphenyl

with vigorous stirring. The beaker was placed in an ice bath
and the contents of the beaker chilled to 5° C. A solution
of sodium nitrite in water was then added slowly (the temp-
erature maintained at 5 - 10° C.) until a positive test with
potassium iodide starch paper was obtained. The diazotiza-
tion proceeded very slowly due to the insolubility of the
amine sulfate. A solution of 125 g. (0.75 moles) of potas-
sium iodide was added, the ice bath removed and the mixture
allowed to stand overnight. The heavy organic layer which
settled to the bottom of the beaker was separated, dissolved
in ether and washed with sodium thiosulfate solution and
water. After drying over magnesium sulfate, the ether was
removed and the residue distilled at a pressure of 1 mm. A
yellow distillate of crude 3-iodo-3'-chlorobiphenyl was
collected at 160 - 170° C. The crude material was dissolved
in 30 - 60° petroleum ether and passed through a column of
activated alumina. The resulting solution was almost color-
less and after redistillation gave 74 g. (50% yield from
3-chloro-3'-nitrobiphenyl) of 3-iodo-3'-chlorobiphenyl.

Preparation of 3-(3-Chlorophenyl)-Δ^2-cyclohexenone.
Into a dry, nitrogen flushed, 500 ml., two neck, round bottom
flask equipped with a magnetic stirrer, dropping funnel and
reflux condenser, were added 3.5 g. (0.15 moles) of magnesium
and 30 ml. of dry ether. With stirring, the addition of 30 g.
(0.16 moles) of m-chlorobromobenzene in 30 ml. of ether was
started. The reaction proceeded smoothly until all the mag-
nesium was consumed, whence, a solution of 20 g. (0.14 moles)
of monoethyl ether of dihydroresorcinol was added. The

Grignard complex was decomposed with 10% sulfuric acid and the resulting mixture steam distilled until no appreciable amount of organic material appeared in the distillate. The residue was extracted with ether, and the extract washed with sodium bicarbonate solution and water. After drying over anhydrous magnesium sulfate, the solution was distilled at a pressure of 1 mm. and the fraction boiling in the range 130 - 145° C. was collected. The liquid obtained was re-distilled at 0.7 mm. and the 3-(3-chlorophenyl)-Δ^2-cyclo-hexenone collected at 135° C. A yield of 14 g. (48%) was obtained. A middle cut of this distillation was analyzed. Anal. Calc'd. for $C_{12}H_{11}OCl$: C, 55.95; H, 3.91. Found: C, 55.97, 55.92; H, 4.21, 4.31.

Preparation of 3,3''-Dichloro-m-terphenyl. The Grignard complex of 3-chlorophenylmagnesium iodide was prepared from 16.2 g. (0.068 moles) of m-chloroiodobenzene, 1.62 g. (0.067 moles) of magnesium, and 40 ml. of dry ether in the manner just described. To the complex was added 12.3 g. (0.060 moles) of 3-(3-chlorophenyl)-Δ^2-cyclohexenone in 20 ml. of dry ether. This reaction mixture was hydrolyzed, steam distilled, extracted, washed and dried by the same methods described in the previous syntheses. The viscous residue obtained from this treatment was distilled on the Hickman apparatus and three fractions were collected. The second and larger fraction was assumed to be the crude 1,3-di-(3-chloro-phenyl)-1,3-cyclohexadiene and a small sample was analyzed. Anal. Calc'd. for $C_{18}H_{14}Cl_2$: C, 71.77; H, 4.68. Found: C, 71.68; H, 5.16.

This diene was prepared primarily to determine whether a compound of this type could be aromatized by the procedure which had been used previously without the occurrence of dehydrohalogenation or dehalogenation. A mixture of 40 ml. of p-cymene and 0.5 g. of 5% palladium on charcoal catalyst was heated until refluxing occurred and then 1.5 g. of the diene dissolved in a small amount of p-cymene was added drop-wise. During this addition and for a period of 1 hour thereafter, strips of moistened blue litmus paper were held at the top of the air condenser. At no time did the color of the litmus paper change, which might indicate the evolution of hydrogen chloride. At the end of this time, the reaction flask was cooled, benzene added and the hot mixture filtered to remove the catalyst. After volatilizing the solvent from the filtrate, the residue could not be induced to crystallize in common solvents. In an attempt to purify it further, five separate fractions were collected by distillation at reduced pressure onto a cold finger. None of the fractions were crystalline or could be crystallized in ordinary solvents. The fifth fraction was analyzed. Anal. Calc'd. for $C_{18}H_{12}Cl_2$: C, 72.25; H, 4.04. Found: C, 71.77, 71.91; H, 4.51, 4.52.

Preparation of 3-(3-(3'-Chloro)-xenyl)-Δ^2-cyclohexenone. The Grignard reagent of 3-chloro-3'-iodobiphenyl was prepared in the usual manner from 17.9 g. (0.057 moles) of the halide and 1.39 g. (0.057 moles) of magnesium. A few additional turnings of magnesium were later added to insure as complete conversion to the Grignard reagent as possible. A solution

of 8.4 g. (0.060 moles) of monoethyl ether of dihydroresor-
cinol in 20 ml. of dry ether was then added. The reaction
mixture was hydrolyzed with a solution of equal parts of
water and saturated ammonium chloride solution. The result-
ing mixture was extracted with ether, followed by successive
treatments of the ether solution with dilute hydrochloric
acid, dilute sodium hydroxide solution, and water. After
drying over anhydrous magnesium sulfate, the ether was dis-
placed by 60 - 80° petroleum ether. This solution afforded
crystals of the desired ketone on standing in the ice box.
The small yield (ca. 20%) of ketone was recrystallized in
60 - 80° petroleum ether to give a product melting at 80 -
81° C. Anal. Calc'd. for $C_{18}H_{15}OCl$: C, 76.44; H, 5.35.
Found: C, 76.23, 76.41; H, 5.70, 5.62.

A red 2,4-dinitrophenylhydrazone was prepared which
melted at 219 - 220° C. Anal. Calc'd for $C_{24}H_{19}O_4N_4Cl$:
C, 62.27; H, 4.14. Found: C, 62.48, 62.37; H, 4.55, 4.15.

Preparation of 3,3''''-Dichloro-m-quinquephenyl. Using
the type of apparatus previously described, the 3'-chloro-3-
biphenylmagnesium iodide was prepared from 31.4 g. (0.1 moles)
of 3-chloro-3'-iodobiphenyl and 2.5 g. (0.1 moles) of magne-
sium. A solution of 9.79 g. (0.034 moles) of 3-(3-(3'-chloro)
-xenylyl)-Δ^2-cyclohexenone in dry ether was then added to
the Grignard reagent. The reaction mixture was allowed to
stand overnight before hydrolysis with 10% sulfuric acid solu-
tion. The contents of the flask was extracted with ether and
the ether extract washed with dilute sodium hydroxide solution
and with water. After drying over anhydrous magnesium sulfate

and removal of the volatile solvent, the residue was distilled on the Hickman apparatus. An 11.5 g. fraction was collected which was assumed to be the intermediate diene. This material set as a glass. After a few unsuccessful attempts to crystallize this glass, it was decided to dehydrogenate the material without further purification.

The aromatization was accomplished by the dropwise addition of 3.2 g. of the diene dissolved in a small amount of p-cymene to a refluxing mixture of 0.5 g. of 5% palladium on charcoal catalyst and 25 ml. of p-cymene. The reflux was continued for 2 hours and the top of the air condenser continuously checked for the evolution of hydrogen chloride. None could be detected. The p-cymene was removed by distillation and benzene added to the residue. Filtration of the hot mixture removed the catalyst. A viscous glassy material was obtained after removal of the benzene. Again, it could not be induced to crystallize. A small sample of the 3, 3''''-dichloro-m-quinquephenyl was collected by distillation onto a cold finger. Anal. Calc'd. for $C_{30}H_{20}Cl_2$: C, 79.82; H, 4.47. Found: C, 79.87; 79.79; H, 5.23, 5.47.

The remainder of the diene was then aromatized in the same manner and the aromatized product similarly isolated.

Wurtz Reaction of 3,3''''-dichloro-m-quinquephenyl. The solvent used for this reaction was xylene, which was purified by passing through a column of activated alumina, followed by distillation from metallic sodium. Three hundred milliliters of the xylene was placed in a 1 l., 3 neck, round bottom flask equipped with a stirrer, dropping funnel, and

reflux condenser. Clean sodium (5 g.) was added and the mixture heated until the xylene refluxed vigorously. The stirring was then started and raised to maximum speed. Maintaining the stirring and reflux, a solution of all the 3,3''''-dichloro-m-quinquephenyl contained in 250 ml. of xylene was added very slowly. The addition required 6.5 hours. The reflux and stirring were then continued overnight. After cooling to approximately 60° C., the reaction mixture was decanted through a gravity funnel plugged with glass wool. The filtrate on cooling yielded a small amount of solid which was collected on a Buchner funnel. The filtrate was concentrated to approximately 75 ml. and an additional small amount of solid material appeared on cooling. This solid was also collected on a Buchner funnel. The balance of the xylene was then distilled from the filtrate and a viscous glassy residue remained. Ether was added to the residue, whence a third solid fraction appeared. This was removed by filtration. Each of these three solid fractions appeared to be similar. They were infuzable up to 300° C., burned only with difficulty in a Bunsen flame, and were insoluble in ordinary solvents. A small amount was placed in distilled water, heated to boiling without any appearance of dissolving, and filtered. The filtrate after being made slightly acidic gave a light precipitate on the addition of silver nitrate solution. It was assumed that these three solid fractions were mixtures of sodium chloride and polymeric material resulting from an intermolecular Wurtz reaction. The original ether filtrate was heated to expel the volatile solvent. The glassy residue

was then distilled onto a cold finger. Ten fractions were collected. The first three fractions of very viscous material could not be crystallized and were assumed to be the unreacted dihalide. The next three fractions appeared to be somewhat more crystalline and were probably a mixture. The last fractions were crystalline and could be conveniently recrystallized from ethanol. The last fraction after two recrystallizations melted at 109 - 110° C. and gave the analysis: C, 93.07; H, 5.89. From the melting point and analysis, it was assumed that this last material was m-quinquephenyl, which would result from dehalogenation of the dihalide. The presence of traces of water could well account for such a reaction.

There was no indication that any product resulting from a ring closure reaction was present.

<u>Ultraviolet Absorption Spectra</u>. The instrument used in this investigation for the determination of the ultraviolet absorption spectra was a Beckman Model DU Photoelectric Quartz Spectrophotometer. The light source was a hydrogen arc. Rigorously purified cyclohexane was used as the solvent. The purification was accomplished by treatment of approximately 2 l. of commercial cyclohexane (duPont) with four successive 500 g. portions of chlorosulfonic acid. The first two portions were shaken vigorously with the cyclohexane in a 6 l. separatory funnel. The last two portions were stirred in the separatory funnel containing the cyclohexane for a period of three hours each. The cyclohexane was washed with concentrated sulfuric acid, water, and dilute sodium hydroxide solution in that order. While still in the

separatory funnel, the cyclohexane was stirred for four hours with an alkaline potassium permanganate solution, additional potassium permanganate being added every hour. The cyclohexane was then separated, washed with water and steam distilled. The steam distillate was separated and the organic layer dried over calcium chloride. After removal of the desiccant by filtration, the cyclohexane was refluxed for a period of time with metallic sodium and finally distilled from this sodium.

The experimental procedure followed was the standard technique for use of this spectrophotometer.

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