THE SYNTHESIS OF SUBSTITUTED TERPHENYLS

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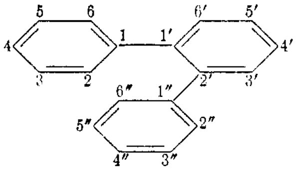
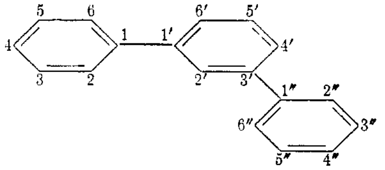
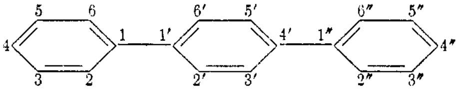
I. INTRODUCTION

Terphenyls are the aromatic hydrocarbons consisting of a chain of three benzene rings. There are three isomers, in which the terminal rings are ortho-, meta-, or para-substituents of the central ring. The conventional (*Chemical Abstracts*) numbering of substituents is shown.

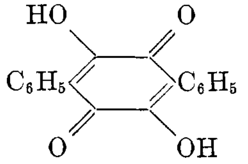




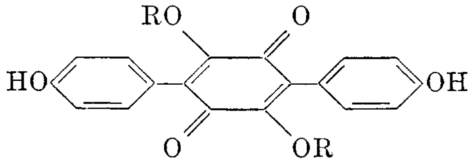


The parent hydrocarbons are commercially available as by-products of the preparation of biphenyl by the pyrolysis of benzene (82). Various procedures have been used: for instance, benzene may be passed through a heated tube (41, 123, 126), heated under pressure (78, 91), or passed over a heated catalyst (3). The individual terphenyls are readily separable by fractionation from the mixture thus obtained.

Very few terphenyl derivatives occur naturally. The known compounds are all hydroxyquinones, which occur as fungal pigments. The simplest, polyporic acid, has the structure I (87), while atromentin (II: R = H) (88, 89) and leucomelone (III) (4) are hydroxy derivatives. Aurantiacin (II: R = C_6H_5CO) (75) is a dibenzoate of atromentin. A more complex derivative of polyporic acid is muscarufin (IV) (90).



I
Polyporic acid



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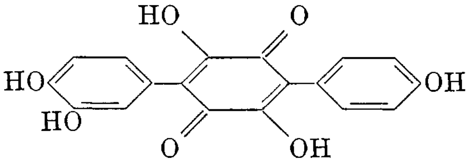
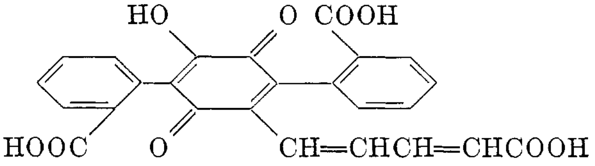


III
Leucomelone



IV
Muscarufin

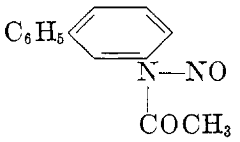
II. GENERAL METHODS FOR THE SYNTHESIS OF SUBSTITUTED TERPHENYLS

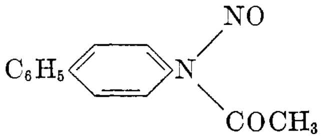
The pyrolysis reaction described above for the parent hydrocarbons cannot normally be applied to substituted terphenyls, as a mixture of products of unknown orientation would be obtained. The general methods by which substituted terphenyls have been obtained can be classified into the following groups: (A) free-radical substitution of an aromatic ring, (B) Ullmann and related reactions, (C) additions to dienes, and (D) condensation reactions of quinones. In addition, many substituted terphenyl compounds have been prepared by methods of more limited scope, and especially by the dehydrogenation of the corresponding cyclohexanes, cyclohexenes, or similar compounds, which can be synthesized by a number of methods.

A. Free-radical substitution of an aromatic ring

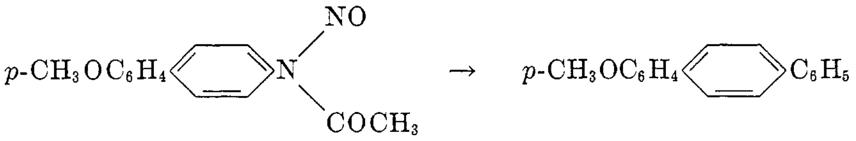
This method consists in the joining of a biphenyl derivative with an aryl compound. It is an extension of the preparation of biphenyl by the reaction of phenyl radicals (for example, from dibenzoyl peroxide) with benzene.

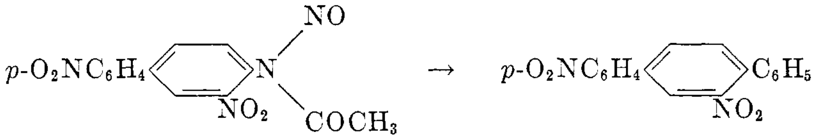
A convenient experimental technique has been developed and used extensively by France, Heilbron, and Hey, in which the free-radical source, an *N*-nitrosoacetanilide, is decomposed in the appropriate aromatic compound as solvent. For example, the becomposition of *N*-nitroso-3-acetylaminobiphenyl (V) or *N*-nitroso-4-acetylaminobiphenyl (VI) in benzene affords *m*-terphenyl (65) or *p*-terphenyl (63) in yields of 63 and 50 per cent, respectively.


V


VI

Substituted terphenyls can be prepared from the appropriate biphenyl compound. Thus, decomposition of 4′-methoxy-*N*-nitroso-4-acetylaminobiphenyl (VII) in benzene gives a 61 per cent yield of 4-methoxy-*p*-terphenyl (VIII) (64). Similarly, 3′,4-dinitro-*p*-terphenyl (X) can be prepared from the dinitro compound (IX) (63).


VII VIII

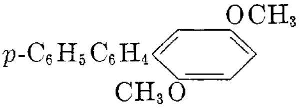

IX X

France, Heilbron, and Hey also prepared 2- and 4-nitro- (63), 4-bromo- (64), and 2- and 4-methyl-*p*-terphenyl (64) by this method.

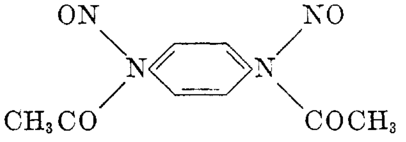
When biphenyl radicals are formed in an aromatic solvent other than benzene, substitution may occur in any of the three possible positions, so that a mixture of isomers is obtained. Thus, *N*-nitroso-4-acetylaminobiphenyl (VI) reacts with chlorobenzene (63) to give 2-, 3-, and 4-chloro-*p*-terphenyl (17, 7, and 11 per cent yields, respectively) and with toluene (64) to give the corresponding methylterphenyls (8, 1, and 9 per cent yields).

In certain cases, however, preferential formation of one or two isomers may occur. For instance, nitrobenzene gives only 4-nitro-*p*-terphenyl (20 per cent yield) (63) and anisole the 2- and 4-methoxy compounds.

With a para-disubstituted benzene, only one isomer is possible; thus the nitrosamide VI reacts with *p*-dimethoxybenzene to give a 15 per cent yield of 2,5-dimethoxy-*p*-terphenyl (XI) (64).


XI

For the synthesis of symmetrically substituted terphenyls, the *N*-acetyl-*N*-nitroso derivative of a phenylenediamine may be used instead of an *N*-acetyl-*N*-nitroso derivative of an aminobiphenyl. In this way, the *N*-acetyl-*N*-nitroso compound XII gives a 59 per cent yield of *p*-terphenyl and an 8 per cent yield of 4,4″-dinitro-*p*-terphenyl (XIII) when treated with benzene or nitrobenzene, respectively (63).

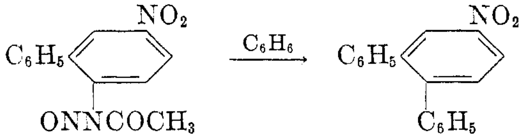


XII

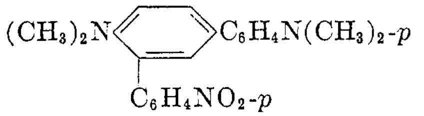
XIII

France, Heilbron, and Hey (66) later reported that *m*-terphenyl could be prepared in 23 per cent yield from the *N*-acetyl-*N*-nitroso derivative of *m*-phenylenediamine.

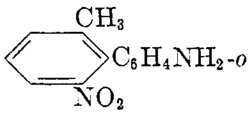
The above method has recently been extended to the synthesis of *o*-terphenyl derivatives by Case (42), who prepared 5′-nitro-*o*-terphenyl in 9 per cent yield from the *N*-acetyl-*N*-nitroso derivative of 2-amino-5-nitrobiphenyl.



Diazonium salts can also be used as the source of aryl radicals. For instance, Allan and Mužík (9) prepared 4,4′-di(dimethylamino)-4″-nitro-*m*-terphenyl (XIV) in 72 per cent yield by the reaction of tetramethylbenzidine with diazotized *p*-nitroaniline.



XIV



XV

Again, DeTar and Howard (48) obtained a 16 per cent yield of 2-methyl-6-nitro-*o*-terphenyl by decomposition of the diazonium salt of the amine XV in benzene.

The patent literature contains a report (140) of the preparation of 3,4-dichloro-*p*-terphenyl via a diazonium salt.

The terphenyls themselves can be obtained by the action of phenyl radicals on biphenyl. Earlier workers reported that phenyl radicals from dibenzoyl peroxide (70, 111) or benzenediazonium chloride (73) reacted with biphenyl to give only *p*-terphenyl; however, Cadogan, Hey, and Williams (40) have now shown that all three isomers are obtained, in approximately 2:1:1 proportions of the ortho, meta, and para isomers, respectively.

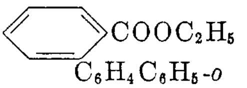
p-Terphenyl is also one of the products of the decomposition of dibenzoyl peroxide in benzene (69) and toluene (according to Dietrich (54)), as well as the reaction between phenylmagnesium bromide, bromobenzene, and cobaltous chloride (86).

There appear to be only two reports of the preparation of a substituted terphenyl by aryl radical substitution of a biphenyl. Grieve and Hey (73) found that diazotized *p*-nitroaniline reacted with biphenyl to give 4-nitro-*p*-terphenyl. Also, Augood, Hey, and Williams (22) obtained a mixture of chloroterphenyls by the decomposition of benzenediazonium chloride in chlorobenzene.

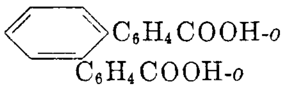
The free-radical substitution of quinones is considered below (page 902).

B. Ullmann and related reactions

The Ullmann reaction which, according to Waters (134), follows a free-radical mechanism, has been used to synthesize terphenyl derivatives. Thus, Sadler and Powell (120) prepared ethyl *o*-terphenyl-2-carboxylate (XVI) from 2-iodobiphenyl and ethyl *o*-bromobenzoate.



XVI

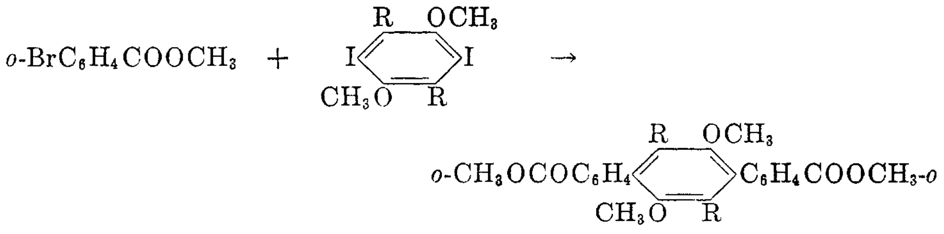


XVII

XVIII

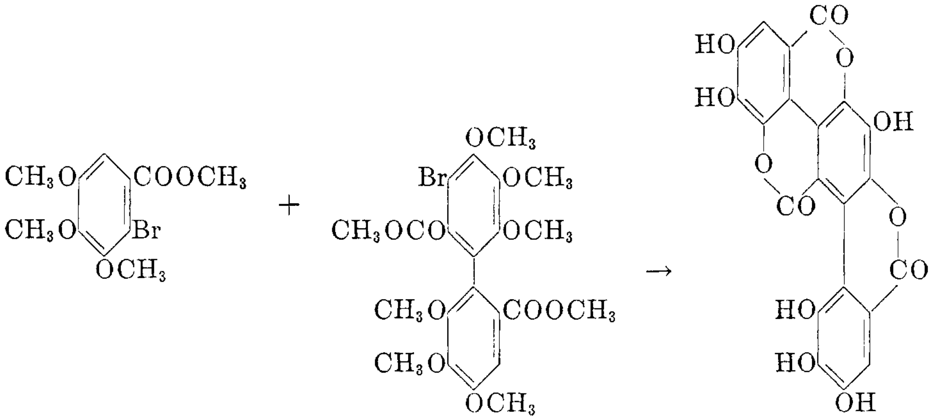
Similarly, Shuttleworth, Rapson, and Stewart (129) obtained an 11 per cent yield of *o*-terphenyl-2,2″-dicarboxylic acid (XVII) by means of an Ullmann reaction between ethyl 2′-iodobiphenyl-2-carboxylate and ethyl *o*-iodobenzoate, followed by hydrolysis. 4-Benzoyl-*o*-terphenyl (XVIII) has been prepared (14) in 15 per cent yield from 2-iodobiphenyl and 4-bromobenzophenone.

Three more applications of the Ullmann reaction to the synthesis of substituted terphenyls have recently been reported. The reaction of methyl *o*-bromobenzoate with 2,5-dimethoxy- and 2,3,5,6-tetramethoxy-1,4-diiodobenzene affords a 48 per cent yield of the ester XIX in which R = H (60) and a 60 per cent yield of the ester XIX in which R = OCH_3 (109).



XIX

Also, flavogallol, which was originally obtained by the action of arsenic acid on gallic acid (28), has been prepared (74) in 24 per cent yield by means of the Ullmann reaction, followed by saponification and demethylation.



Although it is uncertain whether the Wurtz reaction proceeds via an ionic or a radical mechanism (51), it is convenient to consider this method with the Ullmann reaction. There are few examples of the use of this reaction in the preparation of terphenyl compounds. For instance, Riese (119) found that *p*-terphenyl was formed by the action of sodium on a 2:1 mixture of bromobenzene and *p*-dibromobenzene.

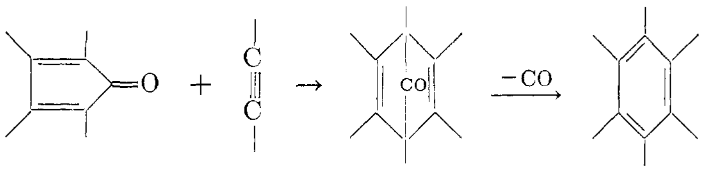
$$2C_6H_5Br + p\text{-}BrC_6H_4Br \rightarrow p\text{-}C_6H_5C_6H_4C_6H_5$$

Similarly, the interaction of sodium, chlorobenzene, *m*-dichlorobenzene, and a small amount of ethyl acetate affords *m*-terphenyl (44). *o*-Terphenyl is obtained by the action of sodium on chlorobenzene (13, 23); benzene, biphenyl, and a small amount of *p*-terphenyl are also produced.

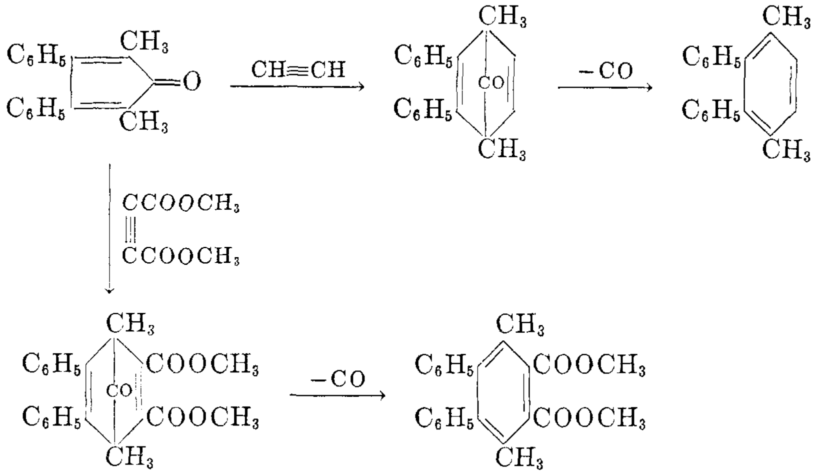
m-Terphenyl (29 per cent yield) is also formed by a related process: namely, the action of phenyllithium on *m*-dichlorobenzene (135). It has been suggested (35) that the product (obtained in 12 per cent yield) from the reaction of phenyllithium with 4,5-dichloroveratrole is 4′,5′-dimethoxy-*o*-terphenyl. (This type of reaction follows an ionic mechanism (33).) Finally, the reaction of *o*-dichlorobenzene with anisylmagnesium bromide yields 4,4″-dimethoxy-*o*-terphenyl (139).

C. Additions to dienes

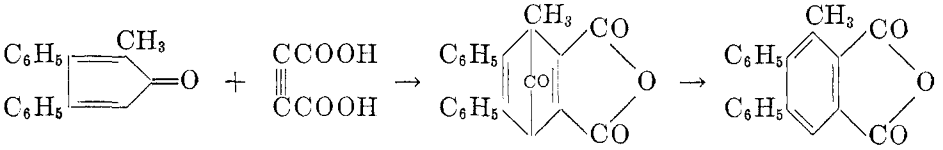
The Diels–Alder reaction, in which a diene is added to an activated double bond, affords tetrahydroaromatic compounds; this approach has been used by a number of workers (see page 911). Similarly, addition of a diene to an acetylene yields a dihydrobenzenoid compound. However, when a cyclopentadienone is added to an acetylene, a carbonyl-bridged ring is formed; the latter loses carbon monoxide on heating, giving an aromatic ring:



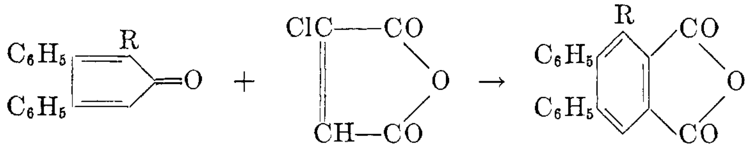
This reaction has been used by Allen and Van Allan (15) to synthesize a number of terphenyl derivatives. For instance, 2,5-dimethyl-3,4-diphenylcyclopentadienone adds to acetylene to give a 51 per cent yield of 3′,6′-dimethyl-*o*-terphenyl, and to dimethyl acetylenedicarboxylate to give a 90 per cent yield of dimethyl 3′,6′-dimethyl-*o*-terphenyl-4′,5′-dicarboxylate.



Again, addition of 2-methyl-3,4-diphenylcyclopentadienone to acetylenedicarboxylic acid affords an *o*-terphenyldicarboxylic acid anhydride (16).

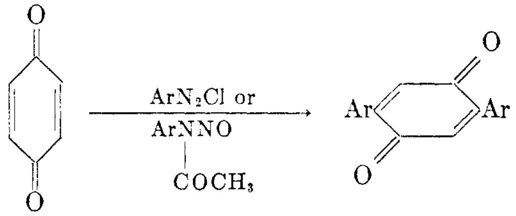


Similar to this is the addition of α-chloromaleic anhydride to a cyclopentadienone (17), in which hydrogen chloride is also eliminated.

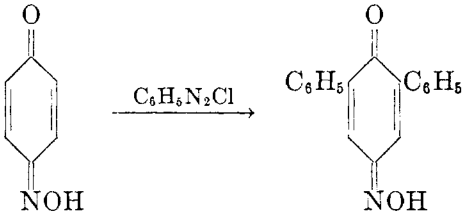


D. Condensation reactions of quinones

Quinonoid and hydroquinonoid terphenyls can be obtained from benzoquinone by substitution or addition reactions. In the substitution reactions benzoquinone is treated with a diazonium salt or with an *N*-nitrosoacetanilide. These reactions have been used by Asano and Kameda (21) and Akagi and Hirose (6), respectively, to prepare 2,5-diarylbenzoquinones:

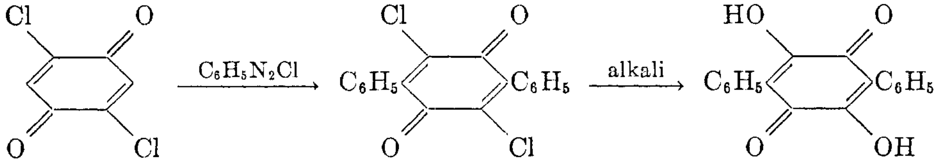


These workers consider that the products obtained are 2,5-diarylbenzoquinones. On the other hand, Borsche (30) assigned structure XX to the product from the reaction of benzoquinone monoöxime and benzenediazonium chloride.



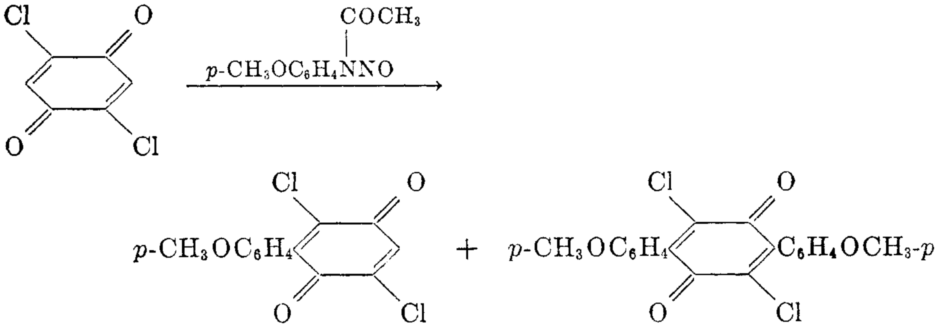
XX

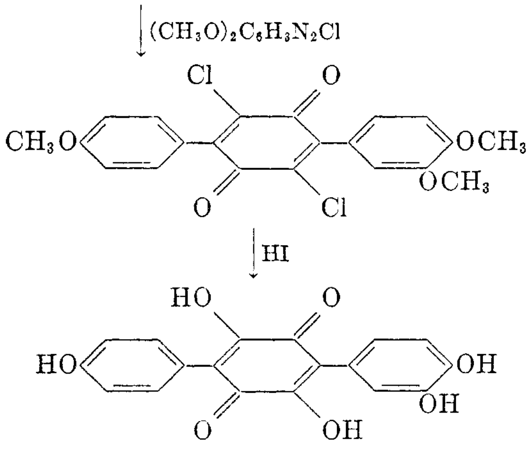
Polyporic acid (I) has been prepared in a two-stage synthesis starting with 2,5-dichlorobenzoquinone (94).



I
Polyporic acid

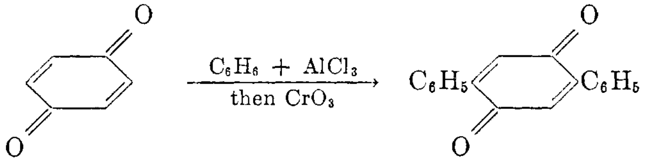
Leucomelone (III) has been prepared (4, 5) similarly.



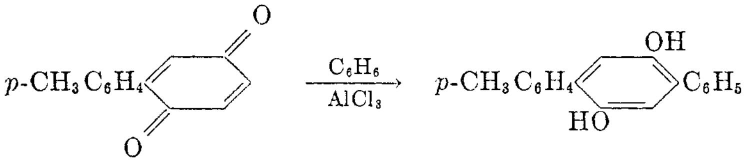


III
Leucomelone

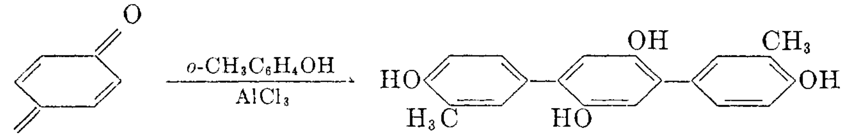
Aluminum chloride catalyzes the addition of the system Ar—H to a quinone. For instance, treatment of benzoquinone with benzene and aluminum chloride, followed by oxidation with chromium trioxide, affords a 72 per cent yield of 2,5-diphenylbenzoquinone (117, 128).



The reaction of benzoquinone with *m*-xylene and mesitylene affords the corresponding tetramethyl- (36) and hexamethyldihydroxy-*p*-terphenyls (127); in each case the yield was 44 per cent. Similarly, 2′,5′-dihydroxy-4-methyl-*p*-terphenyl is obtained from 2-*p*-tolylbenzoquinone (21).

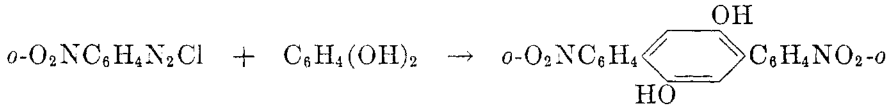


Phenols also undergo aluminum chloride-catalyzed addition to benzoquinone; for example, reaction with *o*-cresol yields the tetrahydroxy compound XXI (116).



XXI

Finally, Dobáš (55) prepared 2′,5′-dihydroxy-2,2″-dinitro-*p*-terphenyl in 16 per cent yield from quinol and the diazonium salt of *o*-nitroaniline.



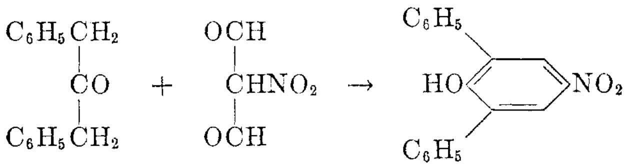
III. OTHER METHODS OF SYNTHESIS

A number of observations mentioned here are of little preparative value, because the terphenyl derivative is formed in poor yield or has not been identified conclusively. For instance, 4,4″-dimethoxy-*p*-terphenyl has been isolated in 0.1 per cent yield from the reaction of anisylmagnesium bromide with 2-chlorocyclopentanone (102). *p*-Terphenyl can be obtained from cinnamaldehyde by successive treatment with thionyl chloride and sodium iodide (124), or by treatment with a zinc–copper couple and distillation (93), as well as by passing benzene over heated potassium (1). Some *o*-terphenyl was found amongst the pyrolysis products of cinnamylidenemalonic acid, $C_6H_5CH{=}CHCH{=}C(COOH)_2$ (13, 56, 57). Treatment of acetophenone with sodium ethoxide and acetone produces 5′-methyl-*m*-terphenyl and other products (68, 130).

Manske and Ledingham (99) treated chlorobenzene with magnesium in the absence of a solvent. Treatment of the organometallic compound with carbon dioxide, followed by esterification, gave a number of products including *p*-terphenyl and an unidentified methyl terphenylcarboxylate. Reaction of the initial product with ethylene oxide also afforded *p*-terphenyl, accompanied by a terphenylethyl alcohol.

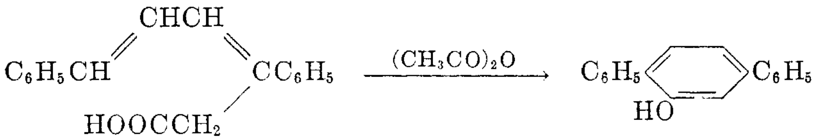
The reaction between chlorobenzene and sodium hydroxide at 300°C. affords a 96 per cent yield of phenol, together with a high-boiling fraction which contains some 2′-hydroxy-*m*-terphenyl (96).

There are comparatively few methods by which a complex substituted terphenyl may be synthesized unambiguously. One such method is that devised by Hill (79, 80), in which a 95 per cent yield of 2′-hydroxy-5′-nitro-*m*-terphenyl is obtained by the condensation of dibenzyl ketone with nitromalondialdehyde.

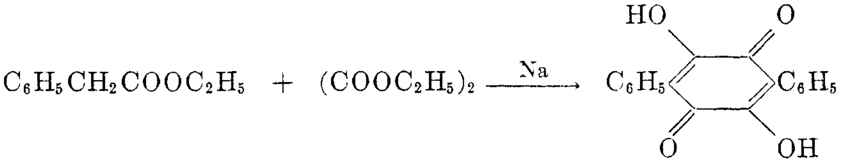


This reaction has been extended to other diaryl acetones (83, 84).

Fichter reported two syntheses of substituted terphenyls in which the central ring is formed in the reaction. Cyclization of 3,6-diphenyl-3,5-hexadienoic acid with acetic anhydride affords 2′-hydroxy-*p*-terphenyl (XXII) (62). Also, polyporic acid (I) can be obtained by the action of sodium on ethyl phenylacetate and diethyl oxalate (61).



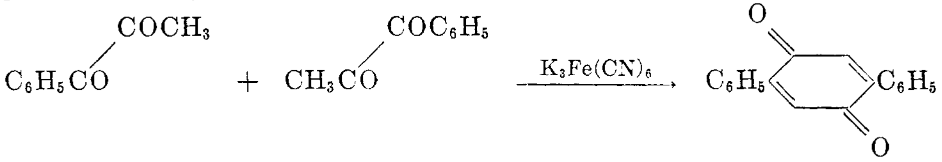
XXII



I

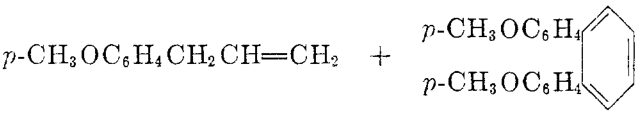
Polyporic acid

2,5-Diphenylbenzoquinone can also be obtained by a reaction in which the central ring is formed: namely, treatment of 1-phenyl-1,2-propanedione with potassium ferricyanide (105).

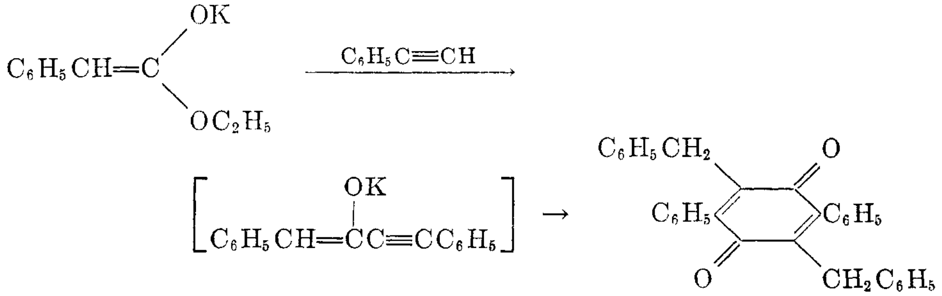


van der Zanden and de Vries (139) found that 4,4″-dimethoxy-*o*-terphenyl is formed as a by-product in the preparation of anisyl-2-propene from anisylmagnesium bromide and allyl bromide. Their confirmatory synthesis of the terphenyl has been described above (page 900).

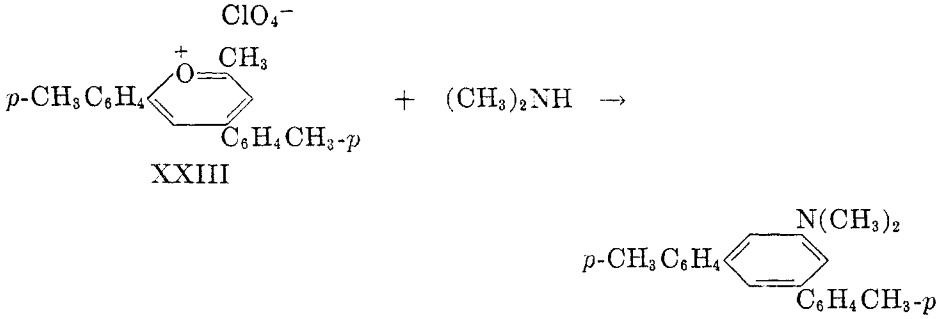
$$p\text{-}CH_3OC_6H_4MgBr + BrCH_2CH{=}CH_2 \rightarrow$$



Cope and Smith (46) isolated *o*-terphenyl (11 per cent yield) and 1,2-diphenylcyclooctatetraene (14 per cent yield) from the reaction of diphenylacetylene with acetylene. Phenylacetylene reacts with iron pentacarbonyl in ethanolamine to give a 22 per cent yield of 2′,5′-dihydroxy-*p*-terphenyl (118), and with the potassium derivative of ethyl phenylacetate to form a 17 per cent yield of a dibenzyldiphenylbenzoquinone (122).

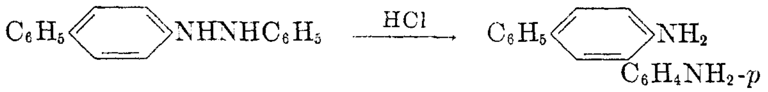


4,4″-Dimethyl-5′-dimethylamino-*m*-terphenyl is formed by the action of dimethylamine on the pyrylium salt XXIII (52).

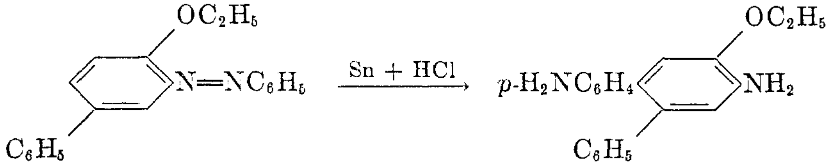


XXIII

In addition to the above preparations in which one of the aromatic rings is formed, there are a number of syntheses in which the rings are joined or reoriented. For example, 4-phenylhydrazobenzene undergoes a Beckmann transformation when treated with hydrochloric acid, yielding 4,6′-diamino-*m*-terphenyl (59).

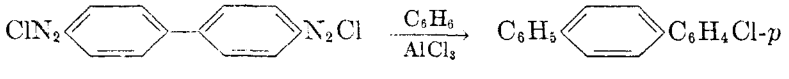


Related to this is the formation of 4,4′-diamino-5′-ethoxy-*o*-terphenyl by the action of tin and hydrochloric acid on 2-ethoxy-5-phenylazobenzene (81).

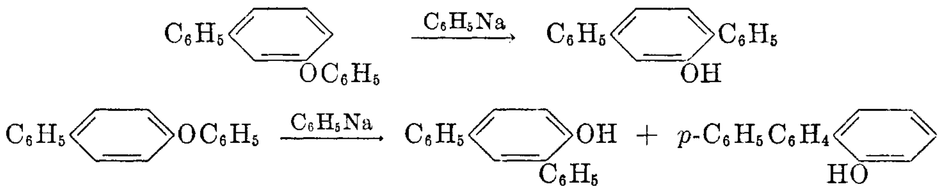


4-Amino-*p*-terphenyl is produced by the action of aluminum chloride on azobenzene and biphenyl (115).

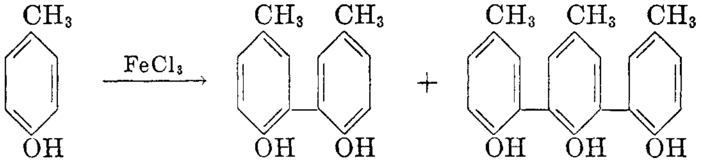
When the tetrazonium salt of benzidine is treated with aluminum chloride and benzene, 4-chloro-*p*-terphenyl is produced (43).



Diaryl ethers undergo rearrangement and substitution when treated with sodium phenyl. One of the products obtained from diphenyl ether is 2′-hydroxy-*m*-terphenyl (10 per cent yield) (97). Other hydroxyterphenyls are formed from 3- and 4-biphenylyl phenyl ether (98).



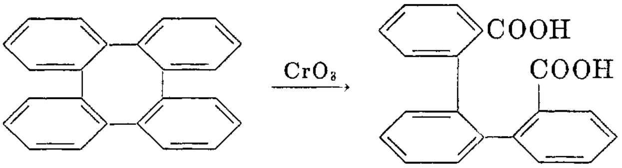
When *p*-cresol is oxidized with ferric chloride, a ring-coupling reaction occurs, 2,2′-dihydroxy-5,5′-dimethylbiphenyl (10 per cent yield) and 2,2′,2″-trihydroxy-5,5′,5″-trimethyl-*m*-terphenyl (6 per cent yield) being produced (31).



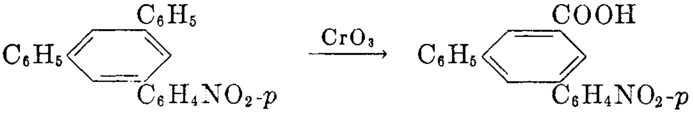
The corresponding triethylterphenyl is obtained in 4 per cent yield by the similar oxidation of *p*-ethylphenol (77).

In 1936 Busch and Weber (38) reported that the catalytic hydrogenation of bromobenzene or *p*-dibromobenzene affords *p*-terphenyl in 1 and 14 per cent yields, respectively; various catalysts were used.

A few substituted terphenyls have been obtained by the degradation of higher polyphenyls. For instance, the oxidation of tetraphenylene with chromic oxide affords *o*-terphenyl-2,2″-dicarboxylic acid (129).



Also, 4-nitro-*m*-terphenyl-5′-carboxylic acid is obtained by similar oxidation of the nitroquaterphenyl (XXIV) (133).



XXIV

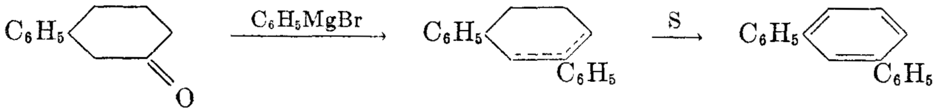
IV. METHODS OF SYNTHESIS BASED ON DEHYDROGENATIONS

These methods can be subdivided according to the method by which the hydrogenated compound was prepared. Four methods have been used to synthesize the terphenyl precursors: use of Grignard reagents, the Friedel–Crafts reaction, the Diels–Alder reaction, and the Michael reaction.

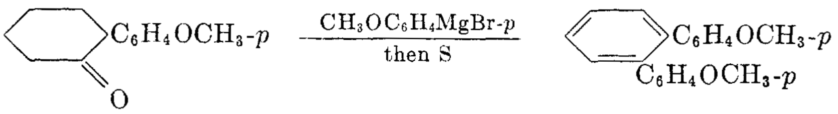
A. Syntheses with Grignard reagents

The reaction of an aryl Grignard reagent with an arylcyclohexanone or alternatively of a biaryl Grignard reagent with a cyclohexanone affords a diarylcyclohexene which can be dehydrogenated to a terphenyl.

The former technique was used by France, Heilbron, and Hey (65) in their synthesis of *m*-terphenyl. 3-Phenylcyclohexanone is treated with phenylmagnesium bromide, and the cyclohexene obtained thereby is dehydrogenated with sulfur.

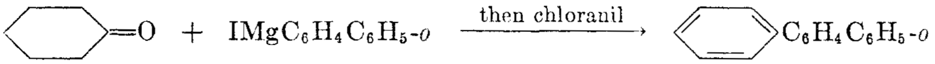


Similarly, anisylmagnesium bromide reacts with 2-anisylcylohexanone to give a cyclohexene which is dehydrogenated by sulfur to give a 15 per cent yield of 4,4″-dimethoxy-*o*-terphenyl (104).

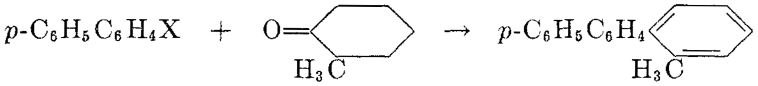


Alternatively, an arylcyclohexenone may be used; thus *m*-terphenyl is obtained by the action of phenylmagnesium bromide on 3-phenylcyclohex-2-enone, followed by dehydrogenation (58).

The second technique, that of reaction of a biaryl Grignard reagent with a cyclohexanone, has been used to prepare *o*-terphenyl (56, 57).



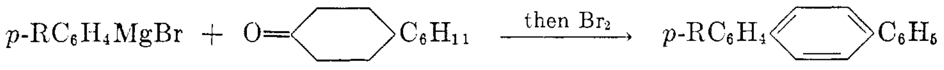
2-Methyl-*p*-terphenyl has been prepared in this way by the treatment of 2-methylcyclohexanone with 4-biphenylylmagnesium bromide (20) or 4-biphenylyllithium (71), followed by dehydrogenation.



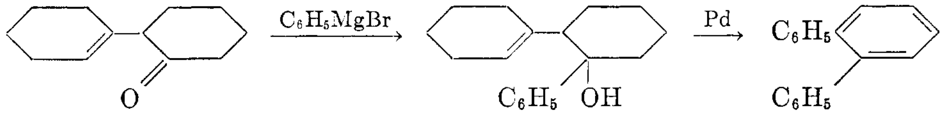
X = MgBr or Li.

3-Methyl-*p*-terphenyl has similarly been synthesized (71).

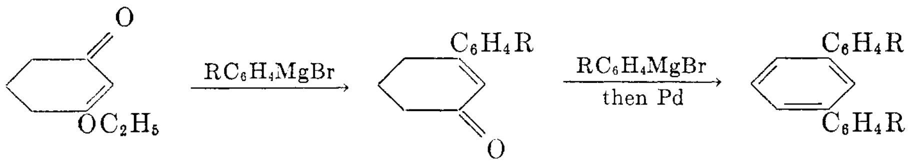
von Braun, Irmisch, and Nelles (35) have reported the synthesis of *p*-terphenyl, and also of 4-methyl-*p*-terphenyl and 4-bromo-*p*-terphenyl, from 4-cyclohexylcyclohexanone and phenylmagnesium bromide, *p*-tolylmagnesium bromide, and the mono-Grignard derivative of *p*-dibromobenzene, respectively. The intermediate compounds were dehydrogenated with bromine.



An attempt (108) to prepare *o*-terphenyl from 2-cyclohexylcyclohexanone afforded only triphenylene; however, it has recently been shown (113) that treatment of 2-cyclohexenylcyclohexanone with phenylmagnesium bromide, followed by dehydrogenation, yields *o*-terphenyl.

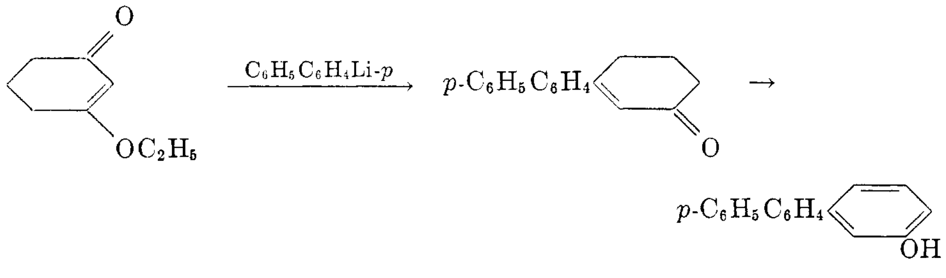


m-Terphenyl derivatives may be synthesized from the enol ether of 1,3-cyclohexanedione; the latter is treated twice with a Grignard reagent, and the resulting cyclohexadiene dehydrogenated. 4,4″-Dimethoxy- (103) and 3,3″-dichloro-*m*-terphenyl (136) have been prepared by this method, the latter in a yield of 15–25 per cent.

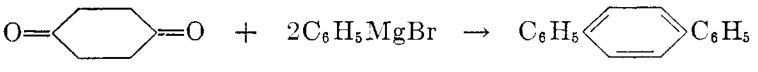


There appears to be no reason why unsymmetrically substituted *m*-terphenyls should not be prepared by this route (by the use of two different Grignard reagents).

The enol ether of 1,3-cyclohexanedione has also been used in a synthesis (137) of 3-hydroxy-*p*-terphenyl from 4-biphenylyllithium.



Analogously, 1,4-cyclohexanedione can be used for the preparation of *p*-terphenyl derivatives, when only two steps are necessary. This is exemplified by the synthesis of *p*-terphenyl by Mayer and Schiffner (100); dehydrogenation of the intermediate cyclohexadiene occurs on distillation.

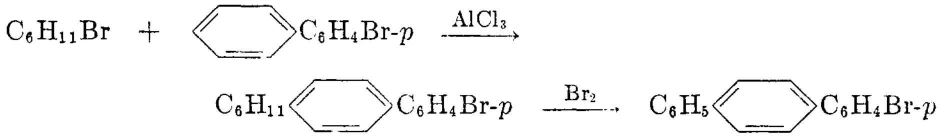


B. Syntheses via the Friedel–Crafts reaction

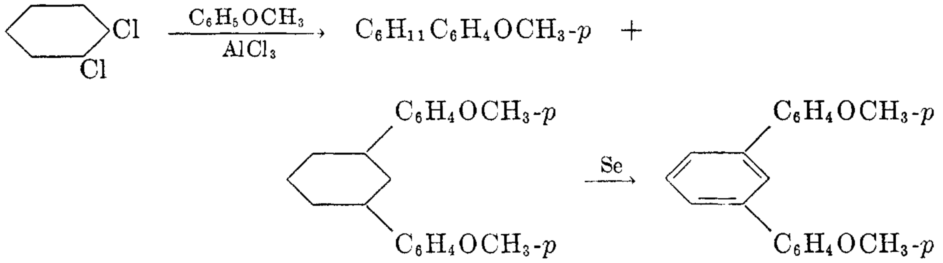
Under Friedel–Crafts conditions, benzene is substituted twice by cyclohexyl bromide. The second substitution occurs wholly para to the first, the sole product being *p*-dicyclohexylbenzene (34). Dehydrogenation of the latter by bromine (34) or selenium (24) affords *p*-terphenyl.

$$C_6H_{11}Br + C_6H_6 \xrightarrow{AlCl_3} C_6H_{11}C_6H_4C_6H_{11}\text{-}p \rightarrow C_6H_5C_6H_4C_6H_5\text{-}p$$

4-Bromo-*p*-terphenyl is obtained when 4-bromo-4′-cyclohexylbiphenyl, obtained by the Friedel-Crafts reaction between cyclohexyl bromide and 4-bromobiphenyl, is dehydrogenated with bromine (25).

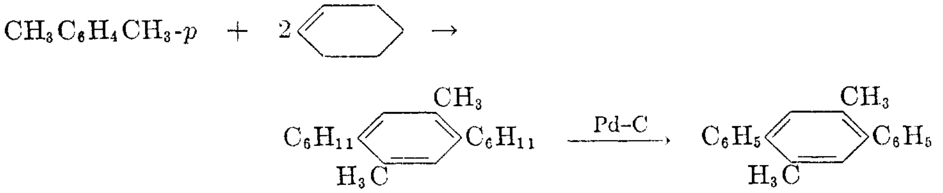


o-Terphenyl derivatives are not formed by the Friedel–Crafts reaction with 1,2-dihalogenocyclohexanes. Thus 1,2-dichloro- and 1,2-dibromocyclohexanes react with benzene and aluminum chloride to give, after dehydrogenation, *m*- and *p*-terphenyl, as well as biphenyl (108). A similar reaction occurs in the case of 1,2-dichlorocyclohexane and anisole (114).



It has been reported (131) that *o*-terphenyl is isomerized to *m*- and *p*-terphenyl by, respectively, brief and prolonged treatment with aluminum chloride.

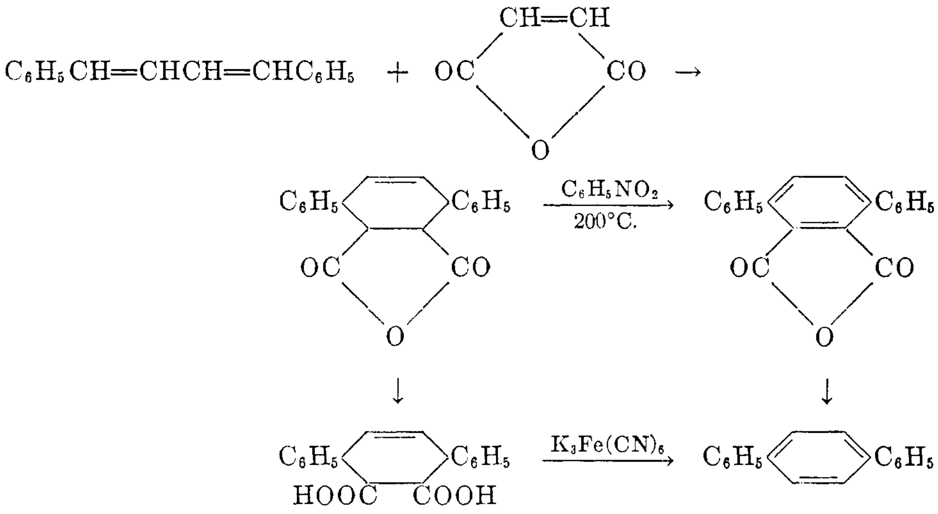
Closely related to the Friedel–Crafts reaction is the aluminum chloride-catalyzed addition of an aromatic compound to a cyclohexene. Examples of this reaction are the formation of 1,2-diphenylcyclohexane from benzene and cyclohexene, and of a mixture of cyclohexylbiphenyls from biphenyl and cyclohexene (29). Also, 2′,5′-dimethyl-*p*-terphenyl has been prepared in 27 per cent yield by the addition of *p*-xylene to 2 moles of cyclohexene followed by dehydrogenation with palladium–charcoal (50).



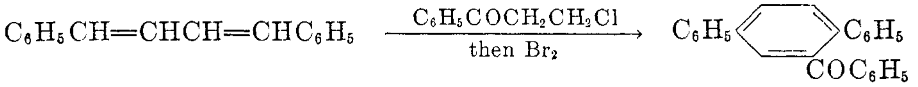
C. Syntheses by the Diels–Alder reaction

The addition of a diarylbutadiene to an activated olefin, followed by dehydrogenation of the resultant diarylcyclohexene, is a convenient method of synthesis of a large number of substituted terphenyls.

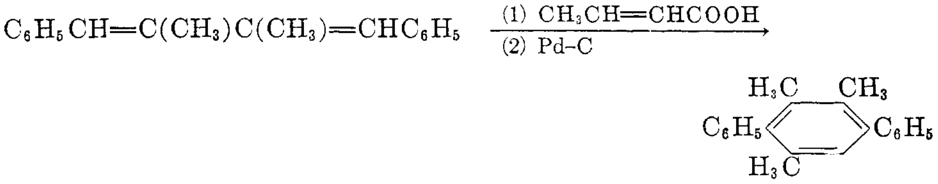
Diels–Alder reactions using 1,4-diphenylbutadiene afford substituted *p*-terphenyls. Thus the addition to maleic anhydride yields 3,6-diphenyltetrahydrophthalic anhydride (53), which may be dehydrogenated by heating in nitrobenzene (26). Oxidation of the tetrahydrophthalic acid with potassium ferricyanide gives *p*-terphenyl (92).



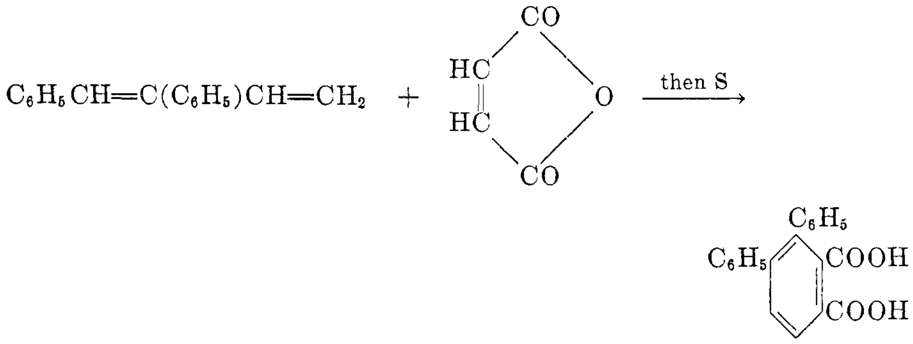
1,4-Diphenylbutadiene also reacts with β-chloropropiophenone; 2′-benzoyl-*p*-terphenyl is obtained on dehydrogenation of the intermediate (10). In effect, this reaction is the addition of the diene to acrylophenone.

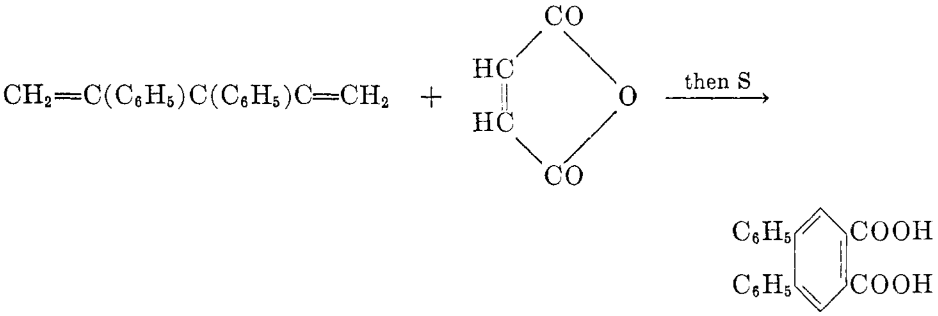


Langer and Wessely (95) have synthesized 2′,3′,5′-trimethyl-*p*-terphenyl in 17–22 per cent yield by the addition of 2,3-dimethyl-1,4-diphenylbutadiene to crotonic acid. The carboxyl group is lost on dehydrogenation.



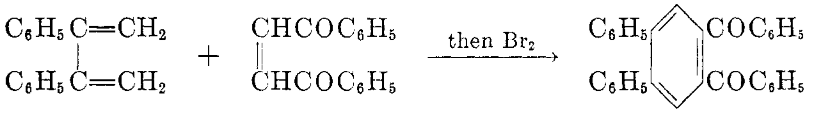
o-Terphenyl derivatives may be prepared from 1,2- and 2,3-diphenylbutadienes. The addition of maleic anhydride to these dienes yields *o*-terphenyl-3′,4′-dicarboxylic acid (8) and *o*-terphenyl-4′,5′-dicarboxylic acid (7), respectively.





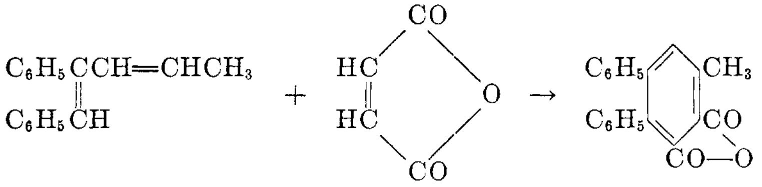
Similarly, the additions with crotonic acid afford *o*-terphenyl-3′-carboxylic acid (8) and *o*-terphenyl-4′-carboxylic acid (7).

In the patent literature there is reported (2) the addition of 2,3-diphenyl-1,3-butadiene to 1,2-dibenzoylethylene; 4′,5′-dibenzoyl-*o*-terphenyl is produced.

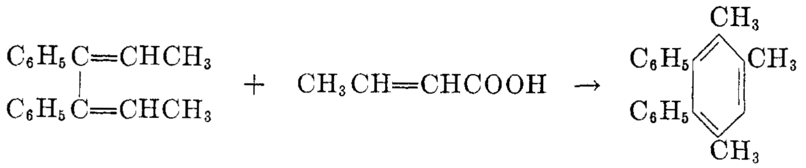


2,3-Diphenylbutadiene also reacts with β-chloropropiophenone in a manner exactly analogous to 1,4-diphenyl-1,3-butadiene (10) (page 911); in this case, 4′-benzoyl-*o*-terphenyl is obtained in 48 per cent yield.

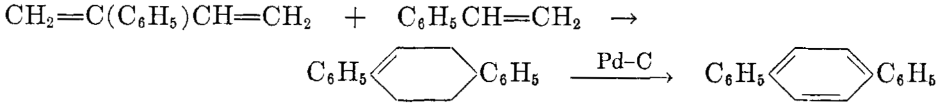
1,2-Diphenyl-1,3-pentadiene reacts with maleic anhydride in the usual way (27); if the reaction is carried out in nitrobenzene at 200°C., dehydrogenation occurs spontaneously.



Addition of 3,4-diphenyl-2,4-hexadiene to crotonic acid, followed by dehydrogenation with palladium–charcoal, affords 3′,4′,6′-trimethyl-*o*-terphenyl in 77–81 per cent yield (95).

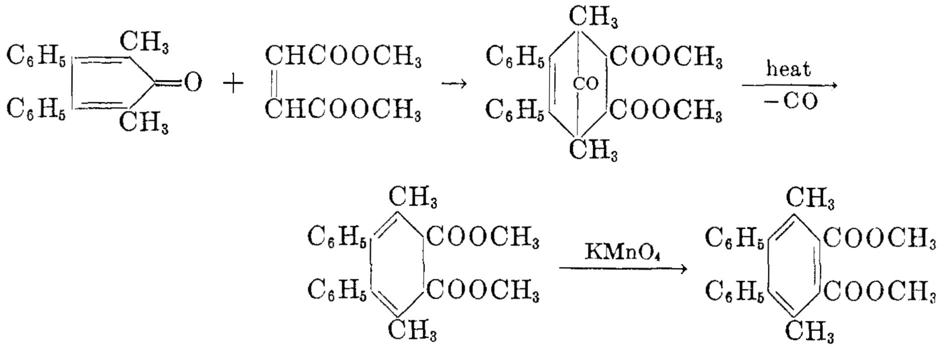


The double bond in styrene is sufficiently activated to participate in the Diels–Alder reaction. Thus 2-phenylbutadiene and styrene react to form a 30 per cent yield of a diphenylcyclohexene (7); the addition is apparently monodirectional, the only product being the para isomer, which is dehydrogenated to *p*-terphenyl.

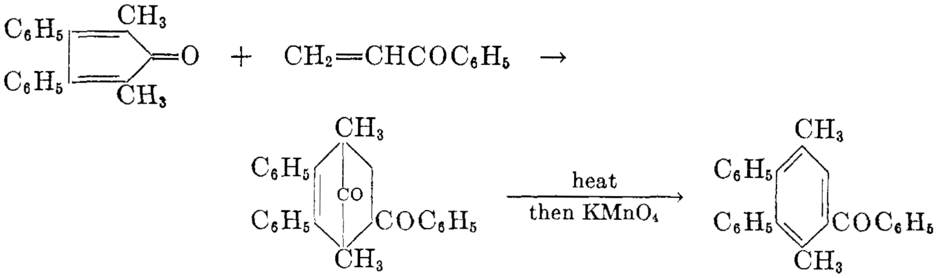


The addition of cyclopentadienones to acetylenic compounds has been discussed above (page 900). Cyclopentadienones also add to activated olefins, giving bridged-ring carbonyl compounds, pyrolysis of which yields cyclohexadienes. The latter are readily oxidizable to aromatic compounds.

Allen and Van Allan (15) have reported a number of addition reactions of 2,5-dimethyl-3,4-diphenylcyclopentadienone with activated olefins, such as dimethyl maleate:



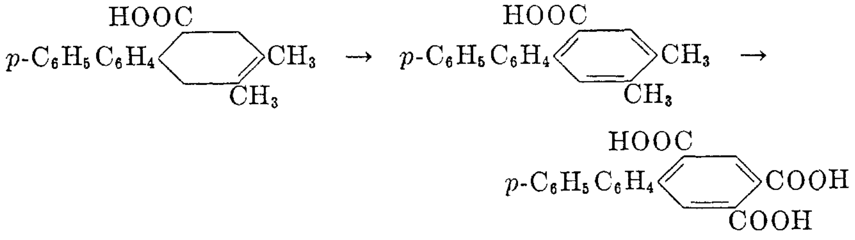
and acrylophenone:



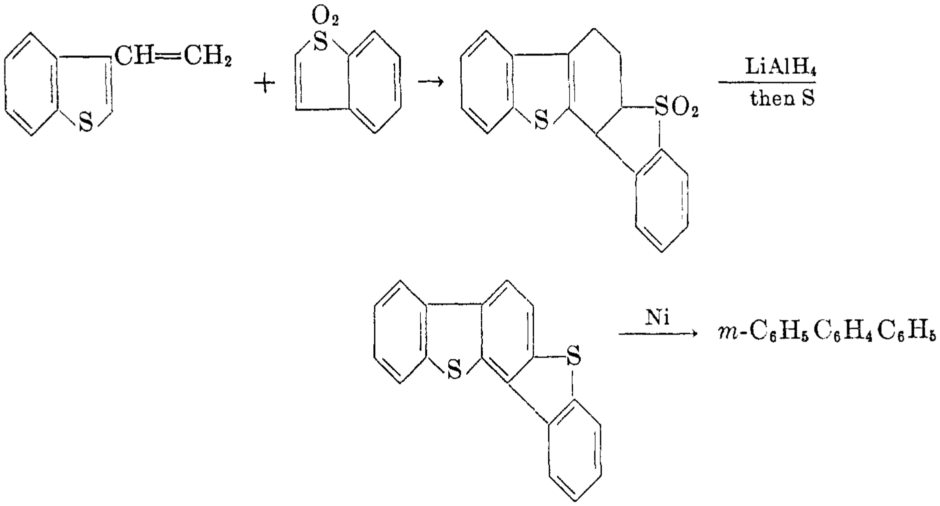
The additions to methyl acrylate and maleic anhydride were also carried out.

In the patent literature there is described (125) the synthesis of *p*-terphenyl-2,4,5-tricarboxylic acid by means of the Diels–Alder reaction.

$$p\text{-}C_6H_5C_6H_4CH{=}CHCOOH + CH_2{=}C(CH_3)C(CH_3){=}CH_2 \rightarrow$$



Finally, the synthesis of *m*-terphenyl has recently been reported (47) by means of a reaction of the Diels–Alder type.

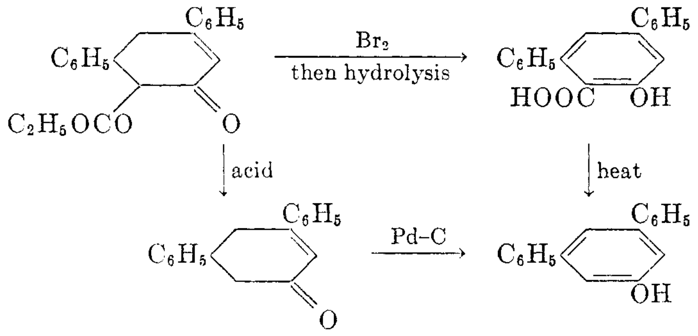


D. Syntheses by the Michael reaction

Until recently, the only applications of the Michael reaction to the preparation of substituted terphenyls have been the syntheses of various *m*-terphenyl derivatives from, initially, chalcones. Addition of β-keto esters to the latter gives carbethoxycyclohexenones.

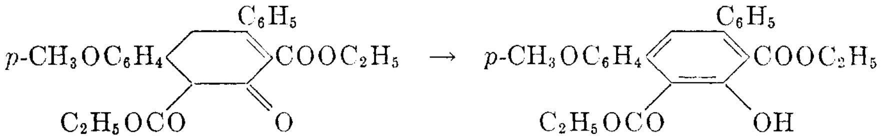
The adduct from chalcone and ethyl acetoacetate can be dehydrogenated by treatment with bromine (85). The diphenylsalicylic acid thus obtained is decarboxylated by heating to 5′-hydroxy-*m*-terphenyl, which had previously been obtained (112) from the same carbethoxycyclohexenone by hydrolysis and dehydrogenation.

$$\underset{\text{Chalcone}}{C_6H_5CH{=}CHCOC_6H_5} + CH_3COCH_2COOC_2H_5 \xrightarrow{C_2H_5ONa}$$

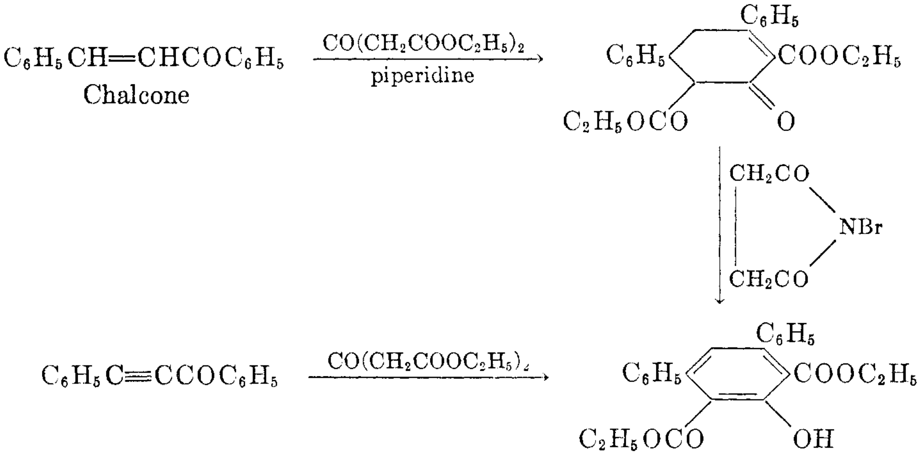


The addition of diethyl β-oxoglutarate to chalcones has also been used as a route to substituted *m*-terphenyls. For instance, the addition to 4-methoxychalcone affords a dihydroaromatic ester, which is oxidized to the corresponding terphenyl by successive treatment with *N*-bromosuccinimide and pyridine; a 28 per cent yield was obtained (76).

$p\text{-}CH_3OC_6H_4CH{=}CHCOC_6H_5 + C_2H_5OCOCH_2COCH_2COOC_2H_5 \rightarrow$



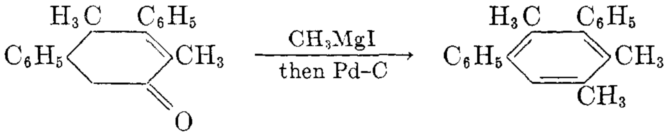
The adduct obtained from chalcone and diethyl β-oxoglutarate can be dehydrogenated by *N*-bromosuccinimide to diethyl 5′-hydroxy-*m*-terphenyl-4′,6′-dicarboxylate (XXV) (49). The ester XXV was also prepared directly, in 38 per cent yield, by the reaction of diethyl β-oxoglutarate with 1,3-diphenyl-1-propyn-3-one.



XXV

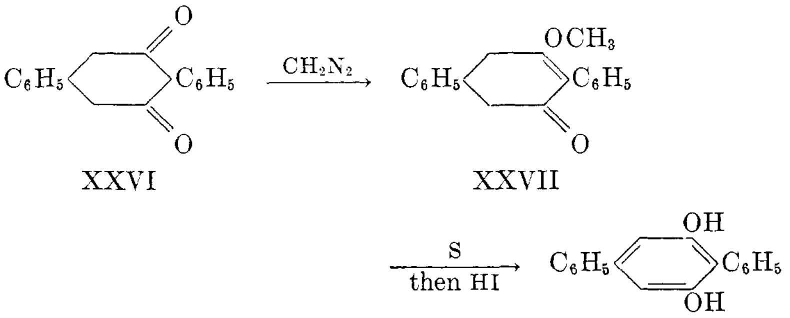
2′,4′,5′-Trimethyl-*m*-terphenyl has been prepared (95) in 15 per cent yield by the addition of ethyl β-oxopentanoate to dypnone, followed by treatment with methylmagnesium iodide and dehydrogenation.

$$\underset{\text{Dypnone}}{C_6H_5CH{=}C(CH_3)COC_6H_5} + CH_3CH_2COCH_2COOC_2H_5 \rightarrow$$

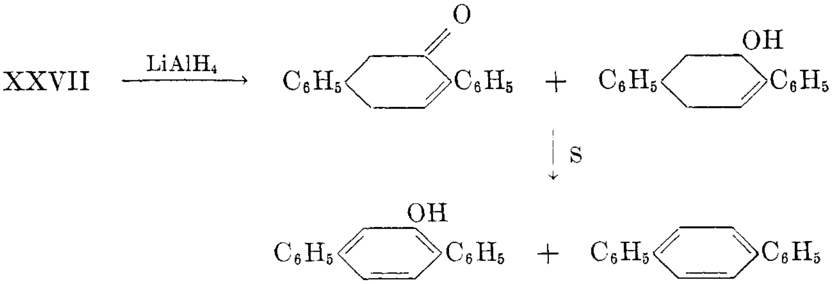


Recently, there has been reported (18) the synthesis of a number of derivatives of *p*-terphenyl from 2,5-diphenyl-1,3-cyclohexanedione (XXVI), prepared by the addition of diethyl malonate to 1,4-diphenyl-1-buten-3-one. Dehydrogenation of the enol ether (XXVII) obtained from XXVI gave, on demethylation, a 34 per cent yield of 2′,6′-dihydroxy-*p*-terphenyl.

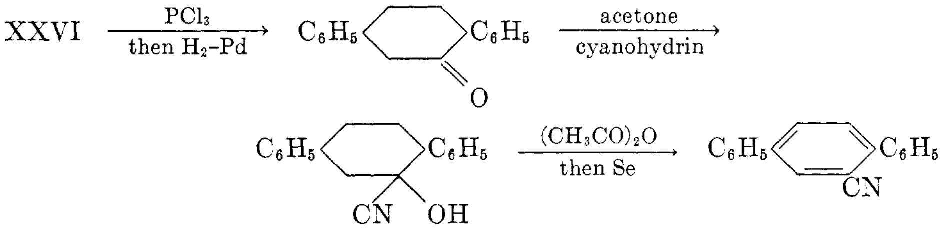
$$C_6H_5CH{=}CHCOCH_2C_6H_5 + CH_2(COOC_2H_5)_2 \xrightarrow{\text{then } Na_2CO_3}$$


XXVI
XXVII

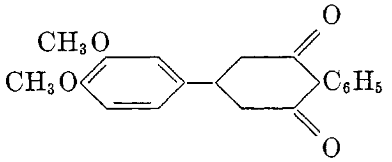
The enol ether (XXVII) was reduced with lithium aluminum hydride and the product, mainly the corresponding cyclohexenone, was dehydrogenated with sulfur to give a 45 per cent yield of 2′-hydroxy-*p*-terphenyl and a 23 per cent yield of *p*-terphenyl.

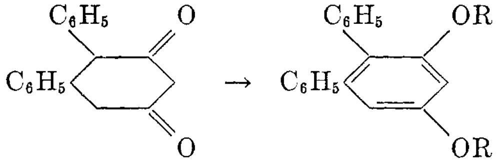


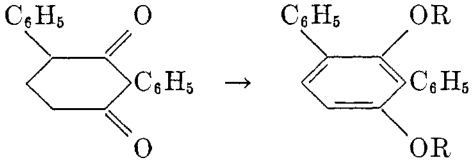
Also 2,5-diphenylcyclohexanone, obtained from XXVI by treatment with phosphorus trichloride and hydrogenation, was converted, via the cyanohydrin, to 2′-cyano-*p*-terphenyl.

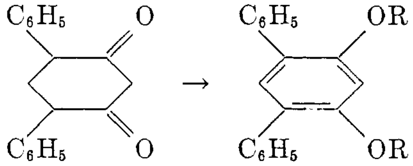


Using these methods, 3,4,3′-trimethoxy-*p*-terphenyl and 3,4,3′,5′-tetramethoxy-*p*-terphenyl have been prepared from the dione XXVIII; also the diphenyl-1,3-cyclohexanediones (XXIX, XXX, and XXXI) have been converted into the corresponding hydroxy and methoxy compounds of the *o*- and *m*-terphenyl series (19).


XXVIII


XXIX


XXX


XXXI

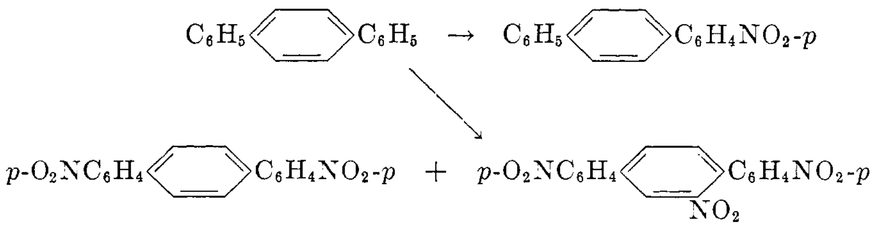
R = H or CH_3.

V. SYNTHESES FROM OTHER TERPHENYLS

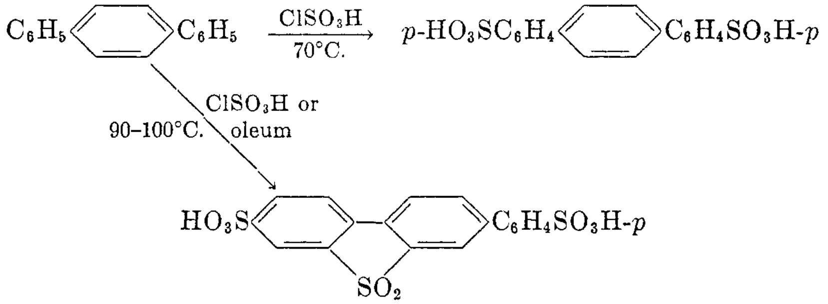
Many substituted terphenyls can be prepared by substitution reactions of the terphenyls, as well as by interconversions using general transformation methods.

A. Substitution reactions of p-terphenyl

Electrophilic substitution of *p*-terphenyl occurs in the 4-position. Thus 4-monosubstituted and 4,4″-disubstituted *p*-terphenyls are produced, according to the conditions. Nitration with fuming nitric acid in acetic acid at 100°C., using moderately small amounts of nitric acid (less than 1 ml. per gram), gives a 72 per cent yield of 4-nitro-*p*-terphenyl (12); with a large excess of nitric acid (6 ml. per gram), a 43 per cent yield of 4,4″-dinitro-*p*-terphenyl and a 28 per cent yield of 4,2′,4″-trinitro-*p*-terphenyl are produced (63).



Treatment of *p*-terphenyl with chlorosulfonic acid at 70°C. affords the 4,4″-disulfonic acid (138), whereas with chlorosulfonic acid or oleum at 90–100°C., a sulfone is produced (132).

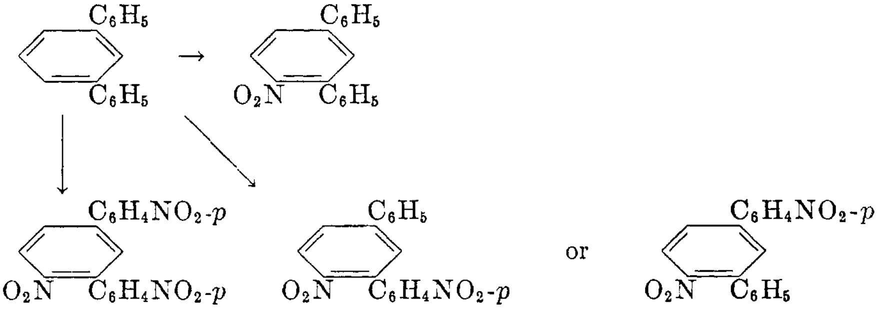


Bromination of *p*-terphenyl gives the 4-bromo and 4,4″-dibromo compounds (35, 63, 110). It has been shown (106, 107) that in the Friedel–Crafts reaction only 4,4″-diacyl derivatives are obtained.

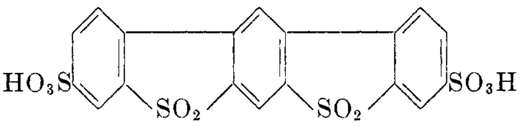
In 1883 Merz and Weith (101) reported that the reaction of *p*-terphenyl with antimony pentachloride gives a perchloro-*p*-terphenyl, $C_{18}Cl_{14}$.

B. Substitution reactions of m-terphenyl

The nitration of this hydrocarbon has been studied by France, Heilbron, and Hey (65). Reaction at 90°C. with concentrated nitric acid in acetic acid and with nitric acid alone gives a 75 per cent yield of 4′-nitro-*m*-terphenyl and a 14 per cent yield of a dinitro-*m*-terphenyl, respectively. Treatment with fuming nitric acid at 100°C. gives a trinitro compound in 64 per cent yield. France, Heilbron, and Hey consider that the dinitro compound is either the 4,4′- or the 4,6′-isomer, and that the trinitro compound is 4,4′,4″-trinitro-*m*-terphenyl.



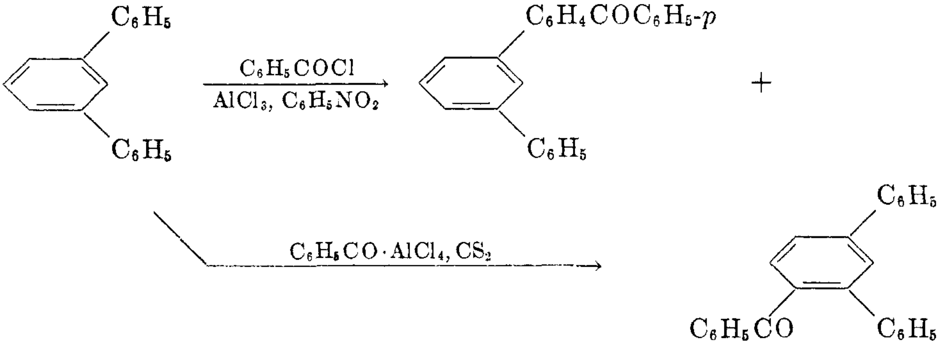
When *m*-terphenyl is treated with sulfuric acid at 100°C., the 4,4″-disulfonic acid is produced (138), while with chlorosulfonic acid or oleum at the same temperature, further substitution occurs, to give a 53 per cent yield of the sulfone (XXXII) (132).



XXXII

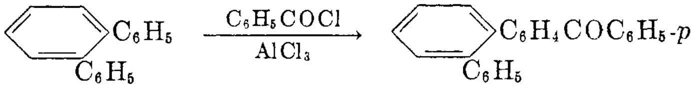
Cook and Cook (148) found that chlorine and bromine react with *m*-terphenyl at the 4′-position; the bromination had been studied earlier (67, 110, 130), when a tetrabromo derivative, probably 3,4,6′,4″-tetrabromo-*m*-terphenyl, was also isolated. Bradsher and Swerlick (32) also prepared 4′-bromo-*m*-terphenyl and reported that it was contaminated with an isomer.

It has been reported (39, 72) that Friedel–Crafts reaction with a number of acyl and aroyl halides gives the corresponding 4-substituted *m*-terphenyls; in one case there was also isolated a diacyl derivative, for which the 4,4″-structure was suggested (72). However, in the case of benzoylation, reaction of *m*-terphenyl with benzoyl chloride and aluminum chloride in nitrobenzene gives a mixture of 4- and 4′-benzoyl-*m*-terphenyls, but if *m*-terphenyl is added to the preformed complex of benzoyl chloride and aluminum chloride in carbon disulfide, only 4′-benzoyl-*m*-terphenyl is produced (32).

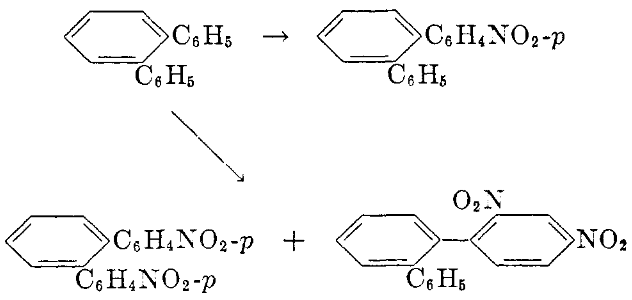


C. *Substitution reactions of o-terphenyl*

The substitution reactions of *o*-terphenyl have been studied by Allen and Pingert (14). Friedel–Crafts reactions give 4-acyl derivatives.



Nitration of *o*-terphenyl with fuming nitric acid in acetic acid at 55–60°C. (12) or with nitric acid in acetic anhydride at 0°C. (14) leads to 4-nitro-*o*-terphenyl. Reaction with fuming nitric acid in acetic anhydride at room temperature yields the 2,4- and 4,4″-dinitro compounds (14).



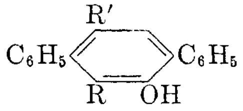
A number of polysubstituted bromo compounds are obtained by the action of bromine on *o*-terphenyl (14); they are 4,4″-dibromo-, 4,4′,4″-tribromo-, and 4,4′,5′,4″-tetrabromo-*o*-terphenyl. A tetrabromotriphenylene is also produced.

With concentrated sulfuric acid, *o*-terphenyl yields the 4-, 4,4″-di-, and 4,4′,4″-trisulfonic acids (11).

D. Further substitution of terphenyl derivatives

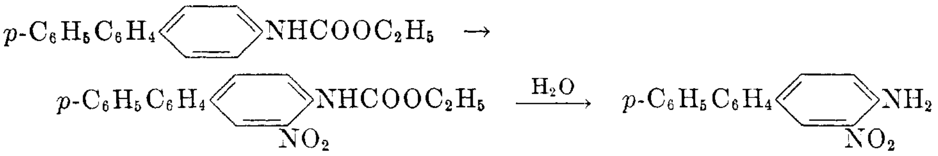
As expected, nitration of mononitroterphenyls gives the same polynitro compounds obtained by more vigorous nitration of the parent hydrocarbon. Thus nitration of 4-nitro-*p*-terphenyl gives the 4,4″-dinitro compound, further nitration of which gives 4,2′,4″-trinitro-*p*-terphenyl (63).

Few examples of the synthesis, by direct substitution, of terphenyls containing two different substituents are recorded in the literature. Nitration of 2′-hydroxy-*p*-terphenyl (XXII) gives the 3′,5′-dinitrophenol XXIIa, while treatment with one mole of bromine gives XXIIb (95).

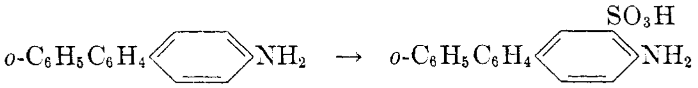


XXII: R = H, R′ = H
XXIIa: R = NO_2, R′ = NO_2
XXIIb: R = H, R′ = Br

Nitration of 4-ethoxycarbonylamino-*p*-terphenyl gives the 3-nitro compound (121), which is hydrolyzed to 4-amino-3-nitro-*p*-terphenyl; the overall yield is 67 per cent.



Finally, sulfonation of 4-amino-*o*-terphenyl gives a 78 per cent yield of the 3-sulfonic acid (11).



Electrophilic substitution in the terphenyl series, therefore, occurs in positions para to one of the other rings, i.e., in the 4-position in *o*-terphenyl and *p*-terphenyl and in the 4′-position in *m*-terphenyl. This is exactly analogous to the corresponding reactions of biphenyl.

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