to precipitate crude dimethyldiphenyladipic acid. The crude product was washed with 200 cc. of hot benzene to remove polymeric acids, and with a large volume of hot water to remove inorganic salts.

After vacuum drying, the washed 2,5-dimethyl-2,5-diphenyladipic acid had a neutral equivalent of 164.5 (theory 163); m.p. 190–214°; yield, 41 g. (50%). This product was largely the low melting (presumably *dl*) isomer. Recrystallization from 550 cc. of acetonitrile yielded 35 g. of the pure acid, m.p. 216–217°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.59; H, 6.79. Found: C, 73.52; H, 7.04.

Accumulation and reworking of several filtrates gave a very small fraction (2–5%) of the product as the *meso* isomer, m.p. 247–449° from methanol.

Anal. Found: C, 73.27; H, 6.97.

The almost complete absence of the *meso* form indicates an interesting stereospecificity of the dimerization step. In the case of diphenyladipic from styrene and of divinyladipic from butadiene, the *dl* product also predominates.

A portion of the disodiodiphenylhexane also was hydrolyzed to give an 88% yield of 2,5-diphenylhexane, b.p. 148–151°/5 mm.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.81; H, 9.34.

2,5-Dimethyl-2,5-dicyclohexyladipic acid. Hydrogenation of racemic dimethyldiphenyladipic acid was carried out in acetic acid solution using palladium-on-carbon catalyst as in the preparation of dicyclohexyladipic acid. The product was recrystallized from methanol to yield pure racemic 2,5-dimethyl-2,5-dicyclohexyladipic acid, m.p. 223–224°.

Anal. Calcd. for $C_{20}H_{32}O_4$: C, 70.96; H, 10.12. Found: C, 70.82; H, 9.89.

Derivatives of diphenyladipic acid. Di-n-butyl-2,5-diphenyladipate. One equivalent (149.6 g.) of 2,5-diphenyladipic acid (m.p. 206–235°), 92.7 g. (1.25 moles) of *n*-butyl alcohol, 0.7 g. of *p*-toluenesulfonic acid and 1.0 g. of Nuchar-CA were refluxed under nitrogen, water produced being collected in a Dean-Starke trap. The reaction was essentially complete in 3.7 hr., final reflux temperature being 142°. The mixture was stirred with 2.0 g. of sodium carbonate and 10 g. of Cellite for 15 min. and filtered. Excess alcohol was removed under reduced pressure and the product finally distilled at 194–196°/0.2 mm.; yield, 181 g. (88%). The diester slowly became a semi-solid at room temperature.

Anal. Calcd. for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35. Found: C, 75.92; H, 8.30.

Hexachlorodiphenyladipic acid. A suspension of 150 g. of diphenyladipic acid (mixed isomers) and 12.8 g. of iodine in 1500 ml. of chloroform was heated to reflux and treated with a rapid stream of chlorine for a period of 5 hr., in the absence of any light. The reaction mixture was filtered to remove any unchanged diphenyladipic acid, and the solvent and catalyst removed by distillation under reduced pressure. The product on cooling to room temperature was an amorphous, glass-like material melting over a broad range beginning at 58°.

Anal. Calcd. for $C_{18}H_{12}O_4Cl_6$: Cl, 42.2%. Found: Cl, 41.4%.

The following observations indicate the product is largely 2,5-dichloro-2,5-bis(3,4-dichlorophenyl)adipic acid: Two of the chlorine atoms in the product were readily removed by refluxing with 10% aqueous caustic, the remaining four chlorines being unaffected. Oxidation of the hexachloro acid with alkaline permanganate yielded 3,4-dichlorobenzoic acid, m.p. 202–204°.

2,5-Diphenylcyclopentanone.[10] A mixture of 233 g. of diphenyladipic acid and 8 g. of finely powdered barium hydroxide was heated under a stream of nitrogen, at 300–320°, until carbon dioxide ceased to be evolved (about 2 hr.). The crude reaction mixture was crystallized first from methanol, then from ethanol to yield 101 g. of product melting at 90.5–91°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.20; H, 6.78. The filtrate contained 54 g. of an oily product which was not identified.

2,5-Dicyclohexylcyclopentanone. A mixture of 28 g. of 2,5-dicyclohexyladipic acid and 0.1 g. of barium hydroxide was heated at 310–320° for 5 hr., at which time evolution of carbon dioxide ceased. The reaction product was cooled, dissolved in diethyl ether and filtered. The solvent was then evaporated leaving a residue of 20.4 g. (91.5% yield) of almost pure *meso* and racemic ketone. This is a new compound. The higher melting form was separated and purified by crystallization from methanol; m.p. 94–95°.

Anal. Calcd. for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 81.88; H, 11.60.

The original methanolic filtrate yielded a residue which on recrystallization from hexane melted at 41–46°.

Anal. Found: C, 82.35; H, 11.17.

CINCINNATI 37, OHIO

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(10) P. Ruggli and J. Schmidlin, *Helv. Chim. Acta*, **29**, 396 (1946).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

Doubly-Branched Polyphenyls

G. FORREST WOODS, J. E. SWENARTON, AND R. B. ISAACSON

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The synthesis of some doubly-branched polyphenyls, including 1,2,3,5-tetraphenylbenzene, is reported. Melting points and ultraviolet absorption data are tabulated.

The earlier papers[1,2] in this series have dealt with the synthesis, properties, and a mode of nomenclature of linear and singly-branched polyphenyls. It was desired to extend this study into the synthesis and determination of some physical properties of some doubly-branched polyphenyls.

One method that was employed for the synthesis of doubly-branched polyphenyls started with the monomethyl ether of 2,5-diphenyldihydroresorcinol.[3]

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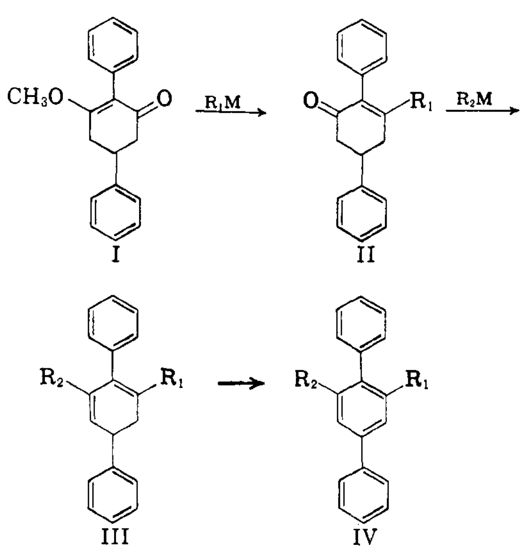
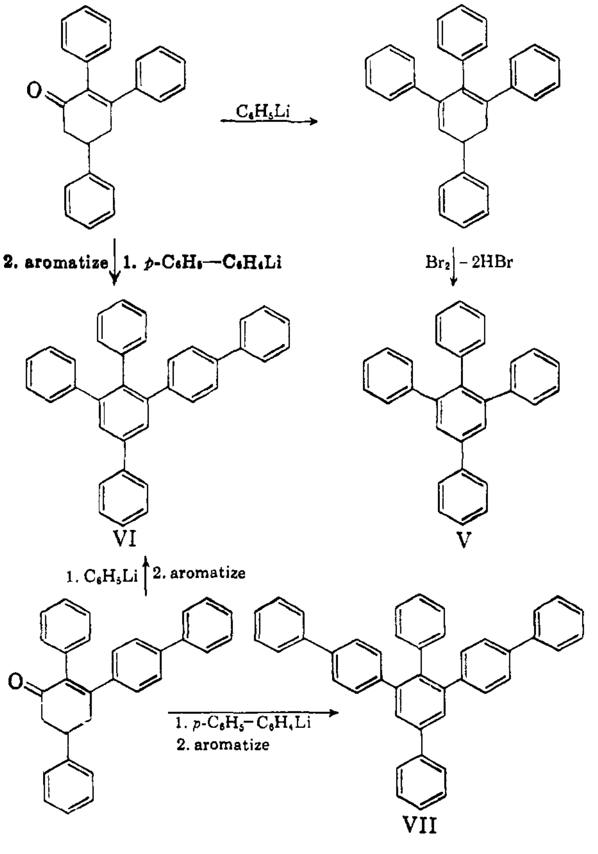
(1) G. Forrest Woods, D. D. Centola, H. E. Ruskie, and C. David Miller, *J. Am. Chem. Soc.*, **82**, 5227 (1960).

(2) G. F. Woods, J. C. Oppelt, and R. B. Isaacson, *J. Am. Chem. Soc.*, in press.

(3) G. R. Ames and W. Davey, *J. Chem. Soc.*, 3480 (1957).



Phenylmagnesium bromide failed to add to enol ether (I); in contrast, phenyllithium and *p*-xenyllithium readily provided II wherein R_1 is C_6H_5- and *p*-$C_6H_5C_6H_4$-. The following reactions were accomplished with the two resulting ketones:



Substance V is of considerable interest since a survey of the literature disclosed that of the three tetraphenylbenzenes, there are conflicting interpretations only for the 1,2,3,5 isomer and that it has not previously been prepared.[4]

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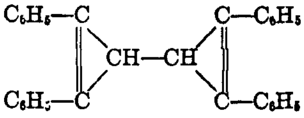
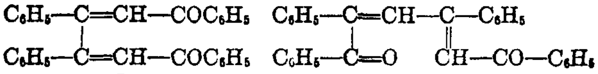
(4) Bogdanowska [V. Bogdanowska, *Ber.*, **25,** 1274 (1892)] treated dibenzylcarbinol with hydroiodic acid–red phosphorus, hydroiodic acid alone, and with methyl iodide, the latter in a sealed tube for three hours at 265°. In the first two instances dibenzylmethane was isolated in good yields. In the last instance a mixture was obtained from which was isolated dibenzylmethane and a hydrocarbon which melted at 268–269°. Bogdanowska assigned the structure VIII to this hydrocarbon. The analytical results for this hydrocarbon were consistent with the formula $C_{30}H_{22}$. Some six years later, Wislicenus and Lehmann [J. Wislicenus and A. Lehmann, *Ann.*, **320,** 195 (1898)] postulated that VIII was actually 1,2,4,5-tetraphenylbenzene. This was



VIII

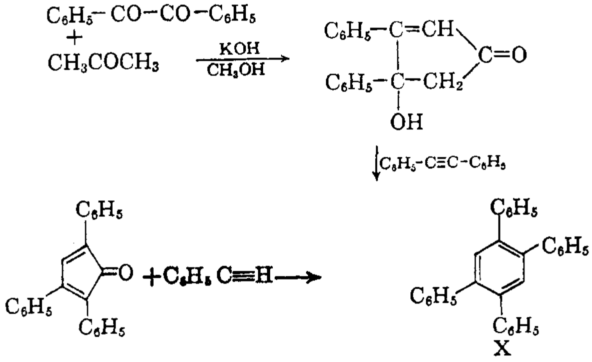
done because Wislicenus and Lehmann condensed benzil with acetophenone in the presence of alcoholic potassium hydroxide and obtained, beside a mono-condensation product, a di-condensation product for which they considered the structures IXa and IXb. Compound IX was treated



$$\begin{array}{l} C_6H_5{-}C{=}CH{-}COC_6H_5 \\ \quad\;\; | \\ C_6H_5{-}C{=}CH{-}COC_6H_5 \end{array} \qquad \begin{array}{l} C_6H_5{-}C{=}CH{-}C{-}C_6H_5 \\ \quad\;\; | \qquad\qquad \| \\ C_6H_5{-}C{=}O \quad\; CH{-}CO{-}C_6H_5 \end{array}$$

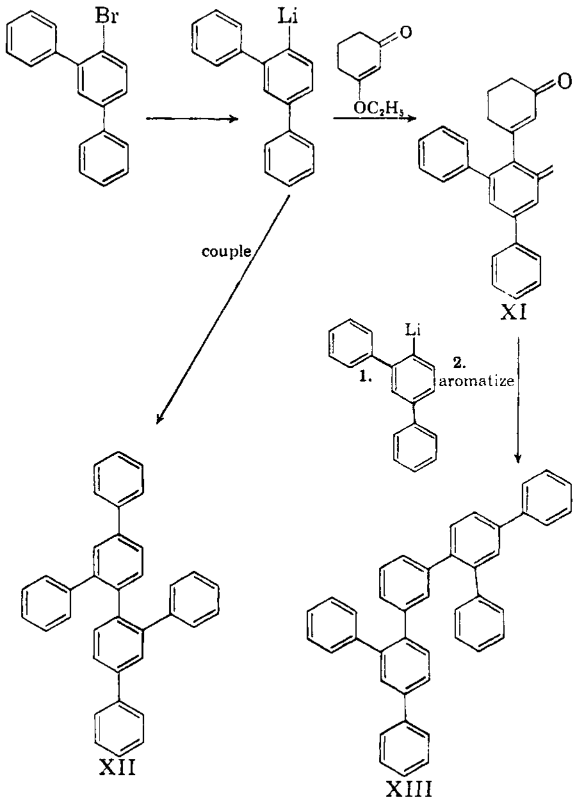
IXa IXb

with hydroiodic acid and red phosphorus to yield a hydrocarbon, m.p. 278° ($C_{30}H_{22}$), assumed to be a tetraphenylbenzene on the basis of the ease with which aromatic compounds are formed and that their isomer was probably the 1,2,3,5-isomer; thus, they believed Bogdanowska's compound must have been 1,2,4,5-tetraphenylbenzene. Schlenk and Bergmann [W. Schlenk and E. Bergmann, *Ann.*, **463,** 96 (1928)] reduced the hydrocarbon obtained by Wislicenus and Lehmann with sodium followed by ethanol and obtained a dihydro derivative, m.p. 208–210°, which upon treatment with palladium (and hydrogen) yielded the original hydrocarbon. Schlenk and Bergmann point out that only an aryl substituted benzene will yield a sodium derivative under these conditions and they designate the hydrocarbon as the 1,2,4,5-isomer. Dilthey [W. Dilthey, *et al.*, *Ber.*, **67,** 2004 (1934); **68,** 1159 (1935)] questioned the assignment by Wislicenus and Lehmann which was made primarily on the basis of melting points. Dilthey employed the following two schemes to obtain 1,2,4,5-tetraphenylbenzene (X).



Dilthey's hydrocarbon, the 1,2,4,5-isomer, is the same as that of Wislicenus and Lehmann. Bogdanowska's is probably the 1,2,4,5-isomer also. It is interesting to note that Egloff *Physical Constants of Hydrocarbons*, Vol. III, p. 593 594, Reinhold Publishing Corp., New York, N. Y., accepts the interpretation of Wislicenus and Lehmann and gives the data of these authors for the 1,2,3,5-tetraphenyl-

A second method available for the preparation of doubly-branched polyphenyls is dependent on branching, not as a consequence of the dihydroresorcinol component, but as a consequence of the organometallic. For this purpose 4′- bromo-*m*-terphenyl[5] was employed, and the following syntheses were accomplished.



EXPERIMENTAL

Preparation of 2,3,5-triphenyl-2-cyclohexenone. A solution of 5 g. of the monomethyl enol ether of 2,5-diphenylcyclohexanedione-1,3 (I) in dry benzene–ether was added slowly to excess phenyllithium. After 1 hr. the addition complex was hydrolyzed with cold dilute sulfuric acid. The organic layer was steam distilled from an acid solution until no further biphenyl could be detected in the distillate. The organic residue was extracted with ether. The ethereal solution was washed with sodium bicarbonate and with water and then dried with magnesium sulfate. The ethereal solution was concentrated and the crystalline material obtained was recrystallized from 95% ethanol. A light yellow solid, m.p. 112-113°, was obtained; yield, 4.6 g. (80%).

Anal. Calcd. for $C_{30}H_{24}O$: C, 88.85; H, 6.22. Found: C, 88.61; H, 6.05.

A *2,4-dinitrophenylhydrazone* derivative was prepared. Orange needles were obtained after two recrystallizations from methanol-benzene, m.p. 230–233°.

Anal. Calcd. for $C_{30}H_{24}N_4O_4$: C, 71.42; H, 4.80. Found: C, 71.40; H, 4.85.

Preparation of 1,2,3,5-tetraphenylbenzene (V). 2,3,5-Triphenyl-2-cyclohexenone (2.55 g.) in dry benzene-ether was added to a phenyllithium solution. The reaction complex was decomposed with dilute sulfuric acid and the whole was submitted to steam distillation. A light brown solid was obtained from the steam distillation residue. It was dissolved in petroleum ether (b.p. 100–120°) and chromatography employing an alumina column was attempted. Only a yellow viscous oil could be obtained.

The oil was dissolved in chloroform and 0.8 g. of bromine (in chloroform) was added. The mixture was kept at 0° throughout. The solution was slowly allowed to warm to room temperature and then it was heated on a steam bath to the boiling point. The solution was washed with dilute aqueous sodium sulfite. The organic layer was filtered through anhydrous calcium chloride and evaporated to dryness. The solid product obtained was recrystallized from petroleum ether (b.p. 100–120°) toluene mixture and from petroleum ether (b.p. 100–120°). White needles, m.p. 224–226°, were isolated; yield, 0.8 g. (27%). Molecular weight[6]: Calcd. 382. Found (cryoscopic), 387. ϵ_{max} 4.7 × 10^4 (λ_{max} 248 mμ, infl. 272).

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.09; H, 5.69.

Preparation of II, II-*diphenyl-[2,5]-quater[3,4]phenyl* (VI). *Method A.* A solution of 2 g. of 2,3,5-triphenyl-2-cyclohexenone in ether was added to an ethereal solution of 0.014 mole of 4-xenyllithium. The reaction complex was decomposed and subsequently treated as described for hydrocarbon V.

The diene obtained was aromatized with 1 g. of bromine as described previously. The aromatic compound was recrystallized from petroleum ether (b.p. 100–120°) affording white crystalline material, m.p. 188.5–190°. At approximately 195° crystals began to appear in the melt and increase in quantity until 206–207° at which temperature they re-melted; yield, 1.9 g. (62%). ϵ_{max} 5.4 × 10^4 (λ_{max} 263 mμ).

Anal. Calcd. for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.05; H, 5.58.

Preparation of 2,5-diphenyl-3-(4-xenyl)-2-cyclohexenone. The monomethyl enol ether of 2,5-diphenylcyclohexenedione-1,3 (3.3 g.) in dry benzene was added to an excess of 4-xenyllithium. The reaction complex was decomposed with cold dilute sulfuric acid and the whole was submitted to steam distillation. The steam distillation residue was extracted with ether. The ethereal solution was washed with aqueous sodium bicarbonate and then with water. The organic layer was dried with magnesium sulfate.

The ether was removed under reduced pressure and the resulting viscous material was taken up in benzene and chromatographed using an alumina column. The first fractions, which were fluorescent, were discarded. A nonfluorescent band of material followed; this gave a positive 2,4-dinitrophenylhydrazone test. This material was collected and recrystallized first from petroleum ether (b.p. 80–100°) and then from petroleum ether (b.p. 100–120°). White crystals, m.p. 117.5–119.5°, were obtained.

Anal. Calcd. for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 89.78; H, 6.17.

A *2,4-dinitrophenylhydrazone* derivative was prepared and was recrystallized from ethyl acetate; orange needles, m.p. 214–216°, were obtained.

Anal. Calcd. for $C_{36}H_{28}N_4O_4$: C, 74.47; H, 4.86. Found: C, 74.67; H, 4.87.

Preparation of II, II-*diphenyl-[2,5]-quater[3,4]phenyl* (VI). (*Method B*). A dry benzene solution of 2,5-diphenyl-3-(4-xenyl)-2-cyclohexenone (2.0 g.) was added to an ethereal phenyllithium solution prepared from 0.5 g. of lithium metal and 5.3 g. of bromobenzene. The reaction complex was hydrolyzed with cold dilute sulfuric acid and the organic

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benzene and the data of Bogdanowska for 1,2,4,5-tetraphenylbenzene. In Beilstein *Handbuch Der Organische Chemie*, Vol. V, p. 755, Julius Springer, Berlin (1922) the hydrocarbon prepared by Wislicenus and Lehmann is designated as the 1,2,4,5-isomer and Bogdanowska's as "unbekannte."

(5) L. Olgiati, *Ber.*, 27, 3387 (1894).

(6) All molecular weight determinations were carried out with *p*-terphenyl as the solvent, and all ultraviolet spectra were determined in iso-octane.

product was treated as described previously for hydrocarbon V.

A chloroform solution of the diene was aromatized with 1 g. of bromine. The organic product isolated was recrystallized from petroleum ether (b.p. 100–120°) affording white crystalline material, m.p. 187.5–188.5°. The melt produced crystals which, upon further heating, melted at 206–207°; yield: 1.2 g. (52%). The mixed melting point with the product obtained by Method A was at 205–207°. Recrystallization of this sample from petroleum ether (b.p. 100–120°) gave crystalline material, m.p. 186–188°.

Preparation of III, III-*diphenyl-[2,5]quinque[4,3,4]phenyl* (VII). 2,5-Diphenyl-3-(4-xenyl)-2-cyclohexenone in dry benzene was added to a 4-xenyllithium solution prepared from bromobenzene and *n*-butyllithium. The reaction complex was decomposed with cold dilute sulfuric acid and the resulting organic product was submitted to steam distillation from dilute sulfuric acid. Isolation of the crude diene was accomplished as described for the preparation of hydrocarbon V.

The diene, in chloroform, was aromatized with 0.8 g. of bromine. The aromatic product was isolated as described previously. The product was recrystallized several times from petroleum ether (b.p. 100–120°) toluene, petroleum ether (b.p. 100–120°), and ethyl acetate, respectively. A white crystalline material, m.p. 230–233°, was obtained; yield, 0.96 g. (36%). ϵ_{max} 7.56 × 10^4 (λ_{max} 268 mμ).

Anal. Calcd. for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.24; H, 5.81.

Preparation of II-*phenyl-[3]*-III-*phenyl-[2]-quater[4,4]-phenyl* (XII). An ethereal solution of 4′-bromo-*m*-terphenyl[5] (10.0 g.) was treated with 19 ml. of 0.86*N* *n*-butyllithium at room temperature. The mixture was cooled to −70° and stirred at this temperature for 1 hr. Cobalt(II) chloride (2.08 g.) was added as a slurry in ether. The mixture was stirred at −70° for several hours and then allowed to warm slowly to room temperature. The reaction mixture was poured onto an ice water–sulfuric acid mixture. The organic product was extracted with ether, washed with sodium bicarbonate and then with water, and finally dried over magnesium sulfate. Upon concentration of the ethereal solution, a viscous material was obtained. This material was chromatographed on alumina with petroleum ether (b.p. 60–80°) as the eluent. Fractions of 30 ml. volume each were collected. The first two fractions contained 6 g. of unchanged 4′-bromo-*m*-terphenyl. Fraction three afforded 1 g. of *m*-terphenyl. Fractions four through six afforded 1.2 g. of a white solid which was recrystallized from petroleum ether (b.p. 60–80°), m.p. 223–225°; ϵ_{max} 3.3 × 10^4 (λ_{max} 286.5 mμ) and ϵ_{max} 6.5 × 10^4 (λ_{max} 249 mμ). Molecular weight: Calcd., 458.6. Found (cryoscopic), 472.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.19; H, 5.99.

An attempt to use atmospheric oxygen to affect the coupling of the 4′-*m*-terphenyllithium yielded considerable phenolic material with no isolable sexiphenyl.

Preparation of II-*phenyl-[3]*-IV-*phenyl[2]quinque[4,3,4]-phenyl* (XIII). *n*-Butyllithium (18 ml. of 0.78*N* solution) was added, with stirring, to 4.3 g. of 4′-bromo-*m*-terphenyl. 1-(3-Keto-2-cyclohexenyl)-2,4-diphenylbenzene (XI)[2] (3.9 g.) was added as a slurry in ether. The addition complex was decomposed in an ice–sulfuric acid mixture. The ethereal layer was washed with sodium bicarbonate and then with water. The ether was concentrated to half its volume. The solid which precipitated upon concentration was filtered and recrystallized from isopropyl alcohol-benzene mixture; yield 4.0 g. of the diene (62%); m.p. 186–188°.

A solution of 1 g. of the diene in 50 ml. of *p*-cymene was refluxed with 0.3 g. of palladium on carbon for 1 hr. This mixture while hot was filtered through a short column of alumina (2 in. long, 1 in. diameter). The resulting clear solution was concentrated, affording white crystalline material. This solid was recrystallized from isopropyl alcohol-benzene; yield: 0.9 g. (82.5% for aromatization), m.p. 266–267°.

Molecular weight: Calcd. 534.7. Found (cryoscopic), 543. ϵ_{max} 6.7 × 10^4 (λ_{max} 247.9 mμ) and ϵ_{max} 4.8 × 10^4 (λ_{max} 276 mμ).

Anal. Calcd. for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.37; H, 5.90.

Acknowledgment. This research was supported in part by the United States Air Force under Contract No. 33(616)–5063, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

College Park, Md.

[Contribution from the Chemical Laboratories of the University of Maryland]

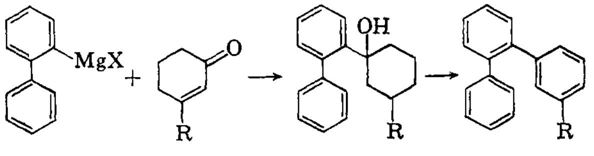
Synthesis of Polyphenyls Containing *ortho* Linkages

G. FORREST WOODS and FRANK SCOTTI

Received May 13, 1960

Two methods are reported for the synthesis of polyphenyls containing *ortho* linkages. Also included are the preparations of some 2-arylcyclohexanones, 1,2-diarylcyclohexanols, 2-aryl-2-cyclohexenones, and some new polyphenyls.

A general method for the introduction of an *ortho* link into a polyphenyl has been dependant on the conversion of a 2-halosubstituted biphenyl to a Grignard reagent and the reaction[1] of the latter with a 3-substituted 2-cyclohexenone as shown below:



This process results in an *ortho* link in the terminal position of the polyphenyl molecule. A method was desired which would make possible the introduction of an *ortho* link not only in the terminal position but in any position within the structure. Synthetic procedures for this have now been developed.

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(1) G. F. Woods, A. L. Van Artsdale, and F. T. Reed, *J. Am. Chem. Soc.*, 72, 3221 (1950).