

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12; mol. wt., 198. Found: C, 84.9, 84.6; H, 6.75, 6.88; mol. wt., 199.

4-Methyl-4'-hydroxydiphenylmethane.—Phenyl-*p*-toluate (m.p. 77.0–77.5°) was made to undergo the Fries rearrangement according to the general directions of Rossemunde and Schnurr.¹⁵ The product was recrystallized from benzene, and 4-methyl-4'-hydroxybenzophenone was obtained in 36% yield in the form of flat needles (m.p. 173–174°).

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.4; H, 6.02.

The ketone was reduced to the diphenylmethane according to the directions of Clemmensen¹⁶ in 50% yield. The product was recrystallized from hexane as a white solid (m.p. 77–78°). Final purification was effected by sublimation and the white solid obtained thereby melted sharply at 81.5–82.0°. The infrared spectrum of this product was identical with that of the *p*-compound obtained *via* interaction of *p*-xylylene with phenol.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.80; H, 7.12. Found: C, 84.6; H, 7.01.

4-Methyl-4'-hydroxydiphenylmethane was also synthesized *via* an alternative route as follows: 4-Methoxy-4'-methylbenzhydrol (m.p. 63–64°) was prepared in 33% yield from 0.30 mole of anisaldehyde, 0.35 mole of magnesium and 0.34 mole *p*-bromotoluene according to the directions of Balfe, *et al.*¹⁷ The corresponding diphenylmethane was then obtained in 30% yield as a colorless liquid (b.p. 139–141° (2 mm.), n_D^{25} 1.5615) by reduction of the benzhydrol with sodium in absolute ethanol according to the procedure indicated by Klages.¹⁸ The liquid slowly crystallized in the form of colorless platelets (m.p. 30–31°). The aromatic ether was then converted to 4-hydroxy-4'-methylidiphenyl-

methane in 30% yield *via* the Ziesel method for demethylation as described by Shriner and Fuson.¹⁹ Final purification was effected by recrystallization from hexane. The compound was obtained in the form of fine white needles (m.p. 80–81°) which showed no depression in melting point when mixed with the 4-hydroxy-4'-methylidiphenylmethane obtained from the reaction of *p*-xylylene with phenol or *via* the above alternative synthesis. A diphenylurethan derivative (m.p. 140–141°) was prepared by causing the aromatic phenol to react with phenyl isocyanate in pyridine.

BF₃-catalyzed Alkylation of Toluene.—A clear solution of *p*-xylylene (0.04 mole) in 0.5 liter of toluene was saturated with gaseous BF₃, and the reaction mixture was kept at –78° for 1.5 hours. Methanol (100 cc.) was then added and the resulting solution was warmed to room temperature. A small amount of insoluble polymeric material (0.20 g.) was removed by filtration. The excess solvent of the mother liquor was removed by distillation at atmospheric pressure, leaving 9.5 g. of non-volatile oil as residue. The presence of a mixture of diphenylmethanes in the non-volatile oil was indicated by its infrared spectrum.²⁰

A second 500-cc. aliquot of the original solution, to which no BF₃ was added, was carried through in parallel as a control experiment. In contrast to the above weight distribution, 2.49 g. of insoluble poly-*p*-xylylene and 3.6 g. of an almost crystalline residue was obtained. The latter was the usual mixture of pyrolysis and subsequent polymerization products.²⁰

Acknowledgments.—The authors are indebted to Drs. H. Dinsmore and H. White, then of the M. W. Kellogg Co., and Dr. J. J. McBrady of the Minnesota Mining and Manufacturing Co. for the interpretation of the infrared spectra.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND, COLLEGE PARK, MD.]

The Synthesis of Some Linear Polyphenyls

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RECEIVED OCTOBER 30, 1959

The synthesis of several aryl-substituted cyclohexenones, linear polyphenyls and halopolyphenyls is reported.

The syntheses of some quater- and quinquephenyls has been reported earlier from this Laboratory.¹ These methods have now been utilized to obtain more complex cyclohexenones, larger polyphenyls and bromopolyphenyls.

4-Bromo-*m*-terphenyl has now been prepared by the two formula sequences (A) and (B).

The products II and IV are indistinguishable, although on the basis of the above reactions they should be isomeric. Aromatization of II and IV was readily accomplished by bromination and dehydrobromination without isolation of the brominated intermediate. In sequence (B) some *p*-phenylenedimagnesium bromide from *p*-dibromobenzene was present since a reasonable amount of the tetrahydro compound V was isolated; V was subsequently aromatized with palladium-charcoal to VIII (R = C₆H₅).

(1) (a) G. F. Woods and I. W. Tucker, *THIS JOURNAL*, **70**, 2174, 3340 (1948); (b) G. F. Woods and F. T. Reed, *ibid.*, **71**, 1348 (1949); (c) G. F. Woods, A. L. Van Artsdale and F. T. Reed, *ibid.*, **72**, 3221 (1950); (d) G. F. Woods, F. T. Reed, T. E. Arthur and H. Ezekiel, *ibid.*, **73**, 3854 (1951).

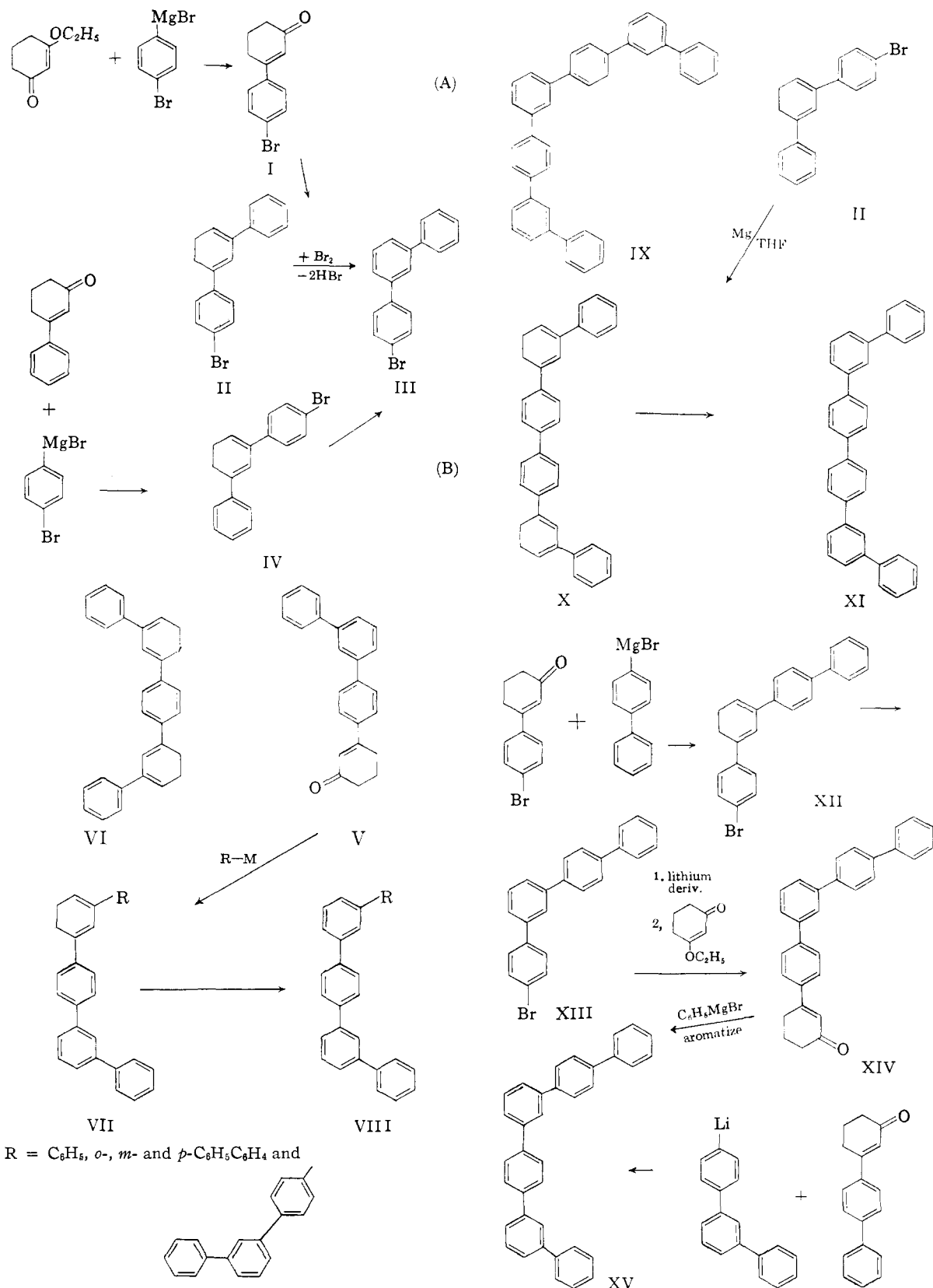
Compound III, 4-bromo-*m*-terphenyl, was found to undergo the interchange reaction with *n*-butyllithium² and subsequent reaction of the aryllithium with the enol ether of dihydroresorcinol provided VI which was then utilized to obtain several new polyphenyls (VIII).

In these reactions R–M was either a Grignard reagent or an aryllithium. Thus, a new quinquephenyl, three sexiphenyls and a septiphenyl, IX, were obtained.

An attempt to prepare the Grignard reagent in tetrahydrofuran from the bromodihydro compound II led to the coupled product X, a tetrahydro compound, which was aromatized to the sexiphenyl XI.

It follows that more complex aryl bromides or ketones will provide intermediates for larger and more complex polyphenyls. Further, since there is no procedure available to prove the structure of the different polyphenyls, alternate methods of

(2) R. G. Jones, in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.

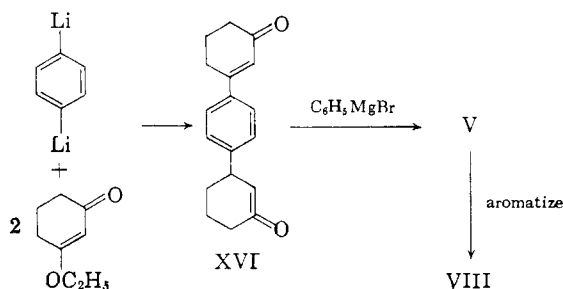


synthesis of certain substances were desired. This was accomplished in part as shown below with the bromoquaterphenyl XIII to obtain the sexiphenyl XV.

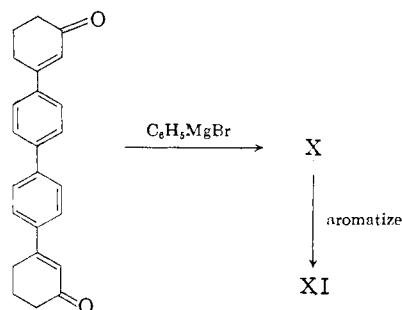
This same sexiphenyl was also prepared by the reaction of 3-[4-xenyl]-2-cyclohexenone with the lithium derivative of 4-bromo-*m*-terphenyl. Sub-

stance XV was earlier prepared as compound VIII (R = *p*-xenyl). The three preparations gave identical material. The diene precursors to XV are isomeric but the dienic structures are in different rings; the two substances melted at 261–263° and 263–265°, respectively.

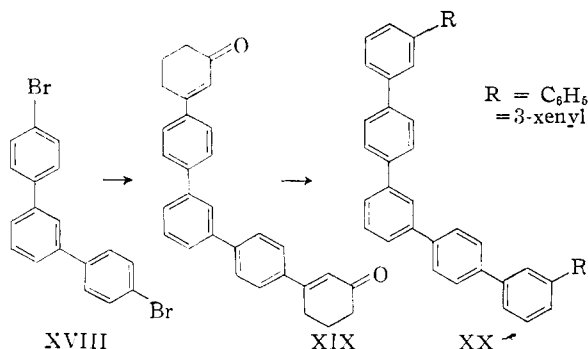
Another successful approach to the polyphenyls is



To explore the generality of this method the 4,4'-dilithium derivative from 4,4'-dibromobiphenyl was prepared and allowed to react with the ethyl enol ether of dihydroresorcinol as above to provide XVII, which was then converted to XI



Treatment of the 3-[4-bromophenyl]-2-cyclohexenone (I) with *p*-bromophenylmagnesium bromide followed by aromatization with bromine resulted in the dibromoterphenyl XVIII. This substance was converted readily to its dilithium derivative and allowed to react with the enol ether of dihydroresorcinol to obtain the pentacyclic diketone XIX.



Reaction of the diketone with phenylmagnesium bromide or with 3-xenyllithium followed by aromatization provided XX. If R is phenyl, the product is a septiphenyl the structure of which is the same as IX, while a noviphenyl containing five *meta* and two *para* linkages results if R is 3-xenyl.

The ultraviolet spectra of the aromatic compounds are all without fine structure as are the spectra of the precursor dienes; however, the latter curves have either a secondary absorption maximum or inflection on the slope toward the red side.

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

Experimental

3-[4-Bromophenyl]-2-cyclohexenone (I).—The Grignard reagent from 379 g. (1.61 moles) of *p*-dibromobenzene and 37.2 g. (1.53 moles) of magnesium was prepared in ether in the usual manner. To the Grignard reagent was added slowly 180 g. (1.28 moles) of 3-ethoxy-2-cyclohexenone dissolved in 200 ml. of ether. The Grignard addition complex was decomposed with cold dilute sulfuric acid and the resulting mixture was submitted to steam distillation. After distillation of organic material had ceased, the steam-pot residue was cooled and the residual bromoketone was extracted with ether. The ether layer was washed with water and with dilute sodium bicarbonate solution and dried with magnesium sulfate. After removal of ether under reduced pressure the ketone was distilled; b.p. 160–170° (0.2–0.7 mm.). The distillate crystallized on standing and was recrystallized from ethyl ether. 3-[4-Bromophenyl]-2-cyclohexenone (197 g., 61%) was obtained, m.p. 82–82.5°, ϵ_{\max} (ethanol) 2.80×10^4 (286 $m\mu$); ϵ_{\max} (isooctane) 2.5×10^4 (273 $m\mu$).

Anal. Calcd. for $C_{12}H_{11}OBr$: C, 57.39; H, 4.42. Found: C, 57.58; H, 4.30.

Its red 2,4-dinitrophenylhydrazone, prepared in the usual manner and recrystallized from *o*-xylene, melted at 212–213°.

Anal. Calcd. for $C_{18}H_{15}N_4O_4Br$: C, 50.13; H, 3.51. Found: C, 50.36; H, 3.64.

1-Phenyl-3-[4-bromophenyl]-benzene (III). Method A.—3-[4-Bromophenyl]-2-cyclohexenone (103 g., 0.41 mole) in 150 ml. of warm benzene was added to an ethereal solution of phenylmagnesium bromide prepared from 125 g. of bromobenzene and 19 g. of magnesium. The Grignard addition complex and excess Grignard reagent were decomposed with dilute sulfuric acid. The aqueous layer was rejected; the ether layer was submitted to steam distillation from a dilute sulfuric acid medium until most of the biphenyl had been removed. The residue solidified on cooling and was recrystallized from absolute ethanol. 4-Bromo-*m*-dihydroterphenyl (II) was obtained in 77% yield, m.p. 104.5–105.5, ϵ_{\max} (ethanol) 1.23×10^4 (316 $m\mu$) and 3.94×10^4 (256 $m\mu$).

Anal. Calcd. for $C_{18}H_{16}Br$: C, 69.46; H, 4.85. Found: C, 69.31; H, 4.98.

Method B.—The mono-Grignard reagent from 236 g. (1 mole) of *p*-dibromobenzene and 27 g. (1.1 moles) of magnesium in 550 ml. of ether was prepared and to this was added 82 g. (0.4 mole) of 3-phenyl-2-cyclohexenone in 250 ml. of ether. The resulting mixture was heated under reflux for an additional 30 minutes. The Grignard addition complex was decomposed and submitted to steam distillation as in method A. The steam-pot residue was a brown viscous oil. As much water was decanted as possible and the residue dissolved in ether; the white crystalline material which did not dissolve was isolated by filtration and treated as described below. The ether filtrate was partially concentrated and chilled in an ice-salt-bath whereupon the bromodihydroterphenyl (IV) crystallized. It was recrystallized and decolorized from ethanol to yield the 4-bromo-*m*-dihydroterphenyl (77%) (essentially the same as in method A) which melted at 104.5–105.5° and gave no depression with the sample from method A.

The white crystalline precipitate (6 g.) isolated above (method B) was recrystallized first from bromobenzene-ethanol then from *o*-xylene to yield compound V, m.p. 225–226°, ϵ_{\max} (ethoxyethanol) 3.06×10^4 (269 $m\mu$) and an inflection at 320 $m\mu$.

Anal. Calcd. for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 92.93; H, 6.54.

TABLE I
DIENES OF FORMULA VII

R (M)	Yield, %	M. p., °C.	Carbon, %		Hydrogen, %		$\epsilon_{\max} \times 10^{-4}$	$\lambda_{\max}, m\mu$	Recrystn. solvent
			Calcd.	Found	Calcd.	Found			
C ₆ H ₅	90	229-230	93.71 ^a	93.61	6.34	6.34	4.26 (ethoxyethanol)	248	<i>o</i> -Xylene
<i>o</i> -Xenyl	51	172-173	93.86 ^b	93.77	6.13	5.81	3.48 (ethoxyethanol)	Inf. 320	Benzene-ethanol
<i>m</i> -Xenyl	60	193-194		93.73		6.30	5.88 (ethoxyethanol)	268	Ethyl benzene
<i>p</i> -Xenyl	63	263-265		93.75		6.07	5.12 (cellosolve-ethanol)	262	Inf. 320
4- <i>m</i> -Terphenyl	42	301-303	93.99 ^c	93.82	6.01	6.14	8.85 (cellosolve-ethanol)	284	Ethyl benzoate
								Inf. 335, 260	
								283	Ethyl benzoate
								Inf. 330, 260	

Formulas: ^a C₃₀H₂₄, ^b C₃₆H₂₈, ^c C₄₂H₃₂.

TABLE II
POLYPHENYLS OF FORMULA VIII

R (M)	M. p., °C.	Carbon, %		Hydrogen, %		$\epsilon_{\max} \times 10^{-4}$	$\lambda_{\max}, m\mu$	Solvent
		Calcd.	Found	Calcd.	Found			
C ₆ H ₅ ^a	235-236	94.20 ^d	94.00	5.80	5.82	5.07 (ethoxyethanol)	261	<i>o</i> -Xylene
<i>o</i> -Xenyl ^b	165-166	94.29 ^e	94.20	5.72	5.69	4.73, 4.51 (ethanol)	263, 240	Benzene-ethanol
<i>m</i> -Xenyl ^b	186-188		94.34		5.71	6.33 (cellosolve-ethanol)	257	<i>o</i> -Xylene
<i>p</i> -Xenyl ^c	268-269		94.19		5.71	5.64 (cellosolve-ethanol)	282	<i>p</i> -Cymene
4- <i>m</i> -Terphenyl	305-306	94.34 ^f	94.20	5.66	5.71	7.40 (ethoxyethanol)	281	<i>p</i> -Cymene

^a This substance is identical with the substance obtained from aromatization of compound V as described earlier in the Experimental section. ^b Aromatized with bromine in chloroform. ^c This polyphenyl was prepared by the alternate procedure: addition of lithium derivative from the interchange of *n*-butyllithium and 4-bromo-*m*-terphenyl with 3-(4-xenyl)-2-cyclohexenone. Diene: m.p. 265-266°. *Anal.* Found: C, 93.62; H, 5.98 (no depression with isomeric dienic compound). Aromatized: m.p. 269-270° (no depression of m.p.). *Anal.* Found: C, 94.29; H, 5.72. Formulas: ^d C₃₀H₂₂, ^e C₃₆H₂₆, ^f C₄₂H₃₀.

Aromatization of V was carried out with 10% palladium-charcoal in boiling *p*-cymene. The mixture was filtered while hot to remove the catalyst. Upon cooling the filtrate, solid material was deposited which was recrystallized from *o*-xylene. 1,4-Di-[3-xenyl]-benzene (VIII, R = C₆H₅) was obtained, m.p. 235-236°.

Anal. Calcd. for C₃₀H₂₂: C, 94.20; H, 5.80. Found: C, 94.00; H, 5.82.

Aromatization of the bromo-*m*-dihydroterphenyl (20 g.) (II or IV) in 60 ml. of chloroform was accomplished by the addition of 70 ml. of 1 *M* solution of bromine in chloroform. The solution, during addition, was chilled in an ice-bath and stirred. After the addition, the solution was warmed on a steam-bath until evolution of hydrogen bromide had ceased and the volume had been reduced by 50%. Absolute ethanol was added and the solution chilled. White crystalline material precipitated which was recrystallized from absolute ethanol to yield 1-phenyl-3-[4-bromophenyl]-benzene (III) (61%), m.p. 86-87°, ϵ_{\max} (ethanol) 5.1 × 10⁴ (249 mμ).

Anal. Calcd. for C₁₅H₁₃Br: C, 69.80; H, 4.21. Found: C, 70.09; H, 4.36.

3-(4-*m*-Terphenyl)-2-cyclohexenone (VI).—To a slight excess of *n*-butyllithium in 44 ml. of ether was added 11.5 g. (0.036 mole) of 4-bromo-*m*-terphenyl in 50 ml. of an equal mixture of ether-benzene. The temperature during addition and for a subsequent 20 minutes was maintained at 10° after which time 9.8 g. (0.07 mole) of 3-ethoxy-2-cyclohexenone in ether was added.

The mixture was stirred for an additional 30 minutes, then decomposed with dilute sulfuric acid. The organic layer was separated and submitted to steam distillation from a dilute sulfuric acid medium until most of the steam-volatile organic material had been removed. The organic residue in the steam-pot solidified on cooling and was isolated by filtration. The ketone (10.3 g., 88%) was recrystallized from absolute ethanol; m.p. 144-145° ϵ_{\max} (ethanol) 3.04 × 10⁵ (308 mμ) and 2.56 × 10⁵ (235 mμ).

Anal. Calcd. for C₂₄H₂₀O: C, 88.85; H, 6.21. Found: C, 89.06; H, 6.32.

Its 2,4-dinitrophenylhydrazone prepared in the usual manner recrystallized from *p*-cymene melted at 242.5-243.5°.

Anal. Calcd. for C₃₀H₂₄N₄O₄: C, 71.41; H, 4.79. Found: C, 71.65; H, 4.96.

Polyphenyls (VIII).—Ketone VI was treated in separate reactions with phenylmagnesium bromide, 2-xenylmagne-

sium iodide, 3-xenylmagnesium bromide and 4-xenyllithium (*n*-butyllithium interchange) and the lithium derivative (interchange) from 4-bromo-*m*-terphenyl. The ketone was added in dilute benzene solution to the organometallic medium. The various addition products were decomposed with dilute sulfuric acid and the whole was submitted to steam distillation. Solid formed in the steam-pot as the distillation proceeded. The solid dienes were isolated and recrystallized as indicated in Table I.

The dienes were aromatized with 10% palladium-charcoal in larger amounts of boiling *p*-cymene. The catalyst was removed by filtration of the hot solution. Concentration of the solution followed by chilling provided crystalline polyphenyl which was recrystallized as indicated in Table II.

Sexiphenyl XI.—A mixture of 11.5 g. of 4-bromo-dihydro-*m*-terphenyl (II), 0.7 g. of magnesium and 20 ml. of tetrahydrofuran was heated under reflux for approximately 36 hours at the end of which time the magnesium had been consumed. The mixture was hydrolyzed with water at which time a precipitate formed. The solid was isolated by filtration and was recrystallized first from dioxane and then from *o*-xylene; m.p. 285-287°, ϵ_{\max} (Cellosolve-ethanol) 4.96 × 10⁴ (297 mμ) and inflection at 260 mμ.

Anal. Calcd. for C₃₆H₃₀: C, 93.46; H, 6.54. Found: C, 93.30; H, 6.24.

This material was aromatized in *p*-cymene with 10% palladium-charcoal. The mixture was filtered while hot. The filtrate was concentrated and cooled whereupon solid crystallized; this was recrystallized from *o*-xylene; m.p. 280-281°, ϵ_{\max} (Cellosolve-ethanol) 5.55 × 10⁴ (299 mμ) and 3.61 × 10⁴ (263 mμ).

Anal. Calcd. for C₃₆H₂₈: C, 94.29; H, 5.72. Found: C, 94.11; H, 6.03.

4-Bromoquaterphenyl (XIII).—To the Grignard reagent prepared in 250 ml. of tetrahydrofuran from 60 g. of 4-xenyl bromide and 6.08 g. of magnesium was added 49 g. of 3-[4-bromophenyl]-2-cyclohexenone dissolved in a minimum of tetrahydrofuran. The complex was decomposed with dilute sulfuric acid and the resulting mixture was submitted to steam distillation. Powdery pale green product (45 g.) formed upon cooling of the steam-pot and was isolated by suction filtration. To remove the color the product was first recrystallized from *o*-xylene, then dissolved in a minimum of petroleum ether (90-100) and passed through an alumina chromatographic column. The product melted at 182-185° and a satisfactory analysis could not be obtained. Apparently aromatization had taken place in part.

Aromatization of the product was accomplished by the addition of an equal molar quantity of bromine in chloroform as described earlier. White crystalline 4-bromoquaterphenyl was obtained which was recrystallized from *o*-xylene; m.p. 180–182°, ϵ_{\max} (isoöctane) 5.2×10^4 (268 $m\mu$).

Anal. Calcd. for $C_{24}H_{17}Br$: C, 74.81; H, 4.45. Found: C, 74.80; H, 4.50.

Sexiphenyl XV.—The above bromoquaterphenyl XIII (7. g.) in an ether slurry was treated with an equivalent amount of *n*-butyllithium in ether and allowed to stand for 2 hours. A slight excess of 3-ethoxy-2-cyclohexenone in ether was added. The mixture was decomposed with dilute sulfuric acid. The product precipitated in the medium and was isolated by filtration and recrystallized from toluene. The product was dissolved in hot *n*-butyl alcohol and decolorized with Norite. Cooling provided white crystalline ketone XIV upon addition of methanol; m.p. 233–235°, insolubility prevented the determination of ϵ_{\max} (isoöctane); but maximum absorption was at 289 $m\mu$.

Anal. Calcd. for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 90.19; H, 6.21.

The above ketone XIV, 3 g., dissolved in benzene was added to excess phenylmagnesium bromide in ether. The product was hydrolyzed with dilute sulfuric acid. The unsaturated hydrocarbon was insoluble in this medium and was isolated (3.1 g.) by filtration and recrystallized from *o*-xylene; m.p. 261–263°.

Anal. Calcd. for $C_{38}H_{28}$: C, 93.86; H, 6.13. Found: C, 93.19; H, 6.18.

It was aromatized with bromine to XV.

An alternate synthesis of XV was accomplished as follows: 4-(*m*-terphenyl)-lithium was prepared from 2.54 g. (0.0082 mole) of 4-bromo-*m*-terphenyl in 30 ml. of anhydrous ether and 0.0088 moles of *n*-butyllithium in 11 ml. of anhydrous ether. To this mixture at 10° was added 1.91 g. (0.0077 mole) of 3-(4-xenyl)-2-cyclohexenone in 25 ml. of dry benzene and temperature of the solution raised to room temperature. The reaction mixture was stirred for an additional hour at room temperature. The complex was hydrolyzed with dilute sulfuric acid and the organic layer separated. The organic layer was steam distilled until a precipitate formed in the steam-pot. The residue was cooled and the solid recovered by filtration. The dienic solid was recrystallized from ethyl benzoate with alcohol washes. Its melting point was 265–266°, ϵ_{\max} (Cellosolve-ethanol) 4.19×10^4 (283 $m\mu$), inflection 325 $m\mu$.

Anal. Calcd. for $C_{36}H_{28}$: C, 93.88; H, 6.13. Found: C, 93.62; H, 5.98.

Aromatization of the diene was accomplished by dissolving the diene in boiling *p*-cymene and adding 10% palladium-charcoal. The mixture was refluxed for 20 minutes and filtered hot. A solid formed upon cooling and was isolated by filtration. The solid was recrystallized from *p*-cymene with alcohol washes; m.p. 269.5–270.5°. Mixed melting point with the compound prepared by the previous method showed no depression.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.29; H, 5.72. Found: C, 94.41; H, 5.84.

This compound was identical with the hydrocarbon VIII wherein R = *p*-xenyl (Table II).

Diketone XVI.—*p*-Dibromobenzene (0.18 mole) was treated with a slight excess of *n*-butyllithium and the mixture was allowed to stand for 36 hours. A slight excess of 3-ethoxy-2-cyclohexenone was added and the resulting complex was decomposed with dilute sulfuric acid. The mixture was submitted to steam distillation and the residue was dissolved in benzene and decolorized with charcoal. Most of the benzene was removed by distillation and petroleum ether (60–80°) was added. On cooling, solid formed (29%) which was recrystallized from benzene-petroleum ether; m.p. 133–134°, ϵ_{\max} (isoöctane) 3.1×10^4 (303 $m\mu$), 0.52×10^4 (250 $m\mu$) and 1.17×10^4 (225 $m\mu$).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.16; H, 6.81. Found: C, 81.13; H, 6.85.

Quinquephenyl VIII.—To an excess of phenylmagnesium bromide was added 1.33 g. of diketone XVI. The product was hydrolyzed with dilute sulfuric acid and steam distilled as described above. Upon cooling, 0.75 g. of solid product was isolated which was recrystallized directly from benzene (m.p. 230°). This material was aromatized with bromine

in chloroform as described above. The product was recrystallized from benzene-petroleum ether (80–100); m.p. 233–234°.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.35; H, 5.82.

This product was identical with the hydrocarbon VIII (R = C_6H_5), Table II.

Diketone XVII.—Excess *n*-butyllithium was added to 9.4 g. of 4,4'-dibromobiphenyl in ether and allowed to stand for 4 hours at the end of which time a slight excess of 3-ethoxy-2-cyclohexenone was added. The diketone precipitated (5 g.) from the medium upon acidification with dilute sulfuric acid and was isolated by filtration and recrystallized from benzene; m.p. 209–212°, ϵ_{\max} (isoöctane) 4.62×10^4 (315 $m\mu$) and 2.53×10^4 (225 $m\mu$).

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6.47. Found: C, 84.38; H, 6.41.

Sexiphenyl XI.—A small sample (1 g.) of diketone XVII dissolved in benzene was added to excess phenylmagnesium bromide in ether. After addition the solution was stirred and then decomposed with dilute sulfuric acid. The unsaturated compound X precipitated and was isolated by filtration. This was aromatized by bromine in the above-described manner to yield XI, m.p. 280–281°. This sample of the sexiphenyl XI was identical with the same substance prepared earlier by the alternate method.

4,4'-Dibromo-*m*-terphenyl (XVIII).—A solution of 3-(4-bromophenyl)-2-cyclohexenone (59 g.) (I) in a minimum of benzene was added to the Grignard reagent prepared from 62.5 g. of *p*-dibromobenzene and 6 g. of magnesium in approximately 200 ml. of ether. The addition complex was decomposed with dilute sulfuric acid and the mixture was submitted to steam distillation. Upon cooling, the residue solidified and was recrystallized from acetone. The dibromodihydro compound, 71 g. (78%), melted at 151–153°, ϵ_{\max} (isoöctane) 3.6×10^4 (261 $m\mu$) and 1.3×10^4 (315 $m\mu$).

Anal. Calcd. for $C_{18}H_{14}Br_2$: C, 55.43; H, 3.59. Found: C, 55.59; H, 3.63.

Aromatization was accomplished by the addition of a stoichiometric amount of bromine dissolved in chloroform to a solution of the dihydro compound in chloroform. After the addition, carried out at 0°, was complete, the solution was concentrated, diluted with petroleum ether (100–120°), and chilled. White crystalline 4,4'-dibromo-*m*-terphenyl precipitated and was recrystallized from isopropyl alcohol; m.p. 147–149°, ϵ_{\max} (isoöctane) 6.1×10^4 (255 $m\mu$).

Anal. Calcd. for $C_{18}H_{12}Br_2$: C, 55.71; H, 3.12. Found: C, 55.71; H, 3.32.

Polyphenyls (XX).—A slurry of 32.2 g. of 4,4'-dibromo-*m*-terphenyl (XVIII) in 200 ml. of anhydrous ether was treated with an ethereal solution of *n*-butyllithium (0.18 mole). The temperature was maintained at 0 and 3° and the resultant clear solution was allowed to warm and stand for 2 hours at room temperature. To this was added with stirring a solution of 30 g. of 3-ethoxy-2-cyclohexenone in 50 ml. of ether. Hydrolysis was effected with dilute sulfuric acid. The mixture was steam distilled and the residue which solidified on cooling was recrystallized from isoamyl alcohol. The diketone XIX, 26 g. (75%), was obtained, m.p. 196–197°. Insolubility prevented the determination of ϵ_{\max} ; λ_{\max} (isoöctane) 310 $m\mu$.

Anal. Calcd. for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 85.97; H, 6.39.

The above ketone (5 g.) dissolved in warm toluene was added to an ethereal solution of phenylmagnesium bromide prepared from 9.4 g. of bromobenzene and 1.45 g. of magnesium. The complex was decomposed with dilute sulfuric acid and the mixture was submitted to steam distillation. The residual yellow solid (4.35 g., 67%) was recrystallized from dimethyl sulfoxide; m.p. 304–305°.

Aromatization of this product in the usual manner with 10% palladium-charcoal in a large amount of *p*-cymene resulted in a product of the same melting point (304–305°) and ultraviolet spectrum as the previous supposed tetrahydro compound; ϵ_{\max} (ethoxyethanol) 7.4×10^4 (280 $m\mu$).

Anal. Calcd. for $C_{32}H_{30}$ (aromatic): C, 94.34; H, 5.66. Found (aromatized product): C, 94.20; H, 5.71. (Supposed tetrahydro compound): C, 94.22; H, 5.64.

The dienic compounds very readily lose hydrogen, probably in reaction with atmospheric oxygen, to yield the

aromatized compound. This septiphenyl was identical with the septiphenyl VIII (R = 4-*m*-terphenyl).

The above diketone XIX, 5 g., dissolved in toluene was added to the Grignard reagent prepared from 14 g. of 3-xenyl bromide and 1.46 g. of magnesium in 25 ml. of ether. The product was treated as above. The stem-pot residue was isolated and recrystallized from dimethyl sulfoxide; yield 5.9 g. (71%), m.p. 247–250°, ϵ_{max} (ethoxyethanol) 8.0×10^4 (265 $m\mu$) and an inflection at 325 $m\mu$.

Anal. Calcd. for $C_{64}H_{42}$: C, 93.87; H, 6.13. Found: C, 93.50; H, 6.21.

Aromatization was effected in a large amount of *p*-cymene with 10% palladium-charcoal in the usual manner. The product was recrystallized from dimethyl sulfoxide; m.p. 249–250°, ϵ_{max} (ethoxyethanol) 10×10^4 (257 $m\mu$).

Anal. Calcd. for $C_{64}H_{38}$: C, 94.42; H, 5.58. Found: C, 94.24; H, 5.56.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND, COLLEGE PARK, MD.]

Branched Polyphenyls

BY G. FORREST WOODS, JOHN C. OPPELT AND ROBERT B. ISAACSON

RECEIVED OCTOBER 30, 1959

Two methods have been developed and employed for the synthesis of several branched polyphenyls.

Previous papers¹ from this Laboratory have dealt with the linear or normal polyphenyls up to the noviphenyls. In this paper, the synthesis and properties of several examples of branched polyphenyls² are reported.

Of the possible methods of synthesis of branched polyphenyls we have explored the reaction of cyclohexenones with aryl Grignard reagents or lithium derivatives. The branching can be a consequence of a structural feature of the ketone (as shown below) or in the organometallic (as is indicated later in the formula sequence I \rightarrow V).

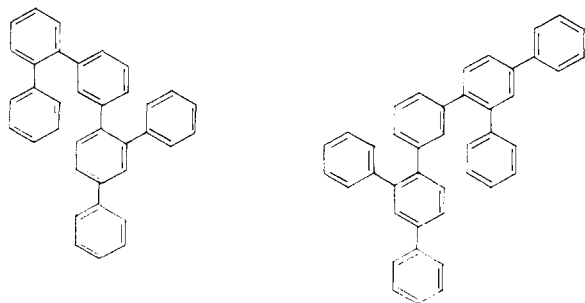
The diketone I³ is converted readily to its enol ether II⁴; and the cyclohexenones III which were prepared by the reaction of II with organometallic reagents are listed in Table I along with certain physical properties.

Treatment of the disubstituted cyclohexenones with the appropriate Grignard reagent or organo-

(1) G. F. Woods, D. D. Centola, H. E. Ruskie and C. D. Miller, *THIS JOURNAL*, **82**, 5227 (1960).

(2) In order to designate the mode of linkages of the aromatic nuclei in the polyphenyls and to locate a substituent on a nucleus in the polyphenyl chain it is recommended that: (1) Arabic numerals be employed to designate the mode (*o*-, *m*-, *p*-) of linkage of the aromatic nuclei; and (2) that Roman numerals be employed to designate the particular ring to which a substituent is attached. It is also suggested that Arabic numerals be used to indicate the position of a substituent on a particular nucleus.

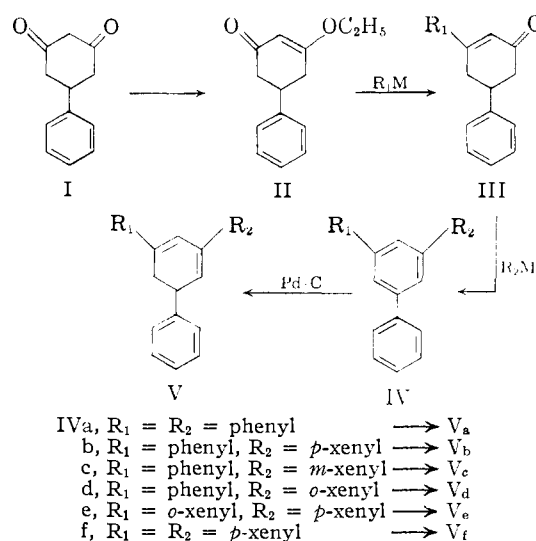
The following two examples make obvious the application of these recommendations which are employed in this and subsequent manuscripts.



II-Phenyl-[3]-quinque[4,3,2]phenyl
II-Phenyl-[3]-
IV-Phenyl-[2]-quinque[4,3,4]phenyl

(3) D. Vorlander, *Ber.*, **27**, 2053 (1894); Q. Michael and P. C. Freer, *J. prakt. Chem.*, **II**, **43**, 390 (1891).

(4) R. L. Frank and H. K. Hall, *THIS JOURNAL*, **72**, 1645 (1950).



lithium compound provided trisubstituted cyclohexadienes IV.

Certain of the dienes could not be induced to crystallize. We believe that certain factors contribute to this: (1) products with *meta* or *ortho* linkages are always more difficult to obtain in a crystalline state. (2) Although we have written a precise dienic structure, no evidence has been obtained which excludes the possibility of rearrangement of ethylenic links. Indeed, alternate preparations of a given diene usually seem to lead to a product of the same composition instead of dienic isomers as shown

