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Polyphenyl Synthesis by Means of the Kharash-type Grignard Cross-coupling Reaction[1)]

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A series of twenty-seven polyphenyls, including quater- to sexiphenyls, was synthesized by the cross-coupling reaction of aryl Grignard reagents with arylene diiodides in the presence of bis(acetylacetonato)nickel(II). Twenty of them were obtained in fairly good yields (50—95%) under mild conditions at temperatures below *ca.* 60°C in ether–benzene solution within a few hours. In the cases of the remaining seven polyphenyls, however, lower yields (1—34%) were inevitable owing to the sterically crowded geometry of the reactant(s). Thus, the Kharash-type Grignard cross-coupling reaction was proved to be an efficient and convenient method for synthesizing a variety of polyphenyls, except in the cases of reactants with remarkably crowded geometry.

The infrared, ultraviolet, and proton magnetic resonance spectral properties of several polyphenyls including three new compounds, 3-(2-biphenylyl)-*o*-quaterphenyl, 6′-(3-biphenylyl)-*m*-quaterphenyl, and 3,4′-di(2-biphenylyl)biphenyl, are presented and discussed.

Keywords——Ni-complex-catalyzed cross-coupling; quaterphenyls; quinquephenyls; sexiphenyls; IR; UV; ^{1}H-NMR; polyphenyls

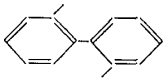
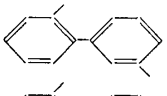
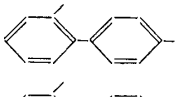
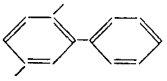
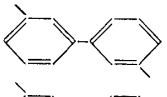
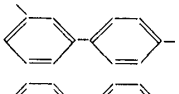
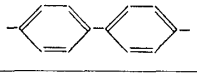
In the previous paper, the cross-coupling reactions of aryl Grignard reagents and aryl halides catalyzed by bis(acetylacetonato)nickel(II) ($Ni(acac)_2$) were extensively investigated to establish efficient syntheses of various types of polyphenyls.[2)] Thus, the standard reaction conditions, which generally resulted in quantitative formation of polyphenyl within a few hours, have been established.

On the basis of the results thus obtained, we have studied the preparation of twenty-seven closely related quater- to sexiphenyls of symmetrical or unsymmetrical type using the Kharash-type Grignard cross-coupling reaction. A series of very pure polyphenyls was obtained in high yields, though a few coupling reactions with reactants having highly crowded geometry gave low yields. The relation between the structures of the reactants and the yields of polyphenyls, and the infrared (IR), ultraviolet (UV), and proton magnetic resonance (^{1}H-NMR) spectral properties of several polyphenyls, including three new compounds, are discussed.

The preparation of polyphenyls (**1**—**27**), ranging from quater- to sexiphenyls, was carried out by the Kharash-type cross-coupling reaction of aryl Grignard reagents and diiodo compounds in the presence of $Ni(acac)_2$. Seven quaterphenyls, *o*-quaterphenyl (**1**), 2-phenyl-*m*- (**2**), 2-phenyl-*p*- (**3**), and 2′-phenyl-*p*-terphenyl (**4**), *m*-quaterphenyl (**5**), 3-phenyl-*p*-terphenyl (**6**), and *p*-quaterphenyl (**7**), were prepared by the coupling reaction of phenylmagnesium bromide (two equivalents) and the corresponding diiodobiphenyl (**28**—**34**) in ether–benzene mixture in the presence of a catalytic amount of $Ni(acac)_2$ (0.5%, based on the Grignard reagent used). Similarly, six quinquephenyls, *o*-quinquephenyl (**8**), 3,3″-diphenyl-*o*-terphenyl (**9**), 2,2″-diphenyl-*m*-terphenyl (**10**), *m*-quinquephenyl (**11**), 2,2″-diphenyl- (**12**), and 3,3″-diphenyl-*p*-terphenyl (**13**), were prepared by the cross-coupling of Grignard reagent (two equivalents) derived from **38** or **39** and the corresponding diiodobenzene (**35**—**37**). Further, fourteen sexiphenyls, *o*-sexiphenyl (**14**), 3,3‴-diphenyl-*o*- (**15**), 3-(2-biphenylyl)-*o*- (**16**), 2-(3-biphenylyl)-*m*- (**17**), 4-(2-biphenylyl)-*o*-quaterphenyl (**18**), 2,4′-di(3-biphenylyl)biphenyl (**19**), 5′-(2-biphenylyl)-*o*- (**20**), 6′-(3-biphenylyl)- (**21**), 2,2‴-diphenyl-*m*-quaterphenyl (**22**), *m*-sexiphenyl (**23**), 3,4′-di(2-biphenylyl)biphenyl (**24**), 4-(3-biphenylyl)-*m*- (**25**), 2,2‴-diphenyl-*p*- (**26**), and 3,3‴-

Table I. Syntheses of Quaterphenyls[a]

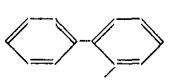
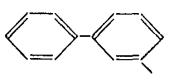
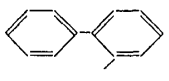
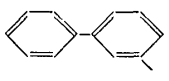
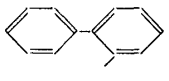
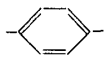
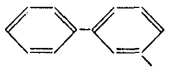
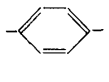
$$Ar\cdot MgBr + I\cdot Ar'\cdot I \xrightarrow[\text{in E-B(1:1)}]{Ni(acac)_2} \underset{A}{Ar\cdot Ar'\cdot Ar} + \underset{B}{Ar\cdot Ar'\cdot I} + Ar\cdot Ar$$

Ar	Ar′	Conversion of I·Ar′·I[b] (%)	Yield, % Ar·Ar′·Ar[c]	A[c]	B[d]
		93[e]	**1**, 12	8[b]	40
		100	**2**, 56	8[b,f]	32
		100	**3**, 84	0	29
		100	**4**, 80	0	32
		100	**5**, 77	0	30
		100	**6**, 84	0	26
		100	**7**, 95	0	7

a) Molar ratio (ArMgBr/IAr′I): 4.
b) Determined by GLPC using an internal standard unless otherwise noted.
c) Based on the IAr′I used.
d) Based on the ArMgBr used.
e) Calculated from recovered IAr′I.
f) Composed of 3-iodo-*o*-terphenyl (3.4%) and 2-iodo-*m*-terphenyl (4.4%).

Table II. Syntheses of Quinquephenyls[a]

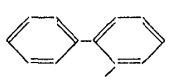
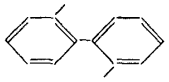
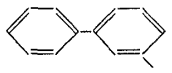
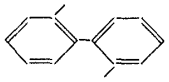
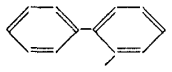
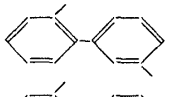
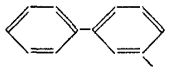
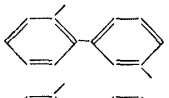
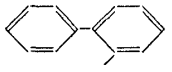
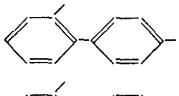
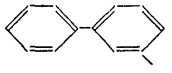
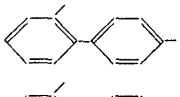
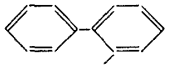
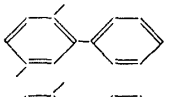
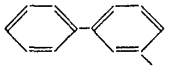
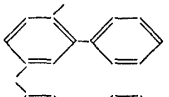
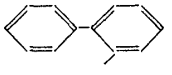
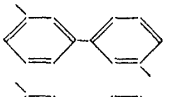
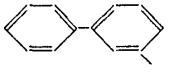
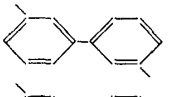
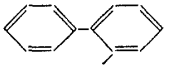
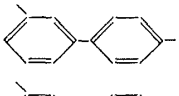
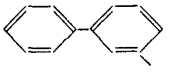
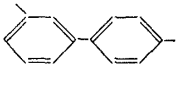
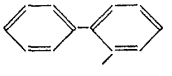
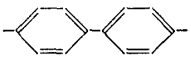
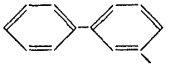
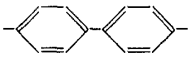
$$Ar\cdot MgBr + I\cdot Ar'\cdot I \xrightarrow[\text{in E-B(1:1)}]{Ni(acac)_2} \underset{A}{Ar\cdot Ar'\cdot Ar} + \underset{B}{Ar\cdot Ar'\cdot I} + \underset{C}{Ar\cdot Ar} + \underset{D}{ArH} + Ar\cdot Ar'H$$

Ar	Ar′	Conversion of I·Ar′·I[b] (%)	Yield, % Ar·Ar′·Ar[c]	A[c]	B[d]	C[d]	D[c]
		100	**8**, 26	0	20	36	24[b]
		100	**9**, 28	0	19	35	17
		100	**10**, 76	0	6	32	0
		100	**11**, 50	2	14	36	0
		100	**12**, 81	0	12	35	0
		100	**13**, 71	0	12	15	0

a—*d*) Refer to the footnotes to Table I.

TABLE III. Syntheses of Sexiphenyls[a)]

$$Ar\cdot MgBr + I\cdot Ar'\cdot I \xrightarrow[\text{in E-B(1:1)}]{Ni(acac)_2} \underset{A}{Ar\cdot Ar'\cdot Ar} + \underset{B}{Ar\cdot Ar'\cdot I} + \underset{C}{Ar\cdot Ar} + ArH$$

Ar	Ar′	Conversion of I·Ar′·I[b)] (%)	Yield, % Ar·Ar′·Ar[c)]	A[c)]	B[d)]	C[d)]
		60	**14**, 1[b)]	0	19[b)]	75[b)]
		57	**15**, 2[b)]	0	20[b)]	78[b)]
		100	**16**, 33	14[e,f)]	22	35
		100	**17**, 34	20[e,g)]	21	37
		100	**18**, 50	13[b,h)]	19	40
		100	**19**, 88	0	18	33
		100	**20**, 58	0	16	19
		100	**21**, 92	0	16	34
		100	**22**, 87	0	20	40
		100	**23**, 84	0	25	35
		100	**24**, 86	0	23	37
		100	**25**, 91	0	21	43
		100	**26**, 77	0	28	36
		100	**27**, 69	0	10	17

a—*d*) Refer to the footnotes to Table I.
e) Calculated from the peak area in GLPC without any calibration.
f) Composed of 3-iodo-*o*-quaterphenyl (3%) and 2-iodo-2″-phenyl-*m*-terphenyl (11%).
g) Composed of 3-iodo-3″-phenyl-*o*-terphenyl (10%) and 2-iodo-*m*-quaterphenyl (10%).
h) Composed of 4-iodo-*o*-quaterphenyl (2%) and 2-iodo-2″-phenyl-*p*-terphenyl (11%).

diphenyl-*p*-quaterphenyl (**27**), were analogously prepared by the cross-coupling of Grignard reagent (two equivalents) derived from **38** or **39** and the corresponding diiodobiphenyl (**28**—**34**). The polyphenyls and by-products thus obtained are summarized in Tables I—III.

These polyphenyls (**1**—**13** and **16**—**27**) were identified from the spectral (IR and UV) data, elemental analysis data, and molecular weight, or by mixed melting point determination and comparison of the IR spectra with those of authentic samples prepared by means of the Ullmann reaction.

The tables show that the yields of twenty polyphenyls are fairly high (50—95%), while

those of the remaining seven congeners (**1**, **8**, **9**, and **14**—**17**) are low (1—34%). The relation between the yields of cross-coupling products and the structures of the reactants may be outlined as follows.

1) In the case of the preparation of quinquephenyls by the use of diiodobenzene, the yield of cross-coupling product decreases in the order *p*->*m*->*o*-diiodobenzene.[3] 2) In the case of the preparation of quater- and sexiphenyls by the use of 2,2′-diiodobiphenyl (**28**), the cross-coupling reaction affords extremely low yields of the corresponding polyphenyls (**1**, 12%; **14**, 1%; **15**, 2%). Under modified forced conditions, however, the yield of **1** could be improved to 52%, while that of **14** was unchanged.[4] 3) In the preparations by the use of 2,3′- (**29**), 2,4′- (**30**), and 2,5-diiodobiphenyl (**31**), the yields of the corresponding polyphenyls increased in the above order of the diiodobiphenyls. On the basis of these results, together with the fact that the cross-coupling using reactants of uncrowded or even slightly crowded geometry generally proceeded stoichiometrically, it could be concluded that the lower yields of the cross-coupling products were due to the crowded geometry of the reactants.

In other words, most of the coupling reactions of aryl Grignard reagents ArMgBr (two equivalents) and arylene diiodides $Ar'I_2$ in the presence of a catalytic amount of $Ni(acac)_2$ proceeded highly selectively and almost quantitatively within a few hours under mild conditions at temperatures below *ca.* 60°C in ether–benzene solution. Furthermore, since the usual by-products Ar·Ar and/or Ar·H were readily separable by column chromatography, the desired polyphenyls could be obtained in high purity.

Thus, the Kharash-type Grignard cross-coupling reaction was established as an efficient and convenient method[5] for laboratory syntheses of a variety of polyphenyls, except in the case of reactants of extremely crowded geometry.

Table IV. Positions and Tentative Assignments of Characteristic Bands in the IR Spectra (690—920 cm^{-1}) of Polyphenyls[a]

4	698	s	γ_{C-C}
	715	w	
	743	m	γ_{C-H}(M)
	756	s	
	771	m	
	781	m	
	837	m	γ_{C-H}(as)
	845	w	
	903	m	γ_{C-H}(as)
	912	w	γ_{C-H}(M)
	921	w	
8	693	s	γ_{C-C}
	698	s	
	704	sh, m	
	721	w	
	739	s	γ_{C-H}(M)
	749	s	
	756	s	
	768	m	γ_{C-H}(*o*)
	776	m	
	867	w	
	873	w	
	907	w	γ_{C-H}(M)
	913	w	
9	691	s	γ_{C-C}
	698	s	
	709	m	
	713	s	
	748	s	γ_{C-H}(M, *o*)
	754	s	
	765	s	
	799	m	γ_{C-H}(*m*)
	813	m	
	833	w	
	842	w	
	898	m	γ_{C-H}(*m*)
16	701	s	γ_{C-C}
	744	s	γ_{C-H}(M)
	755	s	
	772	m	γ_{C-H}(*o*)
	779	s	
	807	m	γ_{C-H}(*m*)
	845	w	
	879	w	
	897	w	γ_{C-H}(*m*)
	910	w	γ_{C-H}(M)
	922	w	
19	703	s	γ_{C-C}
	746	m	γ_{C-H} (M. *o*)
	754	s	
	766	m	
	802	m	γ_{C-H}(*m*)
	807	sh, m	
	843	m	γ_{C-H}(*p*)
	878	vw	γ_{C-H}(*m*)
	897	w	
21	700	s	γ_{C-C}
	742	m	γ_{C-H}(M)
	756	s	
	775	s	
	794	m	γ_{C-H}(*m*)
	802	sh, m	
	836	m	γ_{C-H}(as)
	847	w	
	887	m	γ_{C-H}(*m*, as)
	896	w	
	905	w	
24	703	s	γ_{C-C}
	715	w	
	746	s	γ_{C-H}(M, *o*)
	758	s	
	766	s	
	781	m	γ_{C-H}(*o*)
	800	m	γ_{C-H}(*m*)
	845	m	γ_{C-H}(*p*)
	896	w	γ_{C-H}(*m*)
	916	w	γ_{C-H}(M)

a) v, very; s, strong; m, medium; w, weak; sh, shoulder. γ_{C-C} and γ_{C-H} refer to vibrations which are primarily out-of-plane C–C, and out-of-plane C–H bending motions. M, *o*, *m*, *p*, and as in parentheses refer to mono-, *ortho*-, *meta*-, *para*-, and asymmetrically-substituted rings.

The IR spectra of the polyphenyls were measured by the KBr-disk method. The characteristic bands (690—920 cm^{-1}) of seven polyphenyls (**4**, **8**, **9**, **16**, **19**, **21**, and **24**) are shown in Table IV; these bands are consistent with the kinds of benzene rings constituting each polyphenyl.

A series of strong or medium bands in the 742—781 cm^{-1} region of **4** and **21**, each of which contains 1,2,4-trisubstituted rings, should be assigned to C–H out-of-plane deformation vibrations of five adjacent hydrogens in the terminal rings. Although this region includes absorptions at rather higher frequencies than the 730—770 cm^{-1} region noted by Bellamy[6] and others,[7] the present assignments can be supported on the basis of analogous examples, each of which contains 1,2,4-trisubstituted rings, as discussed previously.[8]

The ^{1}H-NMR spectra of the seven polyphenyls were measured at 80 MHz in $CDCl_3$ solution. The sharp 10H singlet (δ 7.32) in the spectrum of **9** is assignable to the protons of both terminal phenyl rings by analogy with the spectrum of the 3′-phenyl protons of **2** (δ 7.33).[9] The same analogy is also applicable to the assignment of the 5H singlet of **19** (δ 7.30) to the phenyl protons of the *o*-C_6H_4·*m*-C_6H_4·C_6H_5 unit. Further, an apparent 4H AA′BB′-q pattern of **19** (δ 7.29 and 7.52, J=8.6 Hz) can be assigned to the *p*-phenylene protons at the $C_{2',6'}$- and $C_{3'}$, $C_{5'}$-positions, by comparison with the spectrum of the *p*-phenylene protons of **3** (δ 7.20 and 7.47, AA′BB′-q, J=8.6 Hz, 2′-, 6′-H and 3′-, 5′-H).[9]

The spectrum of **21** showed two 5H singlets at δ 7.27 and 7.33 which may be assigned to the phenyl protons of a branched ring and of biphenylyl ring at the 6′-position of the *m*-quaterphenyl skeleton, respectively, by comparison with the spectrum of the 2- and 3′-phenyl protons of **2** (δ 7.22 and 7.33).[9]

In the case of **24**, the spectrum displayed two 5H singlets (δ 7.19 and 7.20), a 4H singlet

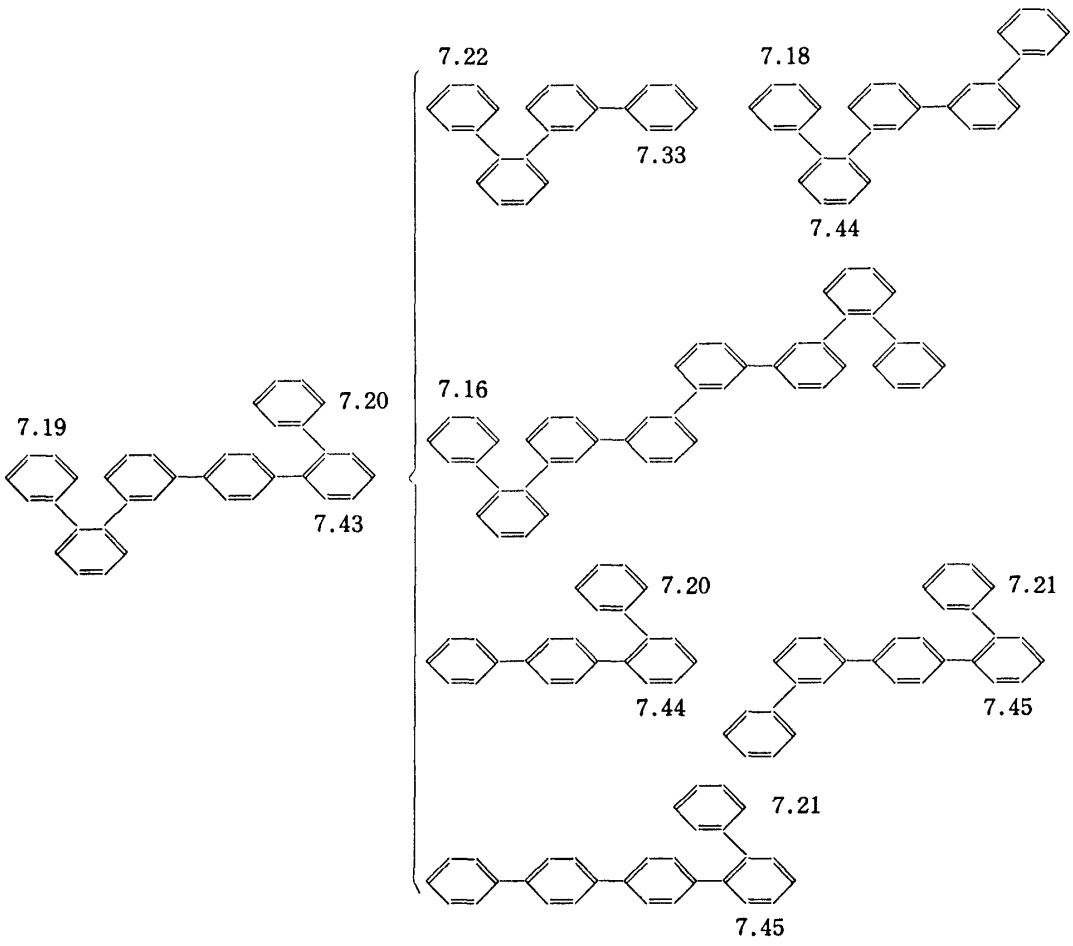


Chart 1

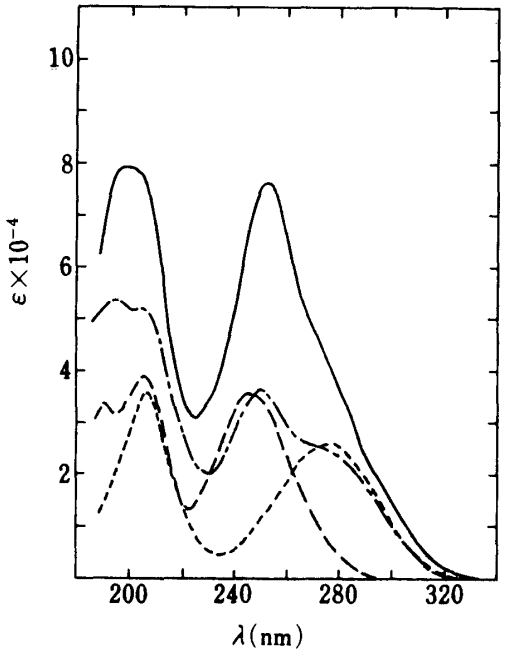


Fig. 1. UV Spectra of Terphenyls, Quaterphenyl, and Sexiphenyl

———: 6′-(3-biphenylyl)-*m*-quaterphenyl (**21**),
—·—·—: 2′-phenyl-*p*-terphenyl (**4**),
– – – –: *m*-terphenyl,
--------: *p*-terphenyl.

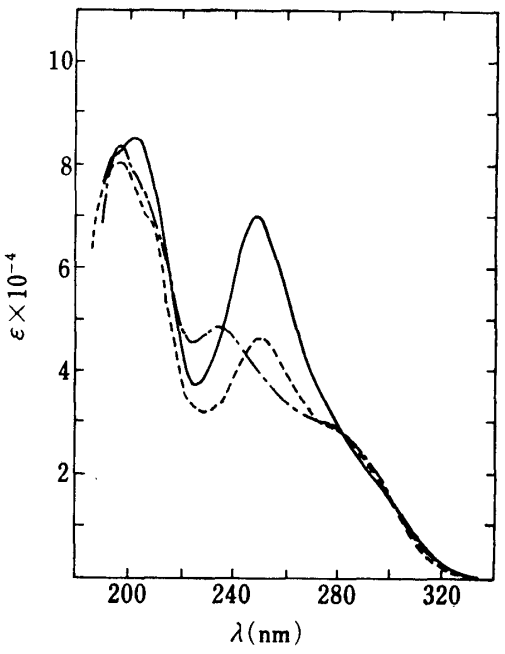


Fig. 2. UV Spectra of Quinquephenyl and Sexiphenyls

———: 2,4′-di(3-biphenylyl)biphenyl (**19**),
—·—·—: 3,4′-di(2-biphenylyl)biphenyl (**24**),
--------: 2,3″-diphenyl-*p*-terphenyl.

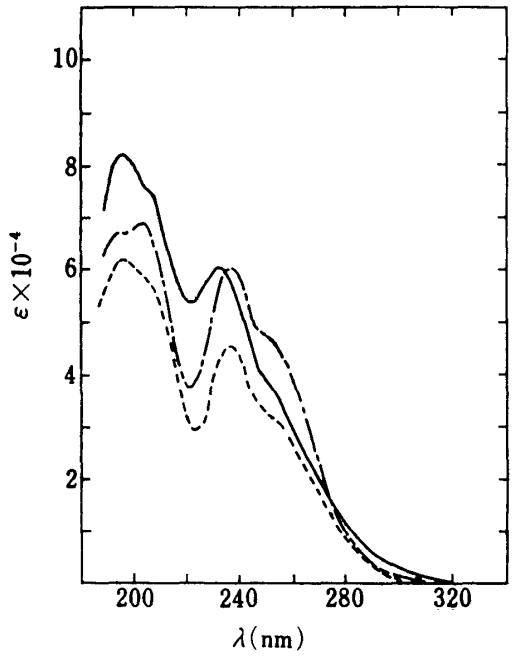


Fig. 3. UV Spectra of Quaterphenyl, Quinquephenyl, and Sexiphenyl

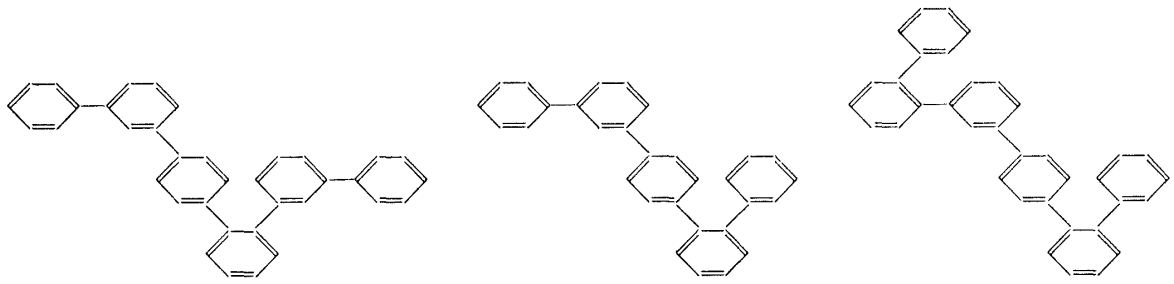
———: 3-(2-biphenylyl)-*o*-quaterphenyl (**16**),
—·—·—: 3,3″-diphenyl-*o*-terphenyl (**9**),
--------: 2-phenyl-*m*-terphenyl (**2**).

(δ 7.43), and a multiplet (δ 6.95—7.55). The three singlets can be assigned as shown in the chart 1 by comparison with the spectra of reference compounds.[8-11] The remaining polyphenyls **8** and **16** showed multiplets which are difficult to assign.

The UV spectra of seven polyphenyls were measured in cyclohexane solution. The absorption curves are shown in Figs. 1—3. The K-band of **4** (250 nm, ε=35500; 266 (sh) nm, 25700), which contains *m*- and *p*-terphenyl units, appeared at wavelengths similar to those of the K-band of *m*-terphenyl (247 nm, 36100) and of *p*-terphenyl (276 nm, 25500) (Fig. 1). The spectral differences between **21** and **4**, an increase in the intensity of the band near 250 nm and diminution of the band near 270 nm to a shoulder in **21**, can reasonably be ascribed to the structural difference, an increase of two *m*-phenylene units at the termini of **4**.

Of the spectra of two sexiphenyls **19** and **24**, which have a common structural unit of 2,3″-diphenyl-*p*-terphenyl (250, 46200; 275 (sh), 29300),[11] the former showed an increase in the intensity of the band near 250 nm (69700) and diminution of the band near 275 nm to a

shoulder as compared with those of the structural unit. On the other hand, the latter showed a remarkable blue shift (237, 49300) of the band near 250 nm, and a similar shoulder near 275 nm (Fig. 2). These spectral differences are fully compatible with the addition of an *m*-phenylene unit to the common structural unit to give an *o*-C_6H_4·*m*-C_6H_4·C_6H_5 moiety and of an *o*-phenylene unit to give a C_6H_5·*o*-C_6H_4·*m*-C_6H_4 moiety, respectively.



19 **24**

Chart 2

The K-bands of **9** (237, 61300; 249 (sh), 48300) and **16** (232, 60900; 250 (sh), 39000) were rather similar to each other and were also closely correlated to that of the common structural unit of 2-phenyl-*m*-terphenyl (**2**) (237, 44000; 251 (sh), 32400) (Fig. 3).

The foregoing results suggest that the unsymmetrical sexiphenyls show absorption curves intimately related to those of quater- or quinquephenyl corresponding to their partial structures.

Experimental

Instruments——The melting points of the polyphenyls were determined with a Mettler FP-51 apparatus except for those above 300°C, which were determined with a Shimadzu DSC-30M differential scanning calorimeter. The UV spectra were measured on a Shimadzu MPS-50L spectrophotometer, and the ^{1}H-NMR spectra on a Varian CFT-20 spectrometer at 80 MHz, using tetramethylsilane as an internal standard. The mass spectra (MS) were recorded on a Hitachi RMU-6E mass spectrometer, and the IR spectra on a Leitz III-G spectrophotometer. Quantitative gas liquid partition chromatography (GLPC) was performed on a Shimadzu GC-5APTF gas chromatograph using a 1 m × 3 mmϕ glass column of 3% Dexil 300GC on Chromosorb W AW-DMCS.

Materials——Among the intermediate diiodo compounds used, 2,2′- (**28**), 2,3′- (**29**), 2,4′- (**30**), 2,5- (**31**), 3,3′-(**32**), 3,4′- (**33**), and 4,4′-diiodobiphenyl (**34**) were prepared by the methods reported previously.[9,12] 2- (**38**) and 3-Bromobiphenyl (**39**) were prepared by means of the Sandmeyer reaction of the corresponding aminobiphenyls.[10] The following materials were obtained commercially. Bromobenzene and *o*-diiodobenzene (**35**) were purified by distillation before use. *m*- (**36**) and *p*-Diiodobenzene (**37**), *o*-, *m*-, and *p*-terphenyl were purified by recrystallization. Diethyl ether and benzene were distilled and dried over sodium wire. Bis(acetylacetonato)nickel(II) was used without further purification. 2-Iodo-*o*-, 3-iodo-*o*-, and 2-iodo-*m*-terphenyl, 4-iodo-*o*-quaterphenyl, 2-iodo-2″-phenyl-*p*-terphenyl, *o*-sexiphenyl, and 3,3‴-diphenyl-*o*-quaterphenyl used were authentic samples prepared previously.[8,13]

General Procedure for the Preparation of Quaterphenyls——Magnesium turnings (0.19 g, 8 mg-atom) were placed in a four-necked round-bottomed flask equipped with a reflux condenser. About one-third of an ethereal solution of bromobenzene (1.26 g, 8 mmol in 20 ml) was added to the flask under a nitrogen atmosphere, and the mixture was stirred and heated, if necessary, to initiate the reaction. The remaining bromobenzene solution was added dropwise rapidly enough to maintain a gentle reflux. After a further 0.5 h of heating, the resulting solution was cooled to 0°C. To this Grignard reagent, a mixture of diiodobiphenyl (0.81 g, 2 mmol) and bis(acetylacetonato)nickel(II) (0.006 g, 0.02 mmol) in benzene (20 ml) was added all at once. The whole was stirred at 0°C for 1 h and then refluxed for 3 h. The mixture was hydrolyzed with dilute hydrochloric acid and then extracted with benzene. The organic layer was separated, washed with dilute hydrochloric acid, sodium carbonate solution, sodium thiosulfate solution, and finally with water, then dried. To a twentieth part of this solution, a known quantity of *m*-terphenyl or an appropriate internal standard calibrated against pure authentic samples was added, and the mixture was subjected to GLPC for determination of the products and starting materials. The remainder of the dried organic layer was subjected to isolation of the products. After the removal of the solvent, the resulting solid was

chromatographed on alumina using cyclohexane and cyclohexane–benzene mixtures as eluents to afford each quaterphenyl and by-products.

o-Quaterphenyl (**1**): 2,2′-Diiodobiphenyl (**28**) was treated with phenylmagnesium bromide and worked up as described in the general procedure. The eluate with cyclohexane gave biphenyl (**40**) as colorless leaves (from methanol), mp 70.1°C, 236 mg (40%) [55%].[14] The eluate with a cyclohexane–benzene (9: 1, v/v) mixture (C–B (9: 1)) provided unchanged **28** as pale yellow needles (ethanol), mp 108.4°C, 54 mg (7.0%) [4.9%] and **1**. Besides these, the formation of 2-iodo-*o*-terphenyl was confirmed by GLPC [8.4%]. **1**: Colorless cubes (ethanol), mp 118.5°C (lit.[12] mp 118—119°C, lit.[15] mp 118°C), 72 mg (12%) [10%].

2-Phenyl-*m*-terphenyl (**2**): 2,3′-Diiodobiphenyl (**29**) was treated with phenylmagnesium bromide and worked up as in the general procedure. The eluate with C–B (9: 1) gave **40** (32%) [33%]. The eluates with C–B (9: 1) and C–B (4: 1) afforded **2**. Besides these, 3-iodo-*o*- [3.4%] and 2-iodo-*m*-terphenyl [4.4%] were confirmed to be present by GLPC. **2**: Colorless needles (ethanol), mp 91.8°C (lit.[13] mp 91—92°C, lit.[16] mp 88.7—89.2°C), 327 mg (56%) [56%].

2-Phenyl-*p*-terphenyl (**3**): 2,4′-Diiodobiphenyl (**30**) was treated with phenylmagnesium bromide. The eluate with C–B (9: 1) gave **40** (29%) [35%]. The eluates with C–B (4: 1) and C–B (2: 1) afforded **3**. **3**: Colorless needles (ethanol), mp 119.7°C (lit.[12] mp 116—118°C, lit.[17] mp 119—119.5°C), 486 mg (84%) [85%].

2′-Phenyl-*p*-terphenyl (**4**): 2,5-Diiodobiphenyl (**31**) was treated with phenylmagnesium bromide. The eluate with cyclohexane gave **40** (32%) [31%]. The eluates with C–B (9: 1) and C–B (4: 1) afforded **4**. **4**: Colorless needles (ethanol), mp 99.8°C (lit.[18] mp 99—100°C, lit.[7] mp 96—97°C), 465 mg (80%) [81%]. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 193 (53300), 204 (51700), 250 (35500), 266 (sh) (25700). ^{1}H-NMR ($CDCl_3$) δ: 7.20 (5H, s, 1′-C_6H_5), 7.22 (5H, s, 2′-C_6H_5), 7.32—7.71 (8H, m, C_6H_3 and 4′-C_6H_5). *Anal.* Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.28; H, 6.19. MS *m/e*: 306 (M^+).

m-Quaterphenyl (**5**): 3,3′-Diiodobiphenyl (**32**) was treated with phenylmagnesium bromide. The eluate with cyclohexane gave **40** (30%) [29%]. The eluates with C–B (9: 1) and C–B (4: 1) afforded **5**. **5**: Colorless needles (ethanol), mp 89.1°C (lit.[12] mp 86—87°C, lit.[19] mp 86.5—87.3°C), 447 mg (77%) [85%].

3-Phenyl-*p*-terphenyl (**6**): 3,4′-Diiodobiphenyl (**33**) was treated with phenylmagnesium bromide. The eluate with C–B (9: 1) gave **40** (26%) [29%]. The eluates with C–B (2: 1) and C–B (1: 1) afforded **6**. **6**: Colorless cubes (ethanol–benzene), mp 167.1°C (lit.[12] mp 164—165°C, lit.[20] mp 166—167°C), 490 mg (84%) [82%].

p-Quaterphenyl (**7**): 4,4′-Diiodobiphenyl (**34**) was treated with phenylmagnesium bromide. The eluate with benzene gave **40** (6.6%) [6.1%] and **7**. **7**: Colorless leaves (benzene), mp 319°C (lit.[12] mp 318—319°C, lit.[21] mp 317.7—318.7°C), 552 mg (95%) [97%].

General Procedure for the Preparation of Quinquephenyls——An ethereal solution of biphenylylmagnesium bromide was prepared from biphenylyl bromide (1.86 g, 8 mmol), magnesium turnings (0.19 g, 8 mgatom), and absolute ether (20 ml) under a nitrogen atmosphere. To this Grignard reagent, a mixture of diiodobenzene (0.66 g, 2 mmol) and bis(acetylacetonato)nickel(II) (0.009 g, 0.035 mmol) in benzene (20 ml) was added all at once. The whole was stirred for 1 h at 0°C, then refluxed for 3 h. The reaction mixture was worked up as described for quaterphenyl preparation.

o-Quinquephenyl (**8**): *o*-Diiodobenzene (**35**) was treated with Grignard reagent prepared from 2-bromobiphenyl (**38**) and worked up as described in the general procedure. The eluates with cyclohexane and C–B (9: 1) gave **40** (36%) [36%] and **1** (20%) [18%], respectively. The eluates with C–B (9: 1) and C–B (4: 1) afforded **8**. Beside these, the formation of *o*-terphenyl was confirmed by GLPC [24%]. **8**: Colorless needles (ethanol–benzene), mp 152.4°C (lit.[22] mp 154—156.5°C), 188 mg (26%) [24%]. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 197 (70800), 237 (46200). ^{1}H-NMR ($CDCl_3$) δ: 5.93—7.43 (22H, m, all protons). *Anal.* Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.27; H, 5.89. MS *m/e*: 382 (M^+).

3,3″-Diphenyl-*o*-terphenyl (**9**): *o*-Diiodobenzene (**35**) was treated with Grignard reagent prepared from 3-bromobiphenyl (**39**) and worked up as described above. The eluate with cyclohexane gave **40** (35%) [34%] and *m*-terphenyl, mp 85.8°C, 74 mg (17%) [27%]. The eluate with C–B (9: 1) gave **5** (19%) [16%]. The eluates with C–B (9: 1) and C–B (4: 1) afforded **9**. **9**: Colorless cubes (ethanol–benzene), mp 127.4°C (lit.[23] mp 125.6—125.9°C), 206 mg (28%) [27%]. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 193 (sh) (67000), 203 (70000), 237 (61300), 249 (sh) (48300). ^{1}H-NMR ($CDCl_3$) δ: 7.12—7.55 (12H, m, C_6H_4), 7.32 (10H, s, C_6H_5). *Anal.* Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.24; H, 5.99. MS *m/e*: 382 (M^+).

2,2″-Diphenyl-*m*-terphenyl (**10**): *m*-Diiodobenzene (**36**) was treated with Grignard reagent prepared from **38**. The eluate with C–B (9: 1) gave **40** (32%) [33%] and **1** (5.8%) [4.8%]. The eluates with C–B (9: 1) and C–B (4: 1) afforded **10**. **10**: Colorless prisms (ethanol), mp 164.2°C (lit.[11] mp 164.2°C, lit.[24] mp 155.5—156.6°C), 552 mg (76%) [80%].

m-Quinquephenyl (**11**): *m*-Diiodobenzene (**36**) was treated with Grignard reagent prepared from **39**. The eluate with cyclohexane gave **40** (36%) [30%]. The eluate with C–B (9: 1) gave 3-iodo-*m*-terphenyl as light yellow prisms (ethanol), mp 61.3°C (lit.[10] mp 61—62°C), 12 mg (1.8%) [2.3%], and **5** (14%) [14%]. The eluates with C–B (9: 1) and C–B (4: 1) afforded **11**. **11**: Colorless needles (ethanol), mp 114.5°C (lit.[11] mp 114.0°C, lit.[25] mp 114—115°C), 361 mg (50%) [56%].

2,2″-Diphenyl-*p*-terphenyl (**12**): *p*-Diiodobenzene (**37**) was treated with Grignard reagent prepared from **38**. The eluate with C–B (5: 1) gave **40** (35%) [33%] and **1** (12%) [10%]. The eluates with C–B (5: 1)

and C–B (5: 2) afforded **12**. **12**: Colorless needles (ethanol–benzene), mp 185.8°C (lit.[11] mp 185.8°C, lit.[26] mp 185.6—185.8°C), 586 mg (81%) [78%].

3,3″-Diphenyl-*p*-terphenyl (**13**): *p*-Diiodobenzene (**37**) was treated with Grignard reagent prepared from **39**. The eluate with C–B (5: 1) gave **40** (15%) [14%] and **5** (12%) [17%]. The eluates with C–B (5: 2) and C–B (5: 3) afforded **13**. **13**: Colorless needles (ethanol–benzene), mp 235.7°C (lit.[11] mp 235.7°C, lit.[26] mp 236.1—236.3°C), 518 mg (71%) [73%].

General Procedure for the Preparation of Sexiphenyls——An ethereal solution of biphenylylmagnesium bromide was prepared from biphenylyl bromide (1.86 g, 8 mmol), magnesium turnings (0.19 g, 8 mg-atom), and absolute ether (20 ml) under a nitrogen atmosphere. To this Grignard reagent, a mixture of diiodobiphenyl (0.81 g, 2 mmol) and bis(acetylacetonato)nickel(II) (0.009 g, 0.035 mmol) in benzene (20 ml) was added all at once. The whole was stirred at 0°C for 1 h and then refluxed for 3 h. The reaction mixture was worked up as described for quaterphenyl preparation.

o-Sexiphenyl (**14**): 2,2′-Diiodobiphenyl (**28**) was treated with Grignard reagent prepared from **38**. The reaction products were shown by GLPC to be **40** [75%], **1** [19%], **28** [40%], and **14** [1.2%].

3,3‴-Diphenyl-*o*-quaterphenyl (**15**): 2,2′-Diiodobiphenyl (**28**) was treated with Grignard reagent prepared from **39**. The reaction products were shown by GLPC to be **40** [78%], **5** [20%], **28** [43%], and **15** [1.7%].

3-(2-Biphenylyl)-*o*-quaterphenyl (**16**): 2,3′-Diiodobiphenyl (**29**) was treated with Grignard reagent prepared from **38**. The eluate with C–B (5: 1) gave **40** (35%) [30%] and **1** (22%) [21%]. Besides these, the presence of 3-iodo-*o*-quaterphenyl [3.0%] and 2-iodo-2″-phenyl-*m*-terphenyl [11%] was determined by GLPC [from the peak areas].[27] The eluate with C–B (5: 2) afforded **16**. **16**: Colorless needles (ethanol–benzene), mp 182.4°C, 290 mg (33%) [30%]. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 195 (83000), 205 (sh) (76400), 232 (60900), 250 (sh) (39000). ^{1}H-NMR ($CDCl_3$) δ: 6.36—7.46 (26H, m, all protons). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.50; H, 5.83. MS *m/e*: 458 (M^+).

2-(3-Biphenylyl)-*m*-quaterphenyl (**17**): 2,3′-Diiodobiphenyl (**29**) was treated with Grignard reagent prepared from **39**. The eluate with C–B (5: 1) gave **40** (37%) [34%] and **5** (21%) [18%]. Besides these, the presence of 3-iodo-3″-phenyl-*o*-terphenyl [10%] and 2-iodo-*m*-quaterphenyl [10%] was determined by GLPC [from the peak areas].[27] The eluate with C–B (5: 2) afforded **17**. **17**: Colorless cubes (ethanol–benzene), mp 55.8°C (lit.[28] mp 60.3°C, lit.[10] mp 58—60°C), 295 mg (34%) [42%].

4-(2-Biphenylyl)-*o*-quaterphenyl (**18**): 2,4′-Diiodobiphenyl (**30**) was treated with Grignard reagent prepared from **38**. The eluate with C–B (5: 1) gave **40** (40%) [37%] and **1** (19%) [17%]. The eluate with C–B (5: 2) afforded **18**. Besides these, 4-iodo-*o*-quaterphenyl [2.0%] and 2-iodo-2″-phenyl-*p*-terphenyl [11%] were confirmed by GLPC. **18**: Colorless prisms (ethanol–benzene), mp 154.1°C (lit.[28] mp 154.9°C), 434 mg (50%) [48%].

2,4′-Di(3-biphenylyl)biphenyl (**19**): 2,4′-Diiodobiphenyl (**30**) was treated with Grignard reagent prepared from **39**. The eluate with C–B (5: 1) gave **40** (33%) [30%] and **5** (18%) [16%]. The eluate with C–B (5: 2) afforded **19**. **19**: Colorless needles (ethanol–benzene), mp 135.7°C (lit.[7] mp 128—130°C, lit.[23] mp 134.0—134.3°C), 764 mg (88%) [90%]. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 195 (sh) (81700), 203 (85100), 249 (69700). ^{1}H-NMR ($CDCl_3$) δ: 7.30 (5H, s, *o*-C_6H_4·*m*-C_6H_4·$C_6\underline{H}_5$), 7.29 and 7.52 (4H, AA′BB′-q, J=8.6 Hz, $C_{2'}$,$C_{6'}$–H and $C_{3'}$,$C_{5'}$–H), 7.76—7.82 (1H, m, *p*-C_6H_4·$C_6\underline{H}$·C_6H_5), 7.16—7.71 (16H, m, other protons). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.58; H, 5.79. MS *m/e*: 458 (M^+).

5′-(2-Biphenylyl)-*o*-quaterphenyl (**20**): 2,5-Diiodobiphenyl (**31**) was treated with Grignard reagent prepared from **38**. The eluate with C–B (5: 1) gave **40** (19%) [18%] and **1** (16%) [19%]. The eluates with C–B (5: 1) and C–B (5: 2) afforded **20**. **20**: Colorless needles (hexane), mp 165.1°C (lit.[28] mp 164.7°C), 505 mg (58%) [68%].

6′-(3-Biphenylyl)-*m*-quaterphenyl (**21**): 2,5-Diiodobiphenyl (**31**) was treated with Grignard reagent prepared from **39**. The eluate with C–B (5: 1) gave **40** (34%) [44%] and **5** (16%) [11%]. The eluates with C–B (5: 1) and C–B (5: 2) afforded **21**. **21**: Colorless needles (ethanol–benzene), mp 174.8°C, 800 mg (92%) [90%]. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 198 (79800), 252 (76200), 273 (infl) (41700). ^{1}H-NMR ($CDCl_3$) δ: 7.27 (5H, s, C_6H_3·$C_6\underline{H}_5$), 7.33 (5H, s, 6′-C_6H_4·$C_6\underline{H}_5$), 7.85—7.93 (1H, m, $C_{2'}$–H), 7.21—7.79 (15H, m, other protons). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.50; H, 5.72. MS *m/e*: 458 (M^+).

2,2‴-Diphenyl-*m*-quaterphenyl (**22**): 3,3′-Diiodobiphenyl (**32**) was treated with Grignard reagent prepared from **38**. The eluate with C–B (5: 1) gave **40** (40%) [41%] and **1** (20%) [18%]. The eluates with C–B (5: 2) and C–B (5: 3) afforded **22**. **22**: Colorless cubes (ethanol–benzene), mp 154.3°C (lit.[12] mp 151.5—152.0°C, lit.[8] mp 151—152°C), 757 mg (87%) [85%].

m-Sexiphenyl (**23**): 3,3′-Diiodobiphenyl (**32**) was treated with Grignard reagent prepared from **39**. The eluate with C–B (5: 2) gave **40** (35%) [41%] and **5** (25%) [27%]. The eluates with C–B (5: 2) and C–B (5: 3) afforded **23**. **23**: Colorless needles (ethanol–benzene), mp 148.8°C (lit.[12] mp 145—146°C, lit.[29] 146—147°C), 730 mg (84%) [92%].

3,4′-Di(2-biphenylyl)biphenyl (**24**): 3,4′-Diiodobiphenyl (**33**) was treated with Grignard reagent prepared from **38**. The eluate with C–B (5: 2) gave **40** (37%) [36%] and **1** (23%) [22%]. The eluates with C–B (5: 2) and C–B (5: 3) afforded **24**. **24**: Colorless cubes (ethanol–benzene), mp 136.7°C, 747 mg (86%) [85%]. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 196 (81500), 203 (sh) (75300), 235 (47500), 248 (sh) (39500), 272 (sh) (30000).

^{1}H-NMR ($CDCl_3$) δ: 7.19 (5H, s, *m*-C_6H_4·*o*-C_6H_4·$C_6\underline{H}_5$), 7.20 (5H, s, *p*-C_6H_4·*o*-C_6H_4·$C_6\underline{H}_5$), 7.43 (4H, s, *p*-C_6H_4·*o*-$C_6\underline{H}_4$), 6.95—7.55 (12H, m, other protons). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.07; H, 5.44. MS *m/e*: 458 (M^+).

4-(3-Biphenylyl)-*m*-quaterphenyl (**25**): 3,4′-Diiodobiphenyl (**33**) was treated with Grignard reagent prepared from **39**. The eluate with C–B (5: 3) gave **40** (43%) [42%] and **5** (21%) [16%]. The eluates with C–B (5: 3), C–B (1: 1), and C–B (1: 2) afforded **25**. **25**: Colorless cubes (benzene), mp 197.5°C (lit.[28] mp 197.0°C, lit.[23] mp 194.0—195.3°C, lit.[18] mp 186—188°C), 791 mg (91%) [94%].

2,2‴-Diphenyl-*p*-quaterphenyl (**26**): 4,4′-Diiodobiphenyl (**34**) was treated with Grignard reagent prepared from **38**. The eluate with C–B (5: 3) gave **40** (36%) [34%] and **1** (8.6%) [7.5%]. The eluates with C–B (5: 3) and C–B (1: 1) afforded **26**. **26**: Colorless needles (benzene), mp 236.1°C (lit.[11] mp 236.1°C, lit.[26] mp 237.9—238.1°C), 670 mg (77%) [86%].

3,3‴-Diphenyl-*p*-quaterphenyl (**27**): 4,4′-Diiodobiphenyl (**34**) was treated with Grignard reagent prepared from **39**. The eluate with C–B (1: 5) gave **40** (18%) [17%] and **5** (10%) [14%]. The eluate with benzene afforded **27**. **27**: Colorless needles (benzene), mp 290.3°C (lit.[12] mp 287—288°C, lit.[30] mp 280—281°C), 599 mg (69%) [75%].

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References and Notes

1) This paper forms Part VIII of "Studies of Polyphenyls and Polyphenylenes." The preceding paper, Part VII: Ref. 2.
2) E. Ibuki, S. Ozasa, Y. Fujioka, and Y. Yanagihara, *Chem. Pharm. Bull.*, **30**, 802 (1982).
3) A preliminary terphenyl preparation by the cross-coupling reaction of phenylmagnesium bromide and each of the diiodobenzenes (**35**—**37**) gave similar results. Thus, the yields of *p*-, *m*-, and *o*-terphenyl were 92, 85, and 35%, respectively.
4) The forcing cross-coupling of phenylmagnesium iodide (three equivalents) and **28** in a hot ether–benzene solution in the presence of $Ni(acac)_2$ (1%) gave **1** in 52% yield. However, under similar forcing conditions but with a more efficient catalyst, Ni(acaen), instead of $Ni(acac)_2$, the coupling of 2-biphenylylmagnesium iodide (three equivalents) and **28** afforded **14** in only 2% yield (*cf.* E. Ibuki, S, Ozasa, Y. Fujioka, and H. Mizutani, *Bull. Chem. Soc. Jpn.*, **55**, 845 (1982).
5) The Ullmann cross-coupling of aryl iodides and arylene diiodides has generally afforded lower yields of polyphenyls as compared with those of the corresponding Grignard cross-coupling reaction (*cf.* Refs. 11 and 12).
6) L.J. Bellamy, "The Infrared Spectra of Complex Molecules," 3rd ed. Chapman and Hall, London, 1975 p. 72.
7) R.C. Doss and P.W. Solomon, *J. Org. Chem.*, **29**, 1567 (1964).
8) E. Ibuki, S. Ozasa, Y. Fujioka, and H. Kitamura, *Chem. Pharm. Bull.*, **28**, 1468 (1980).
9) S. Ozasa, Y. Fujioka, M. Okada, H. Izumi, and E. Ibuki, *Chem. Pharm. Bull.*, **29**, 370 (1981).
10) S. Ozasa, Y. Fujioka, M. Fujiwara, and E. Ibuki, *Chem. Pharm. Bull.*, **28**, 3210 (1980).
11) S. Ozasa, N. Hatada, Y. Fujioka, and E. Ibuki, *Bull. Chem. Soc. Jpn.*, **53**, 2610 (1980).
12) E. Ibuki, S. Ozasa, and K. Murai, *Bull. Chem. Soc. Jpn.*, **48**, 1868 (1975).
13) S. Ozasa, Y. Fujioka, M. Tsukada, and E. Ibuki, *Chem. Pharm. Bull.*, **29**, 344 (1981).
14) Values in brackets were determined by GLPC.
15) J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).
16) C. Beaudet, J. Horlait, A. Marcq, and E. Cassart, *Bull. Soc. Chim. Fr.*, **1964**, 1060.
17) G.F. Woods and F. Scotti, *J. Org. Chem.*, **26**, 312 (1961).
18) G.F. Woods, Wright Air Development Center, Technical Report 59-496 (1959), p. 112.
19) R.L. Alexander, Jr., *J. Org. Chem.*, **21**, 1464 (1956).
20) G.F. Woods and I.W. Tucker, *J. Am. Chem. Soc.*, **70**, 3340 (1948).
21) J.J.E. Schmidt and J.A. Krimmel, *J. Org. Chem.*, **25**, 252 (1960).
22) A substance (3 mg), "probably *o*-quinquephenyl," has been reported as a minor product of the reaction of *o*-dilithiobenzene with ferric chloride in ether at −70°C. G. Wittig and F. Bickelhaupt, *Chem. Ber.*, **91**, 883 (1958).
23) C. Beaudet, J. Horlait, and A. Marcq, *EUR* 295.f (1963).
24) G.F. Woods, A.L. Van Artsdale, and F.T. Reed, *J. Am. Chem. Soc.*, **72**, 3221 (1950).
25) N.B. Sunshine and G.F. Woods, *J. Org. Chem.*, **28**, 2517 (1963).
26) C. Beaudet, J. Horlait, A. Marcq, and G. Belpaire, *EUR* 31.f (1962).
27) The two iodoquaterphenyls were identified on the following basis: i) reasonable formation of intermediate iodo compounds in the preparations of **2** and **18**, ii) the relationship between relative retention

time and structure of polyphenyls and their iodo compounds.
28) S. Ozasa, Y. Fujioka, and E. Ibuki, *Chem. Pharm. Bull.*, **30**, in press.
29) J.A. Cade and A. Pilbeam, *J. Chem. Soc.*, **1964**, 114.
30) G.F. Woods, D.D. Centola, H.E. Ruskie, and C.D. Miller, *J. Am. Chem. Soc.*, **82**, 5227 (1960).