⌈Chem. Pharm. Bull.⌉
⌊29(2) 370—378 (1981)⌋

Syntheses and Physical Properties of Several Deuterium-labelled Polyphenyls[1)]

SHIGERU OZASA,* YASUHIRO FUJIOKA, MOTOFUMI OKADA,
HIROMI IZUMI, and EIICHI IBUKI

Kyoto College of Pharmacy, Misasagi-nakauchi-cho, Yamashina-ku, Kyoto 607, Japan

(Received August 9, 1980)

A Kharash-type Grignard cross-coupling reaction of phenyl-d_5-magnesium bromide and an appropriate diiodo compound in the presence of bis(acetylacetonato)nickel(II) was successfully employed for the syntheses of twelve new decadeuterated polyphenyls, each of which has phenyl-d_5 rings at both termini. On the basis of the nuclear magnetic resonance spectra of the deuterated and normal polyphenyls, close correlations between the apparent signal patterns of phenyl or phenylene groups and the structures of the adjacent groups became apparent. The mass spectral studies revealed that the deuterated polyphenyls containing *o*-linkage(s) were less stable to electron bombardment than those containing no *o*-linkage. Inspection of the ultraviolet spectra of the deuterated polyphenyls showed that the isotope effect in their K-bands was hardly detectable.

Keywords——deuterated polyphenyls; Ni-complex-catalyzed cross-coupling; NMR; MS; UV

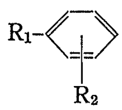
Deuterium labeling has proved to be of great value for the study of reaction mechanisms and for the determination of the structures of chemical substances by means of mass (MS), infrared (IR), or nuclear magnetic resonance (NMR) spectroscopy. However, few studies have been reported on the deuterated polyphenyls, except for work on some deuterated bi- and terphenyls.[2)]

In the previous work,[3)] a series of closely related polyphenyls including quinque- to octiphenyls was synthesized and the relationship between their structures and physical properties was discussed. The present study was undertaken to develop a convenient synthetic method for suitably deuterated polyphenyls, and to elucidate their structure-property correlations, together with their isotope effects. Thus, twelve new decadeuterated polyphenyls (**1a**—**12a**) were synthesized, and their UV, NMR, and MS spectral characteristics were investigated.

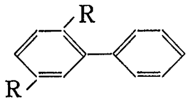
Although the deuterium labeling of organic compounds has now been quite extensively studied,[4)] few reports on syntheses of deuterated polyphenyls have appeared. Methods so far used for deuterated biphenyls and terphenyls are based on the following reactions. 1) Replacement of metal by deuterium.[2a,c)] 2) Replacement of hydrogen by deuterium.[2b,c)] 3) Partial replacement of deuterium by hydrogen *via* intermediates to provide a less-deuterated compound.[2b)] 4) Homo-coupling of a Grignard reagent derived from a deuterated bromo compound.[2a,c)] 5) Grignard reaction: an appropriate Grignard reagent derived from a deuterated bromoaryl is reacted with a deuterated arylcyclohexanone followed by dehydrogenation with bromine.[2c)] Among them, methods 1—4 have the disadvantage of limited applicability to compounds of specific structure. Method 5 is inferior to the other methods because it requires many steps and hence offers a very low overall yield.

Recently, Corriu and Masse[5)] have developed a synthetic method for *p*-terphenyl by the reaction of phenylmagnesium bromide and *p*-dibromobenzene in the presence of nickel(II) complex. More recently, this Kharash-type Grignard cross-coupling reaction has been applied to the syntheses of several octiphenyls in our laboratory.[3d,e)]

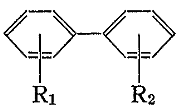
In the present study, the Kharash-type reaction was also employed for the effective syntheses of deuterated polyphenyls. Thus, the attempted Grignard cross-coupling reaction of the Grignard reagent derived from bromobenzene-d_5 (**15**) and appropriate diiodo aromatics



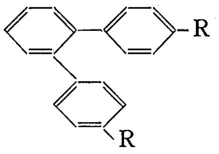
1a: $R_1=C_6D_5$, $R_2=2\text{-}C_6D_5$
1b: $R_1=C_6H_5$, $R_2=2\text{-}C_6H_5$
2a: $R_1=C_6D_5$, $R_2=3\text{-}C_6D_5$
2b: $R_1=C_6H_5$, $R_2=3\text{-}C_6H_5$
3a: $R_1=C_6D_5$, $R_2=4\text{-}C_6D_5$
3b: $R_1=C_6H_5$, $R_2=4\text{-}C_6H_5$
16: $R_1=I$, $R_2=2\text{-}I$
17: $R_1=I$, $R_2=3\text{-}I$
18: $R_1=I$, $R_2=4\text{-}I$



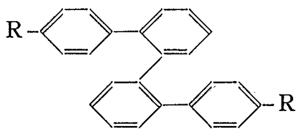
10a: $R=C_6D_5$
10b: $R=C_6H_5$
25: $R=I$



4a: $R_1=2\text{-}C_6D_5$, $R_2=2'\text{-}C_6D_5$
4b: $R_1=2\text{-}C_6H_5$, $R_2=2'\text{-}C_6H_5$
5a: $R_1=3\text{-}C_6D_5$, $R_2=3'\text{-}C_6D_5$
5b: $R_1=3\text{-}C_6H_5$, $R_2=3'\text{-}C_6H_5$
6a: $R_1=4\text{-}C_6D_5$, $R_2=4'\text{-}C_6D_5$
6b: $R_1=4\text{-}C_6H_5$, $R_2=4'\text{-}C_6H_5$
7a: $R_1=2\text{-}C_6D_5$, $R_2=3'\text{-}C_6D_5$
7b: $R_1=2\text{-}C_6H_5$, $R_2=3'\text{-}C_6H_5$
8a: $R_1=2\text{-}C_6D_5$, $R_2=4'\text{-}C_6D_5$
8b: $R_1=2\text{-}C_6H_5$, $R_2=4'\text{-}C_6H_5$
9a: $R_1=3\text{-}C_6D_5$, $R_2=4'\text{-}C_6D_5$
9b: $R_1=3\text{-}C_6H_5$, $R_2=4'\text{-}C_6H_5$
13b: $R_1=R_2=H$
19: $R_1=2\text{-}I$, $R_2=2'\text{-}I$
20: $R_1=3\text{-}I$, $R_2=3'\text{-}I$
21: $R_1=4\text{-}I$, $R_2=4'\text{-}I$
22: $R_1=2\text{-}I$, $R_2=3'\text{-}I$
23: $R_1=2\text{-}I$, $R_2=4'\text{-}I$
24: $R_1=3\text{-}I$, $R_2=4'\text{-}I$



11a: $R=C_6D_5$
11b: $R=C_6H_5$
26: $R=I$



12a: $R=C_6D_5$
12b: $R=C_6H_5$
27: $R=I$

Chart

in the presence of bis(acetylacetonato)nickel(II) proceeded successfully to provide twelve decadeuterated polyphenyls (**1a**—**12a**), each of which has phenyl-d_5 rings at both termini.

The intermediate diiodo compounds **16**—**21** and **27** were prepared by the methods reported previously.[3a,b,d] For the preparation of **22**—**24**, the corresponding dinitrobiphenyls were reduced with activated iron followed by conversion of the products to **22**—**24** by the usual method. Similarly, **25** was prepared by the usual method after direct iodination[6] of 2-aminobiphenyl. Further, **26** was obtained by direct iodination[6] of *o*-terphenyl.

The deuterated polyphenyls (**1a**—**12a**) and by-products, biphenyl-d_{10} (**13a**) and triphenylene-1,2,3,4-d_4 (**14a**),[7] are listed in Table I. The deuterated polyphenyls (except for **1a** and **4a**) were obtained in fairly good yields (73—93%). The lower yields of **1a** and **4a** (53 and 60%) may be ascribed to steric factors of **16** and **19**, respectively. In all preparations, small amounts of **13a** were isolated as a common by-product.[8] A minor by-product, **14a**, was presumably

Table I. Syntheses of Decadeuterated Polyphenyls

Reactant		Polyphenyl-d_{10} (yield, %)	By-product (yield, %)
15+	**16**	**1a** (53)[a]	**13a** (36)[b]
	17	**2a** (93)	**13a** (14)
	18	**3a** (78)	**13a** (14)
	19	**4a** (60)	**13a** (23), **14a** (2)[a]
	20	**5a** (92)	**13a** (8)
	21	**6a** (91)	**13a** (8)
	22	**7a** (83)	**13a** (8)
	23	**8a** (73)	**13a** (13)
	24	**9a** (89)	**13a** (8)
	25	**10a** (83)	**13a** (9)
	26	**11a** (81)	**13a** (8)
	27	**12a** (77)	**13a** (14)

a) Based on the diiodo compound used.
b) Based on the C_6D_5Br used.

formed by partial coupling of the Grignard reagent with **19**, followed by the apparent intramolecular elimination of deuterium iodide.

The deuterated polyphenyls (**1a**—**12a**) thus prepared,[9] gave satisfactory analytical results and spectral (MS and UV) data consistent with the indicated structures. The isotopic contents of **1a**—**12a** were determined by mass spectrometry at 10 eV,[10] an ionizing voltage great enough to ionize the molecules but too small to remove hydrogen atoms from the molecules.[11] The isotopic purities thus obtained are shown in Table II. Since **15** used in the preparations contained 1 atom % hydrogen, the theoretical maximum purity is also given in the table. The table suggests that, in order to improve the content of d_{10}-compound, it is necessary to use **15** of a higher isotopic purity than 99 atom%. Compounds **1a**—**12a** all showed very similar solubility and crystal form, and practically identical melting point compared with the corresponding polyphenyls **1b**—**12b**. Furthermore, mixed-melting-point determination of the corresponding deuterated compound (**a**) and normal polyphenyl (**b**) showed no depression, suggesting apparent identity of **a** and **b**.

TABLE II. Isotopic Purities of Deuterated Compounds

Compd. No.	Isotopic composition											Total D content (Atom %)	
	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	Max.[a]	Found
1a						3.5	0.3	0.1	0.6	8.8	86.7	70.72	69.36
2a						3.1	0.3	0.1	0.2	7.6	88.7	70.72	69.65
3a						2.4	0.3	0.5	0.9	7.8	88.1	70.72	69.69
4a	9.6	4.4	1.2	0.4		1.2	0.4		0.4	7.3	75.1	55.00	46.46
5a						2.2			0.2	7.8	89.8	55.00	54.49
6a						3.5	0.1		0.1	7.9	88.4	55.00	54.10
7a										7.7	92.3	55.00	55.13
8a						0.9		0.1	0.3	8.0	90.7	55.00	54.80
9a						3.7			0.1	7.7	88.5	55.00	54.09
10a						0.3				7.8	91.9	55.00	55.04
11a						1.4			0.1	8.1	90.4	45.00	44.76
12a						1.4			0.1	9.4	89.1	38.08	37.82
13a						4.4			0.5	8.0	87.1	99.00	96.90
14a	1.5		0.1	4.1	94.3							33.00	32.48

[a] Theoretical maximum purity: (number of D-atoms / number of D- and H-atoms) × atom % of D in C_6D_5Br.

The present results suggest that the Kharash-type Grignard cross-coupling reaction may be an efficient synthetic method for a wide variety of deuterated polyphenyls.

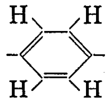
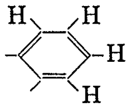
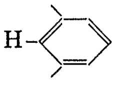
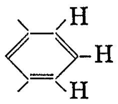
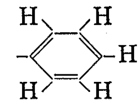
The NMR spectra of the deuterated (**1a**—**12a**) and normal polyphenyls (**1b**—**12b**) were measured at 80 MHz in $CDCl_3$ solution.

Most of the peaks in the spectra of **1a**—**12a** were assigned to *o*-, *m*-, and *p*-phenylene proton signals. Since these assignments can also be applied to the spectra of **1b**—**12b**, the difference between the spectra of the corresponding **a** and **b** was attributed to the phenyl proton signal. The assignments thus deduced are summarized in Table III.[12]

The spectrum of **7b** showed two singlets and a multiplet. The latter was attributed to the signal of *o*- and *m*-phenylene protons by comparison with the identical multiplet in the spectrum of **7a**. The two singlets (δ 7.22 and 7.33) can reasonably be assigned to the phenyl proton signals of $C_6H_5 \cdot o\text{-}C_6H_4$– and $C_6H_5 \cdot m\text{-}C_6H_4$– by analogy with those of **1b** (δ 7.17) and 3,3″-diphenyl-*o*-terphenyl (δ 7.32),[13] respectively.

The spectrum of **10b** also displayed two singlets and a multiplet. Of the two singlets (δ 7.22 and 7.20) (similar to the phenyl proton signal of **1b**), the former was assigned to protons of the 2-phenyl group by comparison with that of **10a** (δ 7.22), and therefore the latter was

TABLE III. NMR Spectral Data for Deuterated (**1a**—**12a**) and Normal Polyphenyls (**1b**—**12b**) in $CDCl_3$ a)

Compd. No.					
1a	—	7.42(4H, s)	—	—	—
1b	—	7.41(4H, s)	—	—	7.17(10H, s)
2a	—	—	7.79—7.84 (1H, m)	7.51—7.61 (3H, m)	—
2b	—	—	7.78—7.83 (1H, m)	7.27—7.72 (13H, m)	
3a	7.68(4H, s)	—	—	—	—
3b	7.68(4H, s)	—	—	—	7.33—7.71(10H, m)
4a	—	7.12—7.43 (8H, m)	—	—	—
4b	—	7.12—7.43 (8H, m)	—	—	6.51—7.08(10H, m)
5a	—	—	7.81—7.88 (2H, m)	7.54—7.64 (6H, m)	—
5b	—	—	7.81—7.88 (2H, m)	7.32—7.74 (16H, m)	
6a	7.72(8H, s)	—	—	—	—
6b	7.71(8H, s)	—	—	—	7.34—7.68(10H, m)
7a	—	7.07—7.53(8H, m)			—
7b	—	7.07—7.53(8H, m)			7.22(5H, s, $o\text{-}C_6H_4\cdot C_6\underline{H}_5$) 7.33(5H, s, $m\text{-}C_6H_4\cdot C_6\underline{H}_5$)
8a	7.21 and 7.46(4H, AA′BB′-q, $J=8.6$ Hz, $C_{2'},C_{6'}$–H and $C_{3'},C_{5'}$–H)	7.44(4H, s)	—	—	—
8b	7.21 and 7.46(4H, AA′BB′-q, $J=8.6$ Hz, $C_{2'},C_{6'}$–H and $C_{3'},C_{5'}$–H)	7.44(4H, s)	—	—	7.20(5H, s, $o\text{-}C_6H_4\cdot C_6\underline{H}_5$) 7.29—7.66(5H, m, $p\text{-}C_6H_4\cdot C_6\underline{H}_5$)
9a	7.71(4H, s)	—	7.82—7.88 (1H, m)	7.53—7.64 (3H, m)	—
9b	7.71(4H, s)	—	7.83—7.88 (1H, m)	7.30—7.74 (13H, m)	
11a	7.26 and 7.48(8H, AA′BB′-q, $J=8.6$ Hz, C_2,C_6–H and C_3,C_5–H)	7.47(4H, s)	—	—	—
11b	7.26 and 7.48(8H, AA′BB′-q, $J=8.6$ Hz, C_2,C_6–H and C_3,C_5–H)	7.47(4H, s)	—	—	7.32—7.66(10H, m)
12a	6.66 and 7.23(8H, AA′BB′-q, $J=8.6$ Hz, C_2,C_6–H and C_3,C_5–H)	7.11—7.52 (8H, m)	—	—	—
12b	6.66 and 7.23(8H, AA′BB′-q, $J=8.5$ Hz, C_2,C_6–H and C_3,C_5–H)		—	—	7.11—7.64(18H, m, $o\text{-}C_6H_4$ and C_6H_5)
10a			7.32—7.71(3H, m, C_6H_3)		7.22(5H, s, 2-C_6H_5)
10b					7.32—7.71(8H, m, C_6H_3 and 4-C_6H_5) 7.20(5H, s, 1-C_6H_5) 7.22(5H, s, 2-C_6H_5)

a) δ (ppm) from internal standard TMS.

assignable to protons of the 1-phenyl group. The multiplet (δ 7.32—7.71) may be attributable to the 4-phenyl and trisubstituted benzene ring protons.

The foregoing results (80 MHz, $CDCl_3$) indicate close correlations between the apparent signal patterns of phenyl and phenylene groups and the structures of the adjacent groups. The correlations may be summarized as follows.

1) *o*-Phenylene ring: In the case of an *o*-phenylene ring linked to two identical or different groups (phenyl or *p*-phenylene), the proton signal is generally observed as a singlet near δ 7.45. In other cases, however, the proton signal is generally observed as a multiplet.

2) *m*-Phenylene ring: The isolated proton signal of an *m*-phenylene ring, to which no *o*-phenylene ring is linked, is generally observed as a multiplet within a narrow region at the most downfield position (δ 7.80—7.90) in the spectra of polyphenyls. The adjacent three-proton signal of the *m*-phenylene ring, observed substantially as a multiplet, is generally difficult to differentiate from other proton signals.

3) *p*-Phenylene ring: The proton signal of a *p*-phenylene ring, to which two identical or different groups (phenyl or phenylenes except *o*-phenylene) are linked, is generally observed as a singlet near δ 7.7. However, in the case of a *p*-phenylene ring linked by two different groups (phenyl or phenylenes), of which one is an *o*-phenylene ring, the proton signal is generally observed as an AA'BB'-q pattern.

4) Phenyl ring: The phenyl proton signal is observed as a singlet near δ 7.2 or a multiplet, depending upon the structure of the adjacent group.

The correlations summarized above should be of use in assigning the NMR spectra of various new polyphenyls.

The MS spectra of the deuterated compounds (**1a**—**14a**) were measured at 70 eV. All of the spectra showed a molecular ion as the most abundant ion. The next most abundant ion was found to be a doubly charged parent ion M^{2+} in the spectra of **3a**, **5a**, **6a**, and **9a**, which contain no *o*-linkage, but was $(M-1)^+$ in the spectra of **4a**, **7a**, **8a**, **10a**, and **11a**, which contain *o*-linkage(s).

Table IV shows the sum of the singly and doubly charged parent ions ($M^+ + M^{2+}$) as a percentage of total ionization, and the ratio of the doubly charged parent to the parent ion (M^{2+}/M^+). The value of $M^+ + M^{2+}$ as a percentage of total ionization was found to be rather low in the spectra of **1a**, **4a**, **7a**, **8a**, and **10a**—**12a**, which contain *o*-linkage(s), as compared with those of **2a**, **3a**, **5a**, **6a**, and **9a**, which contain no *o*-linkage. Moreover, a lower value of the ratio of M^{2+}/M^+ was observed in the spectra of deuterated polyphenyls containing

TABLE IV. Total Ionization of Parent Singly and Doubly Charged Ions (%) and the Ratio of M^{2+} to M^+

Compd. No.	Mol wt	Total ionization of $M^+ + M^{2+}$ (%)	Ratio M^{2+}/M^+
1a	240	24.1	0.05
2a	240	42.2	0.10
3a	240	46.5	0.13
4a	316	21.4	0.04
5a	316	49.0	0.17
6a	316	48.8	0.21
7a	316	27.1	0.04
8a	316	29.7	0.04
9a	316	45.6	0.19
10a	316	30.2	0.04
11a	392	29.9	0.09
12a	468	28.4	0.13
13a	164	31.7	0.06
14a	232	41.1	0.18

Table V. Contribution of Fragment Ions to One-half Parent Mass

Compd. No.	Measd. $\frac{(M+1)^{2+}}{M^{2+}+M^+/2}$	M^{2+} (%)	$M^+/2$ (%)	$\frac{(M+1)^+}{M}$	
				Measd.	Clacd.
1a	0.17	83	17	0.21	0.20
2a	0.18	85	15	0.21	0.20
3a	0.18	87	13	0.21	0.20
4a	0.26	92	8	0.28	0.26
5a	0.26	93	7	0.28	0.26
6a	0.26	94	6	0.27	0.26
7a	0.24	87	13	0.27	0.26
8a	0.25	91	9	0.28	0.26
9a	0.26	94	6	0.27	0.26
10a	0.24	87	13	0.27	0.26
11a	0.32	96	4	0.34	0.33
12a	0.40	98	2	0.41	0.40
13a	0.08	55	45	0.14	0.13
14a	0.19	91	9	0.21	0.20

o-linkage(s). In addition, a significant contribution of fragment ions to M^{2+} was observed for the lower members and for the compounds containing *o*-linkage(s) (Table V).

Because the amount of $M^{+}+M^{2+}$ may be regarded as a measure of the stability of a compound to electron bombardment, the stability of deuterated polyphenyls containing *o*-linkage (s) appears to be substantially less than that of the compounds containing no *o*-linkage. These results are quite analogous to the spectral observations of polyphenyls by Staab and Wünsche[14] and others.[15]

From steric considerations, the markedly lower stability of deuterated polyphenyls containing *o*-linkage(s) presumably reflects their smaller resonance stabilization, as expected on the basis of the UV spectral data. Undoubtedly, a minor resonance stabilization should correlate closely with an abundance of fragment ions. In fact, the MS spectra of the deuterated polyphenyls containing *o*-linkage(s) do exhibit a high degree of fragmentation as compared with those of the compounds containing no *o*-linkage.

Few studies on the UV spectra of deuterated polyphenyls, except for that of biphenyl-d_{10}, have been reported.[16] The UV spectra of deuterated (**1a**—**14a**) and normal compounds (**1b**—**13b** and triphenylene (**14b**)) were measured in cyclohexane solution. The K-band revealed very little, if any, difference between corresponding partially deuterated and normal compounds, suggesting that the isotope effect is hardly detectable in the spectra of **1a**—**12a**, as expected.

The IR spectra of the deuterated compounds (**1a**—**14a**) were measured by the KBr-disk method. In all spectra except for that of **13a**, two groups of weak bands in the regions of 3085—3005 and 2260—2225 cm^{-1} were observed. These are assignable to the C–H and C–D stretching vibration bands, respectively, and are consistent with the partially deuterated structures.

Experimental

The melting points of the deuterated polyphenyls were determined with a Mettler FP-51 apparatus, except for those above 300°, which were determined with a Shimadzu DSC-30M differential scanning calorimeter. The UV spectra were measured on Shimadzu MPS-50L and UV-350 spectrophotometers, and the NMR spectra on a Varian CFT-20 spectrometer at 80 MHz with tetramethylsilane as an internal standard. The MS spectra were recorded on a Hitachi RMU-6MG mass spectrometer, and the IR spectra on a Leitz III-G spectrophotometer.

Biphenyl (**13b**) and terphenyls (**1b**—**3b**) were obtained commercially and purified before use, and quater- to sexiphenyls (**4b**—**12b**) and triphenylene (**14b**) were authentic samples prepared previously.[3a,b,d,13] Bromobenzene-d_5 (**15**) was obtained commercially and used without further purification (isotopic purity: 99 atom %, Merck).

o- (**16**), *m*- (**17**), and *p*-Diiodobenzene (**18**), 2,2′- (**19**), 3,3′- (**20**), and 4,4′-diiodobiphenyl (**21**), and 4,4‴-diiodo-*o*-quaterphenyl (**27**) were prepared by the methods reported previously.[3a,b,d]

2,3′-Diiodobiphenyl (22)——2,3′-Dinitrobiphenyl[17] was reduced with activated iron in hot benzene[18] to prepare 2,3′-diaminobiphenyl; bp 187—190° (6 mmHg) (lit.[17] bp 171—180° (2 mmHg)); yield, 83%. The diamine was then converted into **22** in the usual manner. A pale yellow oil; bp 185—189° (5 mmHg); 40%. *Anal.* Calcd for $C_{12}H_8I_2$: C, 35.50; H, 1.99. Found: C, 35.24; H, 2.01.

2,4′-Diiodobiphenyl (23)——2,4′-Dinitrobiphenyl[17] was subjected to reduction[18] to give 2,4′-diaminobiphenyl; mp 54—55.5° (lit.[19] mp 54—54.5°); 94%. The diamine was transformed to **23**; colorless needles from ethanol; mp 41.5—42° (lit.[20] bp 164—165° (2 mmHg)); 46%. *Anal.* Calcd for $C_{12}H_8I_2$: C, 35.50; H, 1.99. Found: C, 35.73; H, 2.04.

3,4′-Diiodobiphenyl (24)——3,4′-Dinitrobiphenyl[17] was converted into **24** *via* the corresponding diamine: mp 86—87° (lit.[21] mp 85.5—86.5°). **24**: Colorless leaves from ethanol; mp 76—77° (lit.[20] mp 75—77°); 39% based on 3,4′-dinitrobiphenyl. *Anal.* Calcd for $C_{12}H_8I_2$: C, 35.50; H, 1.99. Found: C, 35.67; H, 2.05.

2,5-Diiodobiphenyl (25)——2-Aminobiphenyl was subjected to direct iodination[6] to give 2-amino-5-iodobiphenyl; mp 75—76°. The aminoiodo compound was converted into **25**. Colorless needles from ethanol; mp 58—59°; 78%. *Anal.* Calcd for $C_{12}H_8I_2$: C, 35.50; H, 1.99. Found: C, 35.73; H, 2.11.

4,4″-Diiodo-*o*-terphenyl (26)——*o*-Terphenyl was subjected to direct iodination[6] to afford **26**. Colorless cubes from benzene; mp 230—231° (lit.[22] mp 224—226°); 83%. *Anal.* Calcd for $C_{18}H_{12}I_2$: C, 44.81; H_2, 2.49. Found: C, 44.99; H, 2.45.

Preparation of Decadeuterated Terphenyls (1a—3a)——An ethereal solution of phenyl-d_5-magnesium bromide was prepared from **15** (19.44 g, 120 mmol), magnesium turnings (2.92 g, 120 mg-atom), and absolute ether (80 ml) under nitrogen in the usual manner. To the Grignard reagent thus prepared, a solution of one of the diiodobenzenes (**16**—**18**) (9.90 g, 30 mmol) and bis(acetylacetonato)nickel(II) (78 mg, 0.3 mmol) in benzene (120 ml) was added all at once. The mixture was refluxed with stirring for 3 hr, then hydrolyzed with dilute hydrochloric acid. The product was extracted with benzene. The organic layer was separated, washed with water, and then dried. After the removal of the solvent, the residue was chromatographed on alumina with cyclohexane to afford biphenyl-d_{10} (**13a**) (14—36%). Subsequent elution with a cyclohexane-benzene (19: 1, v/v) mixture (C-B(19: 1)) or a C-B(1: 1) mixture provided the corresponding decadeuterated terphenyl (**1a**—**3a**).

1,2-Di(phenyl-d_5)benzene (**1a**): Eluate with C-B(19: 1); colorless needles from methanol; mp 56.9°; yield, 3.82 g (53%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 233 (28000), 251 (sh) (12100) (**1b**: 233 (29100), 251 (sh) (13300)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3020 (C–H), 2260 (C–D). *Anal.* Calcd for $C_{18}H_4D_{10}$: C, 90.00; H and D, 10.00. Found: C, 90.27; H and D, 9.90. MS *m/e*: 240 (M$^+$).

1,3-Di(phenyl-d_5)benzene (**2a**): Eluate with C-B(19: 1); colorless needles from ethanol; mp 87.8°; 6.71 g (93%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 247 (37700) (**2b**: 247 (36100)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3060, 3020 (C–H); 2260 (C–D). *Anal.* Calcd for $C_{18}H_4D_{10}$: C, 90.00; H and D, 10.00. Found: C, 90.29; H and D, 9.91. MS *m/e*: 240 (M$^+$).

1,4-Di(phenyl-d_5)benzene (**3a**): Eluate with C–B(1: 1); colorless plates from C–B(1: 1); mp 213.6°; 5.62 g (78%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 277 (30500) (**3b**: 277 (31600)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3085, 3020 (C–H); 2260, 2250 (C–D). *Anal.* Calcd for $C_{12}H_4D_{10}$: C, 90.00; H and D, 10.00. Found: C, 89.71; H and D, 9.82. MS *m/e*: 240 (M$^+$).

Preparation of Decadeuterated Quaterphenyls (4a—10a)——An ethereal solution of phenyl-d_5-magnesium bromide was prepared from **15** (9.72 g, 60 mmol), magnesium turnings (1.46 g, 60 mg-atom), and absolute ether (40 ml). To the Grignard reagent thus prepared, a solution of one of the diiodobiphenyls (**19**—**25**) (6.09 g, 15 mmol) and bis(acetylacetonato)nickel(II) (39 mg, 0.15 mmol) in benzene (60 ml) was added. The mixture was worked up as described above. The benzene extract was chromatographed on alumina with cyclohexane to give **13a** (8—23%). Subsequent elution with a C–B mixture afforded the corresponding decadeuterated quaterphenyl (**4a**—**10a**) (60—92%). In the preparation of **6a**, the benzene extract was subjected to crystallization from benzene without previous chromatography.

In the preparation of **4a**, triphenylene-1,2,3,4-d_4 (**14a**) was obtained as an additional by-product from the eluate with C-B(4: 1).

2,2′-Di(phenyl-d_5)biphenyl (**4a**): Eluate with C–B(9: 1); colorless cubes from ethanol; mp 118.8°; 2.84 g (60%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 229 (35500), 248 (sh) (25200) (**4b**: 229 (32200), 248 (sh) (22700)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3030 (C–H), 2255 (C–D). *Anal.* Calcd for $C_{24}H_8D_{10}$: C, 91.13; H and D, 8.87. Found: C, 91.03; H and D, 9.09. MS *m/e*: 316 (M$^+$).

14a: Colorless needles from ethanol; mp 198.3°; 0.14 g (2%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 250 (85500), 259 (157900), 274 (19100), 285 (17300) (**14b**: 250 (89700), 259 (178900), 274 (19600), 286 (17500)). *Anal.* Calcd for $C_{18}H_8D_4$: C, 93.08; H and D, 6.92. Found: C, 92.90; H and D, 6.82. MS *m/e*: 232 (M$^+$).

3,3′-Di(phenyl-d_5)biphenyl (**5a**): Eluate with C–B(9: 1); colorless needles from ethanol; mp 89.0°; 4.36 g (92%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 248 (60200) (**5b**: 248 (62700)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3020 (C–H), 2250, 2240 (C–D). *Anal.* Calcd for $C_{24}H_8D_{10}$: C, 91.13; H and D, 8.87. Found: C, 91.32; H and D, 9.11. MS *m/e*:

316 (M$^+$).

4,4′-Di(phenyl-d_5)biphenyl (**6a**): Colorless leaves; mp 319°; 4.31 g (91%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 294 (44600) (**6b**: 294 (44400)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3020, 3005 (C–H); 2260 (C–D). *Anal.* Calcd for $C_{24}H_8D_{10}$: C, 91.13; H and D, 8.87. Found: C, 90.94; H and D, 8.61. MS *m/e*: 316 (M$^+$).

2,3′-Di(phenyl-d_5)biphenyl (**7a**): Eluate with C–B(9:1); colorless needles from ethanol; mp 91.4°; 3.93 g (83%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 236 (46700), 250 (sh) (32900) (**7b**: 237 (45900), 251 (sh) (32400)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3040, 3020 (C–H); 2245, 2230 (C–D). *Anal.* Calcd for $C_{24}H_8D_{10}$: C, 91.13; H and D, 8.87. Found: C, 91.04; H and D, 8.76. MS *m/e*: 316 (M$^+$).

2,4′-Di(phenyl-d_5)biphenyl (**8a**): Eluate with C–B(4:1); colorless prisms from ethanol; mp 120.0°; 3.46 g (73%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 249 (27100), 277 (23000) (**8b**: 249 (29100), 278 (25100)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3040, 3005 (C–H); 2245, 2235 (C–D). *Anal.* Calcd for $C_{24}H_8D_{10}$: C, 91.13; H and D, 8.87. Found: C, 90.96; H and D, 8.91. MS *m/e*: 316 (M$^+$).

3,4′-Di(phenyl-d_5)biphenyl (**9a**): Eluate with C–B(4:1); colorless needles from ethanol; mp 168.4°; 4.22 g (89%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 267 (37700) (**9b**: 268 (38400)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3050, 3020 (C–H); 2235, 2225 (C–D). *Anal.* Calcd for $C_{24}H_8D_{10}$: C, 91.13; H and D, 8.87. Found: C, 91.38; H and D, 9.17. MS *m/e*: 316 (M$^+$).

1,4-Di(phenyl-d_5)-2-phenylbenzene (**10a**): Eluate with C–B(4:1); colorless needles from ethanol; mp 100.4°; 3.93 g (83%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 249 (34300), 267 (sh) (24300) (**10b**: 250 (35500), 266 (sh) (25700). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3005 (C–H), 2235 (C–D). *Anal.* Calcd for $C_{24}H_8D_{10}$: C, 91.13; H and D, 8.87. Found: C, 90.86; H and D, 8.75. MS *m/e*: 316 (M$^+$).

Preparation of 4,4″-Di(phenyl-*d*$_5$)-*o*-terphenyl (11a)——A solution of **26** (2.41 g, 5 mmol) and bis(acetylacetonato)nickel(II) (13 mg, 0.05 mmol) in benzene (50 ml) was added to the Grignard reagent prepared from **15** (3.24 g, 20 mmol), magnesium turnings (0.49 g, 20 mg-atom), and absolute ether (25 ml). The mixture was worked up as described above. The benzene extract was chromatographed on alumina with cyclohexane to give **13a** (8%). Subsequent elution with C–B(1:1) provided **11a**.

11a: Colorless needles from ethanol–benzene; mp 186.1°; 1.59 g (81%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 264 (50200), 285 (sh) (29800) (**11b**: 264 (49800), 284 (sh) (30600)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3005 (C–H), 2230 (C–D). *Anal.* Calcd for $C_{30}H_{12}D_{10}$: C, 91.82; H and D, 8.18. Found: C, 92.02; H and D, 8.36. MS *m/e*: 392 (M$^+$).

13a: Colorless leaves from methanol; mp 68.5° (lit.[26] mp 69—70°). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 247 (18100) (**13b**: 248 (17400)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 2260 (C–D). *Anal.* Calcd for $C_{12}D_{10}$: C, 87.81; D, 12.19. Found: C, 87.74; D, 12.30. MS *m/e*: 164 (M$^+$).

Preparation of 4,4‴-Di(phenyl-*d*$_5$)-*o*-quaterphenyl (12a)——A solution of **27** (1.68 g, 3 mmol) and bis-(acetylacetonato)nickel(II) (7.8 mg, 0.03 mmol) in benzene (30 ml) was added to the Grignard reagent prepared from **15** (1.94 g, 12 mmol), magnesium turnings (0.29 g, 12 mg-atom), and ether (15 ml). The mixture was worked up as described above. The benzene extract was chromatographed on alumina with cyclohexane to give **13a** (14%). Subsequent elution with C–B(4:1) afforded **12a**.

12a: Colorless cubes from ethanol–benzene; mp 195.7°; 1.09 g (77%). UV $\lambda_{\max}^{\text{cyclohexane}}$ nm (ε): 239 (sh) (26300), 272 (47400) (**12b**: 240 (sh) (28100), 272 (51200)). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3005 (C–H), 2235 (C–D). *Anal.* Calcd for $C_{36}H_{16}D_{10}$: C, 92.29; H and D, 7.71. Found: C, 92.50; H and D, 7.64. MS *m/e*: 468 (M$^+$).

Acknowledgement The authors are indebted to Nippon Shinyaku Co., Ltd., for performing the measurements of MS and IR spectra. Thanks are due to Dr. K. Umemoto and Mr. Y. Fujiwara of this college for their help in elmental analyses and NMR spectrometric measurements.

References and Notes

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7) These by-products were identified on the basis of satisfactory analytical results and spectral (MS and UV) data consistent with the indicated structures.

8) The by-product **13a** formed during the preparation of **1a** was found to be contaminated with biphenyl-2,3,4,5,6-d_5 (MS spectral evidence). The contaminant formation may be attributable to the partial coupling of the Grignard reagent with **16**, followed by the apparent reduction of the iodo intermediate.

9) Each of the deuterated polyphenyls (**1a**—**12a**) showed a single peak upon gas–liquid chromatography, which was carried out with a Shimadzu GC-5APTF gas chromatograph using a glass column (ϕ3 mm × 1 m) of Shimalite impregnated with Silicone OV-17 (3%).

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