Reaction of Aryl Grignard Reagents with Hexahalobenzenes: Novel Arenes via a Multiple Aryne Sequence

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Received May 22, 1985

New methodology for forming four to six new carbon–carbon bonds to an existing benzene ring in a "one-pot" reaction is described. Reaction of hexabromobenzene (7) or 1,2,4,5-tetrabromo-3,6-dichlorobenzene with excess arylmagnesium bromide in THF gives, after aqueous quench, 1,2,4,5-tetraarylbenzenes in good yield (Table I). The actual product is the corresponding di-Grignard **29**, formed from a tetrahalo di-Grignard (**24**, **31**) through a sequence of organometallic aryne intermediates (Scheme II).

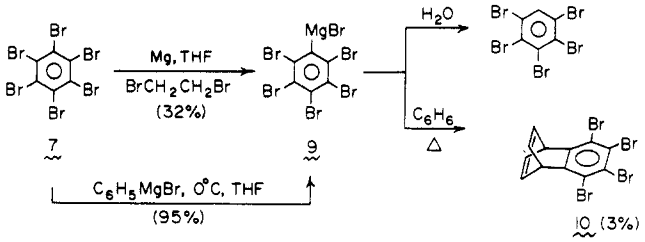
Introduction

We recently described[2] a new *p*-terphenyl synthesis that proceeds according to the sequence in Scheme I. The reaction exhibits several interesting features pertinent to the present work: (a) 4 equiv of aryl Grignard are required per mole of **1**—**2** are used in exchange reactions to form monoGrignard **2** and diGrignard **3**, and 2 furnish the "outside" aryl rings of the product **6**; (b) novel organometallic arynes such as **4** are intermediates; (c) nucleophilic addition to these intermediates (i.e., **4** → **5** and **5** → **6**) is regiospecific and occurs so as to keep like charges in the products (**5** and **6**) as far apart as possible—thus, although *m*-terphenyls are possible reaction products, only *p*-terphenyls **6** are formed; (d) two new aryl–aryl bonds are formed in a good-yield, one-pot reaction.

We describe here the reaction of excess aryl Grignard reagents with certain hexahalobenzenes. The reaction creates *four* new aryl–aryl bonds in a one-pot reaction and yields novel oligoarenes not readily available by any other method.

The seeds of this chemistry are quite old, though until now, they have yielded more weeds than flowers. Durand reported[3] that hexabromobenzene **7** reacts with phenylmagnesium bromide to give hexaphenylbenzene, but shortly afterwards, Dilthey showed[4] through independent synthesis that the product was in fact 1,2,4,5-tetraphenylbenzene (**8**). Geissman[5] confirmed these results and showed, through obtaining 1,2,4,5-tetraphenylbenzene-3,6-dicarboxylic acid on carbonation, that the actual reaction product was the tetraphenyl 1,4-di-Grignard. In these early studies, the solvents were ether, in which **7** is nearly insoluble, or benzene, a poor Grignard solvent. Product yields were well below 10% and considerable tars were formed.

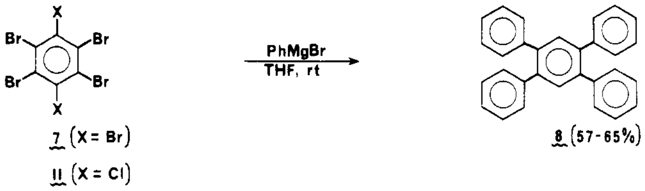
Thirty years later, Berry and Wakefield treated **7** with magnesium in tetrahydrofuran (THF) using 1,2-dibromoethane as the entrainer and obtained pentabromophenylmagnesium bromide **9** in 32% yield (based on aqueous quench to give pentabromobenzene); with ether as solvent, the yield was under 5%. Significant for our work, they found that if the solution of **9** was refluxed with benzene prior to aqueous quench, a 3% yield of tetrabromobenzobarrelene **1** was obtained. Thus, under reflux, **9** eliminated magnesium bromide to give some tetrabromobenzyne. A little later, it was shown that the conversion of **7** to **9** could be greatly improved using exchange with phenyl- or ethylmagnesium bromide.[7]



These seeds blossomed into flowers when we found that by changing the solvent to THF and by using excess aryl Grignard reagent we could improve Durand[3] and Geissman's[5] reaction to give synthetically useful yields of tetraarylbenzenes. Since the reaction product is a di-Grignard reagent, reaction with various electrophiles appreciably broadens the reaction's original scope. We have also deduced by experiment the most probable reaction mechanism.

Results and Discussion

Addition of a THF solution of hexabromobenzene to 8 equiv of phenylmagnesium bromide in the same solvent at room temperature followed by stirring for 12 h gave, after hydrolysis, a 57% yield of 1,2,4,5-tetraphenylbenzene (**8**). The less expensive 1,2,4,5-tetrabromo-3,6-dichlorobenzene (**11**), under the same conditions, gave a 65% yield of **8**; in general, reactions with **11** tended to be cleaner in workup than those with **7**. Other aryl Grignard reagents gave analogous products, as summarized in Table I. In the case of **20**–**22**, the reaction mixture was quenched with bromine in CCl_4 prior to aqueous workup.



Except for the first entry, all of the products in Table I are new compounds. Their structures rest on elemental analysis and mass spectra, on analogy with the first entry, and for those products with methyl substituents, on the symmetry required of their proton NMR spectra. For example, **12**, **13**, and **14** each showed sharp twelve-proton

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[1] On leave from Ube Industries, Ube, Japan.

[2] Hart, H.; Harada, K. *Tetrahedron Lett.* **1985**, *26*, 29; Hart, H.; Harada, K.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 3104.

[3] Durand, J. F.; Hsun, L. W. *C. R. Hebd. Seances Acad. Sci.* **1930**, *191*, 1460; in an earlier report, hexabromobenzene and phenyllithium are said to give a "dark, insoluble powder", Marvel, C. S.; Hager, F. D.; Coffman, D. D. *J. Am. Chem. Soc.* **1927**, *49*, 2323.

[4] Dilthey, W.; Hurtig, G. *Chem. Ber.* **1934**, *67*, 2004.

[5] Geissman, T. A.; Mallatt, R. C. *J. Am. Chem. Soc.* **1939**, *61*, 1788.

[6] Berry, D. J.; Wakefield, B. J. *J. Chem. Soc. C* **1969**, 2342.

[7] Smith, C. F.; Moore, G. J.; Tamborski, C. *J. Organomet. Chem.* **1971**, *33*, C21. These workers also showed that with two equivalents of phenyl- or ethylmagnesium bromide, some 2,3,5,6-tetrabromo-1,4-phenylbis(magnesium bromide) was produced. The amount was usually under 8%; but in one experiment with ethylmagnesium bromide in ether, the yield of di-Grignard was as high as 51%.

[8] Only 6 equiv are required by the stoichiometry, but an excess gives somewhat higher yields.

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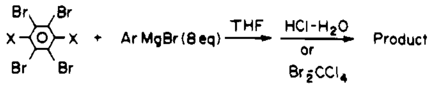
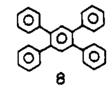
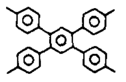
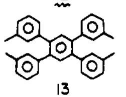
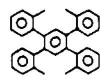
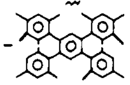
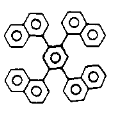
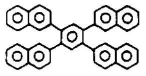
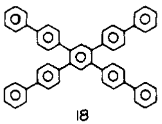
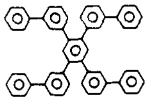
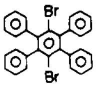
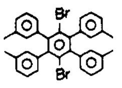
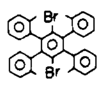
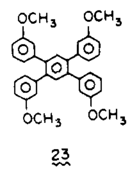
Table I



X	Ar	Product	Yield,%[a]	mp,°C[b]
Br(Cl)	C_6H_5-	 8	57(65)	267-268
Cl	p-$CH_3C_6H_4$-	 12	73	247-249
Cl	m-$CH_3C_6H_4$-	 13	71	157-158
Cl	o-$CH_3C_6H_4$-	 14	70	205-206
Br	2,4,6-$(CH_3)_3$-C_6H_2-	 15	55	258-259
Cl	1-$C_{10}H_7$-	 16	50	352-355
Cl	2-$C_{10}H_7$-	 17	57	324-325
Cl	4-C_6H_4-C_6H_5-	 18	52	380-381
Cl	3-C_6H_4-C_6H_5-	 19	62	257-259
Cl	C_6H_5-	 20	50	423-424
Cl	m-$CH_3C_6H_4$-	 21	55	327-330
Cl	o-$CH_3C_6H_4$-	 22	64	305-310
Cl	m-$CH_3OC_6H_4$-	 23	57	199-200

[a] Isolated yields of purified products [b] Uncorrected

Scheme I

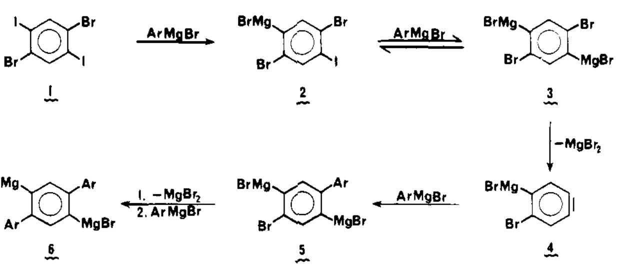
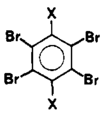
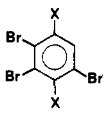
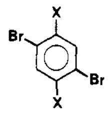
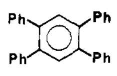


Table II. Reaction of Hexahalobenzenes with Phenylmagnesium Bromide at 7 °C[a]

substrate	products after aqueous quench, %		
			
X=Br	26	32	22
X=Cl	58	27	8

[a] Substrate (2.5 mmol) and phenylmagnesium bromide (15 mmol) in 80 mL of THF were stirred at 7 °C for 4 h and then quenched with water, and the product mixture was analyzed by gas chromatography.

singlets for the methyl protons (at δ 2.33, 2.27, and 2.18, respectively) and **15** showed two such singlets, at δ 2.21 and 1.99 in the ratio of 12:24, respectively. These results clearly establish the 1,2,4,5-orientation of the aryl groups around the central aromatic ring.

The reaction is not particularly susceptible to steric effects. Thus, 1,2,4,5-tetramesitylbenzene (**15**) was prepared in comparable yield to less-hindered analogues. The peripheral rings in **15** are twisted with respect to the central ring and almost certainly not freely rotating. This conclusion is based on our observation that although the methyl signal in 1,2,4,5-tetra-*o*-tolylbenzene (**14**) is a singlet (broad), that signal in the more hindered **22** is, at room temperature, a very complex pattern. Thus, rotation in **22** (which has five possible conformers[9]) is clearly restricted at room temperature; and in **15**, it is expected to be much more so.[10] Indeed, CPK space-filling models of **15** are exceedingly difficult or impossible to construct, even with the mesityl rings at 90° to the central aromatic ring.

Mechanism. The mechanism we propose involves as key intermediates the 1,4-di-Grignard reagent **24** and various organometallic arynes as outlined for hexabromobenzene in Scheme II. Rapid formation of **9** from **7** and phenylmagnesium bromide is well established.[7] We found that with excess phenylmagnesium bromide and lower reaction temperatures, the presence of substantial amounts of the 1,4-di-Grignard can be demonstrated as shown by the quenching results in Table II. When X = Cl, only the bromines exchanged; and the 1,4-di-Grignard was the principal product.[11] The mechanism of such

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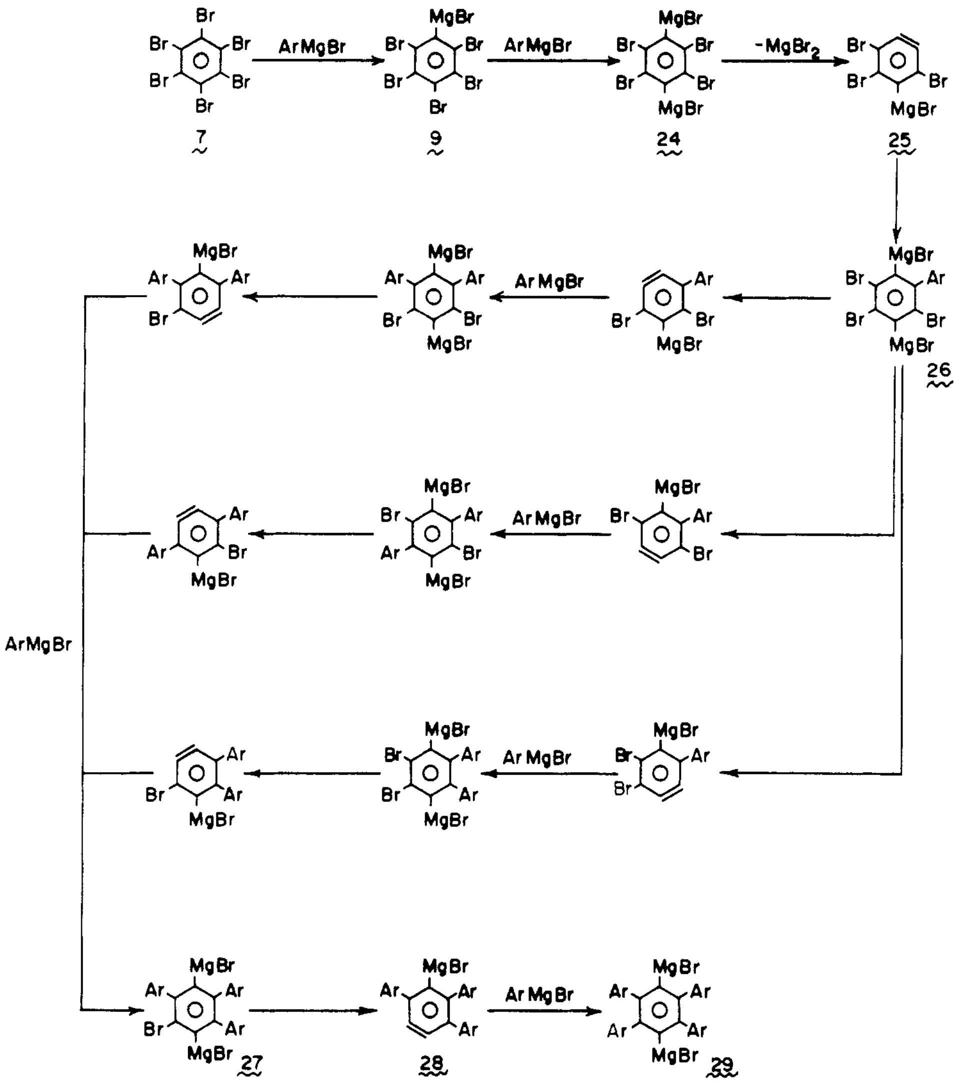
[9] Two more isomers are possible if enantiomers are counted separately. The situation is analogous to the recently described analysis of tetra-*o*-tolylethene conformers; Willem, R.; Pepermans, H.; Hallenga, K.; Gielen, M.; Dams, R.; Geise, H. J. *J. Org. Chem.* **1983**, *48*, 1890; for related studies, see also Willem, R.; Pepermans, H.; Hoogzand, C.; Hallenga, K.; Gielen, M. *J. Am. Chem. Soc.* **1981**, *103*, 2297; Willem, R.; Jans, A.; Hoogzand, C.; Gielen, M.; Van Binst, G.; Pepermans, H. *J. Am. Chem. Soc.* **1985**, *107*, 28.

[10] Studies on the NMR spectra of **14**, **21**, **22**, and related hindered molecules have been initiated in collaboration with Dr. K. Hallenga; see also the Experimental Section for preliminary results.

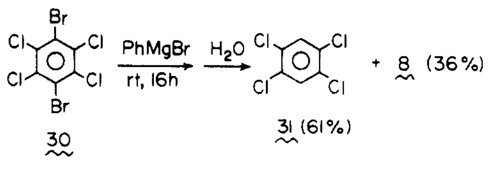
[11] Traces of other isomers may be present, as indicated by very minor peaks in the GC trace. This is especially so when X = Br. Also, some tri-Grignard may be formed in this case.

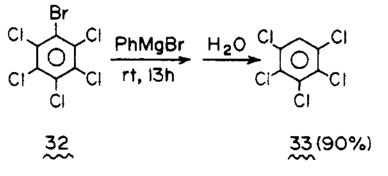
Scheme II



Grignard exchanges is not well established, but we believe that other factors being equal, the isomer with the charges as far apart as possible is preferred.[2,12] The results in Table II show that under the same conditions, more di-Grignard is formed when X = Br than when X = Cl.

The observation that Grignard exchange occurs at bromine but not at chlorine in **11** was used to test the proposal in Scheme II that di-Grignard formation is essential to the tetraarylation reaction. At least two bromines must be present on the bromochloroarene. Thus, dibromotetrachlorobenzene (**30**) reacts to give **8**;[13] on the other hand, bromopentachlorobenzene (**32**) gives, under the same conditions, only pentachlorobenzene **33**.[13] These observations tend to confirm the proposal in Scheme II that the product derives from the di-Grignard **24** and not from the mono-Grignard **9**.





The remaining reactions in Scheme II, once **24** is formed, involve *only a single assumption*, i.e., that addition of arylmagnesium bromide to the intermediate organometallic arynes (i.e., **25**, **28**, and so on) occurs regiospecifically always to give 1,4- (and not 1,3-) di-Grignards. Thus, after aryne formation from **24** and Grignard addition, we obtain only di-Grignard **26** and not its meta regioisomer. Monoaryl di-Grignard **26** may give *three* possible arynes; each of these in turn can give but a single diaryl di-Grignard. Each of these di-Grignards can give only one aryne, and addition of aryl Grignard to any of these three arynes will give a single triaryl di-Grignard **27**!

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[12] Hart, H.; Nwokogu, G. C. *Tetrahedron Lett.* **1983**, *24*, 5721. Of course, meta- and ortho-dimetalated as well as polymetalated benzenes are also known; for a recent reference with examples and leading references, see Crowther, G. P.; Sundberg, R. J.; Sarpeshkar, A. M. *J. Org. Chem.* **1984**, *49*, 4657.

[13] The 1,3- and 1,2-dibromotetrachlorobenzenes also give low yields (10–20%) of 1,2,4,5-tetraphenylbenzene with excess phenylmagnesium bromide; but in these cases, the major product (80–85%) on aqueous quench is the corresponding monobromotetrachlorobenzene. Hexachlorobenzene, under the same conditions, gives pentachlorobenzene (51%) and recovered starting material. A systematic study of the various polyhaloarenes in this reaction will be reported separately; unpublished results with Chi-Jen Frank Du.

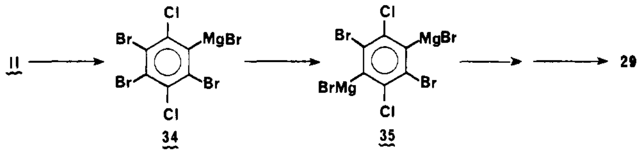
[14] Durand[3] reported low yields of hexamethylbenzene from **7** and excess methylmagnesium iodide; our initial studies of polyhaloarenes with vinyl Grignards indicate that the reaction is complex but potentially useful.

Through two more analogous steps, **27** can give only the observed 1,2,4,5-tetraaryl di-Grignard **29**.

Regiospecificity in the nucleophilic additions of aryl Grignards to the various organometallic arynes in Scheme II may be a consequence of two factors. One is the maintenance of like charges in the di-Grignards as far apart as possible. The second is the electronic effect of substituents (especially the organometallic substituent) on charge distribution in the aryne intermediates. If, of the two aryne carbons, the one most remote from the organometallic substituent is the most negative, then nucleophile will always attack meta to the organometallic substituent giving the para-di-Grignard. Whatever the reason, the observed specificity is remarkable; only 1,2,4,5-tetraarylbenzenes are formed.

Although it is possible to arrive at product **29** from the mono-Grignard **9** by loss of magnesium bromide to give tetrabromobenzyne, this alternative mechanism requires, in its early stages, some arbitrary choices in the regiochemistry of nucleophilic additions to neutral arynes. In later stages, it requires arbitrary regiochemistry in Grignard exchange reactions; and at the di-Grignard stage which is eventually necessary, it requires the same regiospecificity assumption as outlined in Scheme II. Without these multiple assumptions, it would be difficult to rationalize why the two regioisomers of **29** and pentaarylphenylmagnesium bromide are not also observed as products.

We, therefore, believe that Scheme II is essentially correct and consider that di-Grignard **24** is a necessary intermediate in the reaction mechanism. We cannot tell, however, whether all of the multiple paths between **26** and **27** are essential or whether there is a preference among them. Finally, it should be noted that for 1,2,4,5-tetrabromo-3,6-dichlorobenzene **11**, Scheme II must be modified. The first Grignard exchange occurs at bromine to give **34** and the second at the para bromine to give di-Grignard **35**. From **35**, one can proceed to **29** by steps analogous to those in Scheme II except that aryne can be formed from **35** by elimination of either bromide or chloride, making the mechanism similar to but, formally, somewhat more complex than Scheme II.



Since many of the intermediates proposed in Scheme II are nucleophiles, as is the final product **29**, they could replace the original arylmagnesium bromide reagent in adding to the intermediate arynes. The original reagent is, however, present in large excess so its addition predominates. In this way, the good yields reported in Table I are obtained. Some higher molecular weight byproducts are formed, however, perhaps in the manner just indicated. They are easily removed from the desired product through chromatography.

Conclusions. 1,2,4,5-Tetraarylbenzenes are readily prepared in good yield in one step from hexabromobenzene or 1,2,4,5-tetrabromo-3,6-dichlorobenzene in THF at room temperature using 6 to 8 equiv of an aryl Grignard reagent. The aryl Grignard reagent performs two roles; first, through Grignard exchange, it produces a tetrahalo 1,4-di-Grignard intermediate (**24**, **35**) which is the precursor of the first of a series of organometallic aryne intermediates; and second, it acts as a nucleophile and adds to these arynes in a regiospecific manner so as to produce other 1,4-di-Grignards, the last of which is the observed product **29** as shown in Scheme II.

The reaction products are novel and have several interesting features. Some, being highly hindered, show substantial rotational barriers and may be isolable as separate conformers. Since the actual reaction product is a di-Grignard (**29**), it can be trapped by various electrophiles other than protons or bromine as described here. Indeed, with CO_2 trapping Geissman[5] already demonstrated that six new carbon–carbon bonds can be formed by this reaction. With other carbon electrophiles, one can envision adding functionality which can then cyclize on the aryl rings, thus forming polynuclear aromatic compounds. We are actively pursuing these objectives. Finally, we have begun studies extending this reaction to vinyl, heterocyclic, and aliphatic Grignard reagents.

Experimental Section

General Procedures. ^1H NMR spectra were determined on a Varian T-60 or Bruker WM-250 spectrometer in $CDCl_3$ solution containing tetramethylsilane as an internal standard. Chemical shifts are reported in δ units. Mass spectra were recorded at 70 eV on a Finnigan 4000 spectrometer operated by Richard Olsen. Melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. Anhydrous magnesium sulfate was the drying reagent throughout, and the silica gel for chromatography was 230–400 mesh. Analyses are by Spang Microanalytical Laboratory.

Hexabromobenzene (7).[15] A solution of 1,4-dibromobenzene (29.5 g, 125 mmol), bromine (80 g, 500 mmol), and a catalytic amount of iron (1.0 g) and iodine (1.0 g) in 200 mL of oleum (29% SO_3) was vigorously stirred (magnetic) at 60–70 °C for 6 h. The mixture was poured into ice water and the precipitated solid was filtered and washed successively with aqueous sodium bisulfite, sodium bicarbonate, and water. Recrystallization from benzene gave 60 g (89%) of hexabromobenzene (**7**) as white needles, mp 320 °C (lit.[15] 319–321 °C).

1,2,4,5-Tetrabromo-3,6-dichlorobenzene (11).[16] The procedure and workup were essentially the same as for **7**. From 8.2 g (56 mmol) of 1,4-dichlorobenzene, 36 g (225 mmol) of bromine, 0.25 g of iron, and 0.25 g of iodine in 82 mL of oleum (29% SO_3), there was obtained 23.7 g (92%) of **11** as white needles from toluene, mp 279–280 °C (lit.[16] 281 °C).

Typical Procedure for Tetraarylbenzenes (Table I). Preparation of 1,2,4,5-Tetraphenylbenzene (8). A suspension of 1,2,4,5-tetrabromo-3,6-dichlorobenzene 11 (2.2 g, 5 mmol) in 20 mL of THF was added slowly over 30 min to a solution of phenylmagnesium bromide (prepared from 6.28 g, 40 mmol, of bromobenzene, 0.92 g, 40 mmol of magnesium in 80 mL of THF) and the mixture was stirred for an additional 12 h at room temperature. The reaction was quenched with ice and dilute hydrochloric acid, and the mixture was extracted with chloroform. The organic layer was dried and the solvent evaporated under reduced pressure to give a mixture of a solid and an oil. This mixture was washed with hexane and filtered to give 0.85 g of nearly pure 1,2,4,5-tetraphenylbenzene (8). Chromatography of the filtrate using hexane as the eluent gave 0.35 g (18%) of 1,2,4-tribromo-3,6-dichlorobenzene[17] and 0.40 g of additional 8 (total yield 65%), mp 267–268 °C from benzene (lit.[4,5] 263–264 °C); mass spectrum, *m/e* (relative intensity) 384 (4), 383 (28), 382 (M^+, 100), 305 (11), 183 (28), 191 (7).

Procedure for Bromine Quench (Table I). Preparation of 1,4-Dibromo-2,3,5,6-tetraphenylbenzene (20). The standard procedure was followed, but prior to quenching with ice, the reaction mixture was cooled to 10 °C, and a solution of bromine (9.6 g, 60 mmol) in 40 mL of CCl_4 was added, and the mixture was stirred at 10 °C for 1 h. It was then quenched with ice water and worked up as usual to give a solid and oil. This mixture was washed with a little benzene and filtered to give 0.8 g of **20**

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[15] Hennion, G. F.; Anderson, J. G. *J. Am. Chem. Soc.* **1946**, *68*, 424.

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[17] Melting point 124–125 °C; Anal. Calcd for $C_6HBr_3Cl_2$: C, 18.75; H, 0.26. Found: C, 18.89; H, 0.41.

contaminated with a little **11**. Chromatography of the filtrate using hexane–benzene (1:1) as eluent gave 0.5 g of additional **20**. Recrystallization from methylene chloride gave 1.30 g (50%) of pure **20** as white needles, mp 423–424 °C; ^{1}H NMR δ 7.07–7.22 (m, 20 H); mass spectrum, m/e (relative intensity) 542 (21), 540 (47), 538 (20), 380 (38), 302 (45), 273 (21), 271 (47), 269 (21), 182 (100), 181 (97). Anal. Calcd for $C_{30}H_{20}Br_2$: C, 66.69; H, 3.72. Found: C, 66.40; H, 3.81.

Reaction of 1,4-Dibromo-2,3,5,6-tetrachlorobenzene with Phenylmagnesium Bromide. The typical procedure was followed, by using 5 mmol of **30**,[16] 40 mmol of phenylmagnesium bromide and a reaction time of 16 h at room temperature. The usual workup afforded 2.1 g of crude solid product which was chromatographed on silica gel to give first, with petroleum ether as the eluent, 0.66 g (61%) of 1,2,4,5-tetrachlorobenzene which was recrystallized from benzene, mp 138–140 °C (lit.[18] 139–140 °C). Further elution with benzene–petroleum ether (v:v = 40:60) gave 0.69 g (36%) of 1,2,4,5-tetraphenylbenzene with properties identical with those described above.

Reaction of Bromopentachlorobenzene (32) with Phenylmagnesium Bromide. The typical procedure was followed, using 1 mmol of **32**[19] suspended in 10 mL of THF added over 10 min to 8 mmol of phenylmagnesium bromide in 40 mL of THF, with a reaction time of 13 h at room temperature. The usual workup gave, after chromatography on silica gel with hexane as eluent, 225 mg (90%) of pentachlorobenzene. The product was recrystallized from benzene–ethanol to give white needles, mp 84–85 °C (lit.[20] 85–86 °C). No terphenyl was isolated on further elution of the silica gel column.

Data for New Compounds in Table I. 1,2,4,5-Tetra-*p*-tolylbenzene (12): ^{1}H NMR: δ 2.33 (s, 12 H), 7.02–7.12 (m, 16 H), 7.48 (s, 2 H); mass spectrum m/e (relative intensity) 440 (5), 439 (36), 438 (M^+, 100), 219 (5), 204 (13), 196 (16), 189 (16), 130 (18), 85 (20). Anal. Calcd for $C_{34}H_{30}$: C, 93.11; H, 6.89. Found: C, 93.15; H, 6.91. **1,2,4,5-Tetra-*m*-tolylbenzene (13)**: ^{1}H NMR: δ 2.27 (s, 12 H), 6.95–7.15 (m, 16 H), 7.50 (s, 2 H); mass spectrum, m/e (relative intensity) 440 (5), 439 (27), 438 (M^+, 100), 423 (4), 407 (4), 219 (9), 189 (50). Anal. Calcd for $C_{34}H_{30}$: C, 93.11; H, 6.89. Found: C, 92.91; H, 6.91. **1,2,4,5-Tetra-*o*-tolylbenzene (14)**: ^{1}H NMR δ 2.0–2.3 (very broad s, 12 H), 6.88–7.16 (m, 16 H), 7.26 (s, 2 H); at 275 K the methyl signal separates into five peaks and below 250 K into eight peaks;[10] mass spectrum, m/e (relative intensity) 440 (5), 439 (32), 438 (M^+, 100), 423 (4), 397 (2), 347 (4), 333 (4), 219 (40), 189 (16). Anal. Calcd for $C_{34}H_{30}$: C, 93.11; H, 6.89. Found: C, 92.94; H, 6.81. **1,2,4,5-Tetramesitylbenzene (15)**: ^{1}H NMR δ 1.99 (s, 24 H), 2.21 (s, 12 H), 6.73 (s, 8 H), 7.05 (s, 2 H); mass spectrum m/e (relative intensity) 552 (6), 551 (25), 550 (M^+, 88), 535 (12), 520 (3), 430 (3), 275 (4), 85 (100). Anal. Calcd for $C_{42}H_{46}$: C, 91.58; H, 8.42. Found: C, 91.56; H, 8.38. **1,2,4,5-Tetra-1′-naphthylbenzene (16)**: ^{1}H NMR δ 8.03–8.16 (m); mass spectrum, m/e (relative intensity) 584 (2), 583 (11), 582 (M^+, 23), 455 (1), 291 (5), 87 (32), 85 (100). Anal. Calcd for $C_{46}H_{30}$: C, 94.81; H, 5.19. Found: C, 94.66; H, 5.24. **1,2,4,5-Tetra-2′-naphthylbenzene (17)**: ^{1}H NMR δ 2.29 (dd, 4 H), 7.42–7.46 (m, 8 H), 7.59 (d, 4 H), 7.75–7.77 (m, 8 H), 7.85 (s, 2 H), 7.96 (s, 4 H); mass spectrum, m/e (relative intensity) 584 (7), 583 (27), 582 (M^+, 76), 491 (3), 455 (9), 415 (12), 291 (18), 126 (84), 40 (100). Anal. Calcd for $C_{46}H_{30}$: C, 94.81; H, 5.19. Found: C, 94.48; H, 5.23. **1,2,4,5-Tetra-*p*-biphenylylbenzene (18)**: ^{1}H NMR δ 7.32–7.72 (m); mass spectrum, m/e (relative intensity) 686 (M^+, 14), 44 (100). Anal. Calcd for $C_{54}H_{38}$: C, 94.42; H, 5.58. Found: C, 94.26; H, 5.69. **1,2,4,5-Tetra-*m*-biphenylylbenzene (19)**: ^{1}H NMR δ 7.37–7.63 (m, 36 H), 7.73 (s, 2 H); mass spectrum, m/e (relative intensity) 688 (5), 687 (20), 686 (M^+, 58), 595 (4), 143 (8), 77 (11), 57 (12), 55 (12), 44 (100). Anal. Calcd for $C_{54}H_{38}$: C, 94.42; H, 5.58. Found: C, 94.25; H, 5.73. **1,4-Dibromo-2,3,5,6-tetra-*m*-tolylbenzene (21)**: ^{1}H NMR δ 2.22 (s, 6 H), 2.23 (s, 6 H), 6.82–7.00 (m, 12 H), 7.02–7.12 (m, 4 H); mass spectrum, m/e (relative intensity) 598 (16), 596 (50), 594 (22), 436 (17), 420 (11), 218 (11), 210 (29), 203 (33), 202 (23), 201 (15), 200 (12), 195 (100), 188 (47), 187 (21), 182 (30), 163 (22). Anal. Calcd for $C_{34}H_{28}Br_2$: C, 68.47; H, 4.73. Found: C, 68.62; H, 4.74. **1,4-Dibromo-2,3,5,6-tetra-*o*-tolylbenzene (22)**: ^{1}H NMR (300 K) δ 2.11, 2.16, 2.19, 2.25, 2.28 (singlets of nonintegral intensity, 12 H), 6.85–7.15 (m, 16 H); in Me_2SO, 7 peaks are seen which change relative intensities but do not change in number up to 440 K;[10] mass spectrum, m/e (relative intensity) 598 (19), 596 (37), 594 (19), 437 (15), 436 (38), 252 (30), 163 (62), 91 (100). Anal. Calcd for $C_{34}H_{28}Br_2$: C, 68.47; H, 4.73. Found, C, 68.55; H, 4.76. **2,3,5,6-Tetra-*m*-anisylbenzene (23)**: ^{1}H NMR δ 3.63 (s, 12 H), 6.8–7.3 (m, 16 H), 7.56 (s, 2 H); mass spectrum, m/e (relative intensity) 504 (8), 503 (37), 502 (M^+, 100), 396 (2), 78 (8), 43 (9). Anal. Calcd for $C_{34}H_{30}O_4$: C, 81.25; H, 6.02. Found: C, 81.19; H, 6.06.

Acknowledgment. We are indebted to the National Institutes of Health GM15997 for financial support of this research. K.H. also thanks UBE Industries for a leave of absence. We also thank Mr. Chin-hahn Suh for performing preliminary experiments.

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Synthesis and Chiroptical Properties of 5,7-Dioxobicyclo[2.2.2]oct-2-ene and Bicyclo[2.2.2]octane-2,5-dione

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Received June 24, 1985

5,7-Dioxobicyclo[2.2.2]oct-2-ene (**5**) and its dihydro derivative **9** were obtained in racemic form by sequential Diels–Alder addition of maleic anhydride to hydroquinone, hydrolysis of the adduct to diacid **7**, oxidative decarboxylation of **7** with lead tetraacetate, and catalytic hydrogenation. Partial resolution of **7** with brucine or quinine afforded (−)-**5** in 80–86% enantiomeric purity. Ketalization of (±)-**5** with diethyl (*R*,*R*)-(+)-tartrate and subsequent chromatographic separation of the diastereomeric monoketals gave optically pure samples of both antipodes of the enedione. This substance was found to interact powerfully with plane and circularly polarized light. The Cotton effects observed in the ORD and CD spectra of (−)-**5** indicate that its absolute configuration is 1*S*,4*S* when analyzed by the generalized octant rule. It follows that (−)-**9**, its hydrogenation product, is 1*R*,4*R*.

Interest has continued to surround dissymmetric molecules that possess a C_n (Schoenfliess notation) axis of symmetry.[4] Well-known members of this class include spiro compounds (e.g., **1**),[5] allenes such as **2**,[6] and biphenyls