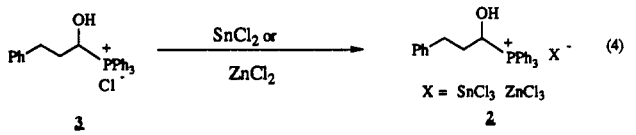
Table I. Selected ^1H NMR Values for Compounds 2 and 3

compd no.	ppm O*H*	*J* (Hz)	ppm P-C-*H*	J_{PCH} (Hz)
3	8.5 (s)	~0	5.9 (d)	10.2
2a	5.0 (t)	8.5	6.2 (m)	3.0
2b	5.1 (dd)	8.0, 9.1	6.3 (dt)	<3.0
2c	5.4 (t)	8.6	6.1 (m)	

in **2b**, suggesting tin was not bonded to this carbon, and (iv) when tin dichloride or zinc dichloride was added to **3**, they yielded compounds **2b** and **2c**, respectively (eq 4). It thus became clear that germanate and stannate anions had not added to hydrocinnamaldehyde but that triphenylphosphine had added instead to form a 1-hydroxy phosphonium salt.



(4)

3 **2**

A comparison of the ^1H NMRs of **2** and **3** revealed some interesting differences. For compound **3** the P-C_1-H coupling was 10.2 Hz, the hydroxyl proton was consistently a singlet at 8.5 ppm, and the C(2) protons were clearly diastereotopic (Table I). For compound **2a** the P-C_1-H coupling was ca. 3 Hz,[11] the hydroxyl proton appeared as a sharp triplet (J = 8.5 Hz) at 5.0 ppm, and the C(2) protons were overlapping. There were also significant differences in the IR spectra of compounds **3** and **2**. Whereas **2** has a hydroxyl stretch at 3380 cm^{-1}, the hydroxyl stretch of **3** resembled that of a carboxylic acid. Thus, there appears to be an interaction between the hydroxy proton and Cl^- in **3**, but no such interaction between the counter ions of the type **2**. Apparently, this interaction also effects the proximal phosphorus-proton couplings. On the other hand, the ^{13}C and ^{31}P spectra were very similar for compounds **2** and **3**.

In summary, triphenylphosphonium salts add to aldehydes, irrespective of the counter ion, yielding 1-hydroxy phosphonium compounds. The ^1H NMR and IR spectra clearly indicate the presence of hydrogen-bonding interactions between the chloride counter ion and the hydroxyl proton, whereas no such interaction is observed between the $^-GeCl_3$, $^-SnCl_3$, or $^-ZnCl_3$ counter ions.

Experimental Section

^1H NMR spectra were recorded at 400 MHz on a Varian XLA-400 spectrometer. ^{13}C NMR spectra were recorded at 100 or 75 MHz. ^{31}P NMR spectra were recorded at 160 MHz. Infrared spectra: all infrared spectra were obtained on a Perkin-Elmer Model 283 IR. C, H, N analyses: analyses were obtained for all new compounds from G. D. Searle, Skokie, IL.

Preparation of (3-Phenyl-1-hydroxypropyl)triphenylphosphonium Trichlorogermanate (2a). Hydrocinnamaldehyde (0.14 g, 1.04 mmol) was added to triphenylphosphonium trichlorogermanate (0.46 g, 1.04 mmol) in methylene chloride (5 mL) and stirred for 2 h. The volume of the reaction was reduced under vacuo, ethyl ether was added (ca. 1:1), and the reaction mixture was placed in a freezer (-30 °C). The crystals were isolated by filtration, washed with ether, and dried under vacuo (0.55 g, 92%): ^1H NMR ($CDCl_3$) δ 7.81-7.65 (m, 15 H), 7.27-7.16 (m, 6 H), 6.20-6.15 (m, 1 H), 5.05-5.00 (t, 1 H, J = 8.5 Hz, OH), 3.15-3.07 (m, 1 H), 3.00-2.93 (m, 1 H), 2.13-2.06 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 140.22, 135.11 (d, $^4J_{PC}$ = 2.9 Hz), 134.21 (d, J_{PC} = 9.1 Hz), 130.43 (d, J_{PC} = 12.1 Hz), 128.66, 128.57, 126.30, 116.75 (d, $^1J_{PC}$ = 81.3 Hz), 67.62 (d, $^1J_{PC}$ = 61.1 Hz), 34.65 (d, $^3J_{PC}$ = 4.9 Hz), 31.86 (d, $^2J_{PC}$ = 13.8 Hz); ^{31}P ($CDCl_3$) δ 23.6 (s); IR (neat, cm^{-1}) 3380 (m), 3060 (w), 3000 (m), 2960 (m), 2920 (m), 2900 (w), 1590 (m), 1480 (w), 1430 (m), 1110 (s), 1060 (m), 990 (m), 520 (m), 480 (m). Anal. Calcd: C, 56.26; H, 4.55. Found: C, 55.87; H, 4.66.

2b: ^1H NMR ($CDCl_3$) δ 7.80-7.76 (m, 9 H), 7.70-7.66 (m, 6 H), 7.26-7.16 (m, 5 H), 6.35-6.30 (dt, 1 H, $^3J_{HH}$ = 5.7, 7.3, 7.9 Hz, $CH_2CHOH(PPh_3)$), 5.13-5.09 (dd, 1 H, $^3J_{HH}$ = 8.0 Hz, $^3J_{PH}$ = 9.1 Hz, OH), 3.15-3.08 (m, 1 H), 3.04-2.94 (m, 1 H), 2.79-2.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 140.37, 135.00 (d, $^4J_{PC}$ = 2.9 Hz), 134.21 (d, J_{PC} = 9.0 Hz), 130.35 (d, J_{PC} = 12.2 Hz), 128.61, 128.47, 126.18, 116.66 (d, $^1J_{PC}$ = 81.4 Hz), 67.16 (d, $^1J_{PC}$ = 60.8 Hz), 34.47 (d, $^3J_{PC}$ = 5.3 Hz), 31.83 (d, $^2J_{PC}$ = 13.9 Hz); ^{31}P ($CDCl_3$) δ 23.72 (s); IR ($CHCl_3$, cm^{-1}) 3320 (m), 2990 (s), 2300 (w), 1440 (w), 1370 (w), 1250 (s), 1100 (m), 890 (m). Anal. Calcd: C, 52.09; H, 4.21. Found: C, 52.02; H, 4.17.

2c: ^1H NMR (CD_2Cl_2) δ 7.8-7.7 (m, 9 H), 7.67-7.63 (m, 6 H), 7.2-7.1 (m, 5 H), 6.11 (br t, 1 H), 5.41 (t, 1 H, J = 8.6 Hz), 3.12-3.02 (m, 1 H), 3.0-2.9 (m, 1 H), 1.8 (m, 2 H); ^{13}C NMR (CD_2Cl_2) δ 140.79, 135.54 (d, $^4J_{PC}$ = 3.0 Hz), 134.69 (d, J_{PC} = 9.0 Hz), 130.93 (d, J_{PC} = 14.0 Hz), 129.09, 128.92, 126.64, 116.99 (d, $^1J_{PC}$ = 81.5 Hz), 68.61 (d, $^1J_{PC}$ = 61.3 Hz), 34.92 (d, $^3J_{PC}$ = 4.9 Hz), 32.26 (d, $^2J_{PC}$ = 14.0 Hz); ^{31}P (CD_2Cl_2) δ 25.68; IR (CH_2Cl_2, cm^{-1}) 3520 (m), 3320 (m), 1600 (w), 1470 (w), 1120 (m). Anal. Calcd: C, 56.97; H, 4.60. Found: C, 56.65; H, 4.63.

Preparation of (3-Phenyl-1-hydroxypropyl)triphenylphosphonium Chloride (3). Hydrogen chloride (1 mL, 1 mmol, 1 M in ethyl ether) was added to a solution of triphenylphosphine (0.26 g, 1 mmol) in methylene chloride (5 mL) at room temperature and stirred for 5 min. Hydrocinnimaldehyde (0.13 g, 1 mmol) was added, and the reaction was stirred for 15 min. The volatiles were removed under vacuo to yield a white solid that was recrystallized form methylene chloride and ethyl ether (ca. 1:1): ^1H NMR ($CDCl_3$) δ 8.51 (s, 1 H, OH), 7.77-7.72 (m, 9 H), 7.65-7.60 (m, 6 H), 7.29-7.25 (m, 5 H), 5.92 (d, 1 H, J_{PH} = 10.17 Hz, $CH_2CHOH(PPh_3)$), 3.19-3.13 (m, 1 H), 2.98-2.90 (m, 1 H), 2.16-2.11 (m, 1 H), 2.00-1.96 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 140.77, 134.74 (d, $^4J_{PC}$ = 2.9 Hz), 134.2 (d, J_{PC} = 8.9 Hz), 130.15 (d, J_{PC} = 12.1 Hz), 128.90, 128.50, 126.10, 117.79 (d, $^1J_{PC}$ = 80.5 Hz), 67.03 (d, $^1J_{PC}$ = 58.8 Hz), 35.09 (d, $^3J_{PC}$ = 6.7 Hz), 31.80 (d, $^2J_{PC}$ = 14.5 Hz); ^{31}P ($CDCl_3$) δ 22.63 (s); IR ($CHCl_3$, cm^{-1}) 3040 (m), 2940 (s), 2800 (m), 1430 (w), 1250 (m), 1190 (m), 1100 (s). Anal. Calcd: C, 74.91; H, 6.05. Found: C, 74.81; H, 6.12.

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Registry No. 1a, 137516-56-4; **1b**, 137516-57-5; **1c**, 137516-58-6; **2a**, 137516-60-0; **2b**, 137516-61-1; **2c**, 137516-62-2; **3**, 137516-55-3; $PhCH_2CH_2CHO$, 104-53-0; PPh_3, 603-35-0.

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Metal-Halogen Exchange between Polybromoanisoles and Aliphatic Grignard Reagents: A Synthesis of Cyclopenta[*b*]benzofurans

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Metal-halogen exchange between aromatic halides and aliphatic organometallic reagents is a versatile method for preparing aromatic organometallic species.[1] Although organolithium reagents are usually used for this purpose,

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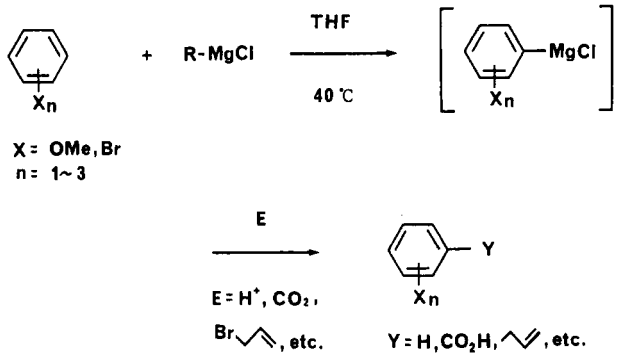
Table I. Metal-Halogen Exchange between Bromoanisoles and Alkyl Grignard Reagents

run	bromoanisole	Grignard reagent (RMgX) R	X (equiv)	reactn time (h)	treatment[a]	product	yield[b] (%)
1	2-bromoanisole (1)	*i*-Pr	Cl (7.5)	16	A	anisole	64[c]
2	4-bromoanisole (2)	*i*-Pr	Cl (7.5)	19	A	anisole	28[c]
3	2,4-dibromoanisole (3)	Me	Br (2.5)	24	A	2	<1
4	3	Et	Br (2.0)	11	A	2	88[c,d]
5	3	*i*-Pr	Cl (2.0)	5	A	2	93[c,d]
6	3	*i*-Pr	Br (2.2)	5	A	2	85[c,d]
7	3	*i*-Pr	Cl (2.5)	5	B	E = allyl	83
8	3	*i*-Pr	Cl (2.5)	5	C	E = COOH	90
9	3	*i*-Pr	Cl (2.5)	3	D	E = I	69
10	3	*i*-Pr	Cl (2.5)	5	E	E = $CH(OH)C_3H_7$	93
11	3	cyclohexyl	Cl (2.5)	5	A	2	93[c,d]
12	2,6-dibromoanisole (4)	*i*-Pr	Cl (2.5)	3	A	1	95
13	2,4,6-tribromoanisole (5)	*i*-Pr	Cl (1.3)	1	A	3	79

[a] A, H_2O; B, allyl bromide (1.0 equiv per equiv of RMgX), CuI (10 mol %, based on the bromoanisole); C, CO_2 gas; D, I_2; E, C_3H_7CHO. [b] Isolated yield unless indicated otherwise. [c] Determined by GLPC. [d] Selectivity: >99%. A trace of 2-bromoanisole was detected (<1%).

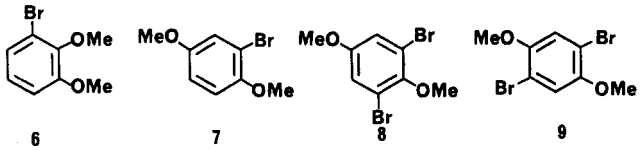
their strong basicity and nucleophilicity can cause problems, e.g., multiple metal–halogen exchanges with polyhalogenated aromatic compounds, alkylation of the aromatic ring. We were therefore interested in the possibility that metal–halogen exchange between polybromoanisoles and alkyl Grignard reagents could be employed as a mild method for generating halogenated aromatic Grignard reagents.[2]



The reaction of various bromoanisoles with an excess (2.0–7.5 equiv) of an alkyl Grignard reagent, RMgX (X = Cl, Br; R = Et, *i*-Pr, cyclohexyl) in tetrahydrofuran (THF) at 40 °C, followed by hydrolysis, gave monodebrominated anisoles. The intermediate aromatic Grignard reagents could be trapped by treatment with carbon dioxide, allyl bromide and CuI, or iodine, which gave the corresponding substituted anisoles. The quantity of the alkyl Grignard reagent that was required and the reaction time are shown in Table I.

A large excess of isopropylmagnesium chloride was required to convert the monobromoanisoles 1 and 2 into the corresponding Grignard reagents, which, on hydrolysis, gave anisole (run 1, 2). In contrast, 2,4- and 2,6-dibromoanisole (3 and 4, respectively) were easily converted into the corresponding anisyl Grignard reagents on treatment with 2.0–2.5 equiv of an alkyl Grignard reagent (RMgX, R = Et, *i*-Pr, cyclohexyl) (runs 4–12). Methylmagnesium bromide reacted relatively slowly with dibromoanisole (run 3), presumably because it is a weaker base than the other alkyl Grignard reagents.

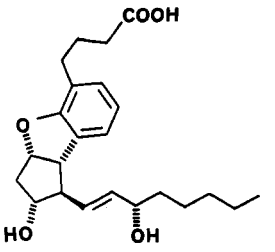
It is quite noteworthy that, *with 2,4-dibromoanisole, only one bromine atom, that ortho to the methoxy group, was exchanged.* In the case of 2,4,6-tribromoanisole (5) also, only one bromine atom, again one of those ortho to the methoxy group, was exchanged (run 13). The structurally similar brominated dimethoxybenzenes 6–9 reacted similarly to give the corresponding monodebrominated Grignard reagents.[3]



6 7 8 9

Pure THF is the solvent of choice. In THF to which another solvent, e.g., diethyl ether, 1,2-dimethoxyethane (DME), cyclohexane, has been added, metal–halogen exchange proceeds more slowly than in pure THF.

We have been interested in a versatile method that could be used to prepare the cyclopenta[*b*]benzofuran skeleton[4] of a key intermediate in a synthesis of the stable prostacyclin analogue 10.[5] Thus, starting from 3,5-*cis*-di-



10

bromo-1-cyclopentene (11)[6] the bis(2-bromophenoxy)-

(1) (a) Gilman, H.; Jacoby, A. *J. Org. Chem.* **1938**, *3*, 103. (b) Wittig, G.; Pockels, U.; Dorge, H. *Chem. Ber.* **1938**, *71*, 1903. (c) For a review: Jones, R. G.; Gilman, H. *Organic Reaction*; John Wiely & Sons, Inc.: New York; **1951**; Vol. 6, p 339.

(2) (a) Gilman, H.; Spatz, S. M. *J. Am. Chem. Soc.* **1941**, *63*, 1553. (b) Gilman, H.; Haubein, A. H. *Ibid.* **1945**, *67*, 1033. (c) Zakharkin, L. I.; Okhlobystin, O. Y.; Bilevitch, K. A. *Tetrahedron* **1965**, *21*, 881. (d) Gilman, H. *J. Organomet. Chem.* **1975**, *100*, 83. (e) Respess, W. L.; Tamborski, C. *Ibid.* **1968**, *11*, 619. (f) Smith, C. F.; Moore, G. J.; Tamborski, C. *Ibid.* **1971**, *33*, C21. (g) Martin, G. J.; Mechin, B.; Leroux, Y.; Paulmier, C.; Meunier, J. C. *Ibid.* **1974**, *67*, 327. (h) Yoshida, Z.; Konishi, H.; Miura, Y.; Ogoshi, H. *Tetrahedron Lett.* **1977**, 4319.

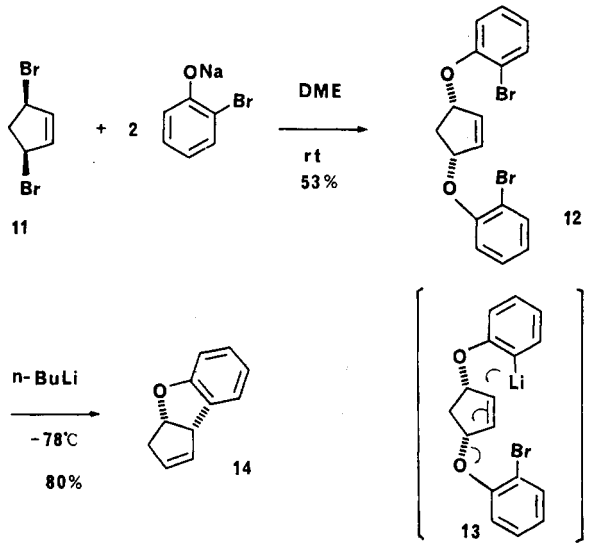
(3) From the reaction with *i*-PrMgCl (3.0–4.0 equiv, 3–6 h, 40 °C, THF), after quenching with water, the yields of the respective monodebrominated products were 84% from 6, 74% from 7, 94% from 8, 84% from 9.

(4) Hosokawa, T.; Miyagi, S.; Murahashi, S.-I.; Sonoda, A. *J. Org. Chem.* **1978**, *43*, 2752.

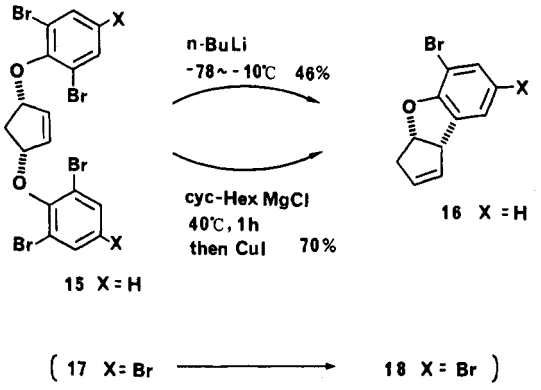
(5) (a) Ohno, K.; Nishiyama, H.; Nagase, H.; Matsumoto, K.; Ishikawa, M. *Tetrahedron Lett.* **1990**, *31*, 4489. (b) Nagase, H.; Matsumoto, K.; Yoshihara, H.; Tajima, A.; Ohno, K. *Ibid.* **1990**, *31*, 4493. (c) Ohno, K.; Nagase, H.; Matsumoto, K.; Nishiyama, H.; Nishio, S. *Advances in Prostaglandin, Thromboxane, and Leukotriene Research*; Raven Press: New York, **1985**; Vol. 15, p 279.

(6) Young, W. G.; Hall, H. K., Jr.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 4338.

cyclopenetene 12 was prepared in 53% yield by the Williamson reaction. Treatment of 12 with *n*-BuLi (1.5 equiv) at −78 °C generated the phenyllithium species 13. That species readily underwent an intramolecular S_N2' reaction at 0 °C to give the desired product of overall syn addition, 3a,8b-*cis*-3*H*-cyclopenta[*b*]benzofuran (14, 80%). Cyclization proceeded very smoothly in the absence of any metal catalyst such as cuprous ion.



However, similar treatment of the bis(2,6-dibromophenoxy)cyclopentene 15 with *n*-BuLi (1.5 equiv) at −50 °C and subsequent cyclization of the product aryllithium at +10 °C gave 5-bromocyclopenta[*b*]furan (16) in only low yield (46%), together with bromine-free 14 (ca. 20%). In this case it is apparent than the strongly basic alkyllithium was not a suitable reagent for effecting metal–halogen exchange. Therefore, in an attempt to improve both the yield and the selectivity of the metal–halogen exchange, cyclohexylmagnesium chloride was employed. CuI was used to catalyze the subsequent cyclization. Thus, successive treatment of the bis(2,6-dibromophenoxy)cyclopentene 15[7] with the Grignard reagent (2.0 equiv, 40 °C, 1 h) and CuI (10 mol %) gave the desired cyclic product, 5-bromocyclopenta[*b*]benzofuran (16), in 70% yield.



(17 X = Br ⟶ 18 X = Br)

The bis(2,4,6-tribromophenoxy)cyclopentene 17 was similarly converted to the dibromocyclopenta[*b*]benzofuran 18 in good yield (69%).

Thus, an effective method for achieving metal–halogen exchange between polybromoanisoles and alkyl Grignard reagents was found. Furthermore, its utility was demonstrated by applying it to the synthesis of the cyclopenta[*b*]benzofuran skeleton. Because only one bromine atom of a polybromoanisole is exchanged on reaction with an alkyl Grignard reagent, the reaction represents a new type of selective organic functional group transformation.

(7) The cyclopentenes 18 and 20 were synthesized in essentially the same manner as was 15. See the Experimental Section.

Experimental Section

General. ^1H NMR spectra of $CDCl_3$ solutions were recorded with JEOL JMR-PMX60 and JEOL JNM-FX100 spectrometers. ^{13}C NMR spectra were recorded with a JEOL GX-270. Infrared spectra were recorded with a JASCO A-3 spectrometer. High-resolution mass spectra (HRMS) were recorded with a JEOL JMS D-300 spectrometer. GLPC analyses were performed with a Shimadzu GC-3BT equipped with a 2 m × 3 mm 10% PEG 20M column. Helium served as the carrier gas. Microanalyses were performed at the Microanalysis Center of Kyoto University. Analytical TLC was performed with Merck precoated (0.25 mm) silica gel plates. Column chromatography was performed with Merck silica gel Art 7734. THF was distilled from $LiAlH_4$. 2,4-Dibromoanisole and 2,4,6-tribromoanisole were prepared from the corresponding phenols by successive reaction with NaH and CH_3I.

Reaction of 2,4-Dibromoanisole with *i*-PrMgCl and Subsequent Treatment with H_2O, Allyl Bromide, CO_2, C_3H_7CHO, and I_2. To *i*-PrMgCl (5 mL of a 1.0 N solution in THF, 5 mmol) at 40 °C was slowly added a solution of 2,4-dibromoanisole (0.53 g, 2.0 mmol) in THF (5 mL). The reaction was monitored by GLPC. After 5 h of stirring, the mixture was cooled to 0 °C and was treated with water (1 mL). The mixture was then extracted with Et_2O (5 mL). GLPC analysis of the extract showed the presence of 4-bromoanisole (93% yield) and trace amounts (<1%) of 2-bromoanisole.

To the Grignard reagent prepared in the same manner from 2,4-dibromoanisole (5 h reaction time), allyl bromide (0.43 mL, 3.0 mmol) and CuI (38 mg, 0.2 mmol) were added at 0 °C. The mixture was stirred for 2 h, and then it was treated with water (1 mL). The whole was extracted with ether (5 mL). The extract was concentrated, and the residue was purified by column chromatography on silica gel (hexane/ether, 9:1) to give 377 mg (1.66 mmol, 83%) of 2-allyl-4-bromoanisole: ^1H NMR (60 MHz) δ 3.30 (d, J = 7 Hz, 2 H), 3.76 (s, 3 H), 4.90–5.20 (m, 2 H), 5.90 (m, 1 H); IR (film) 915, 990 cm^{-1}; HRMS calcd for $C_{10}H_{11}OBr$ (78.9183) 225.9992, found 225.9992.

Into a THF solution of the Grignard reagent prepared from 2,4-dibromoanisole (5 h reaction time) was passed CO_2 gas at rt for 30 min. (The CO_2 gas was generated from dry ice and was passed through concd H_2SO_4 before it was introduced into the reaction mixture.) After workup as described above, the crude product was purified by column chromatography on silica gel (hexane/ether, 9:1) to give 360 mg (1.8 mm,ol, 90%) of 5-bromo-2-methoxybenzoic acid: mp 116–119 °C; ^1H NMR (60 MHz) δ 4.01 (s, 3 H), 4.6 (broad, 1 H), 6.83 (d, J = 9.0 Hz, 1 H), 7.53 (dd, J = 9.0, 3.0 Hz, 1 H), 8.16 (d, J = 3.0 Hz, 1 H); IR (KBr) 3320–2730, 1701 cm^{-1}. Anal. Calcd for $C_7H_7O_3Br$: C, 41.59; H, 3.05. Found C, 41.52; H, 2.81.

The reaction of the Grignard derived from 2,4-dibromoanisole (2.0 mmol) with C_3H_7CHO (0.35 g, 4.8 mmol) and I_2 (0.65 g, 2.6 mmol) gave 4-bromo-2-(1-hydroxy-*n*-butyl)anisole (486 mg, 1.86 mmol, 93%) and 4-bromo-2-iodoanisole (425 mg, 1.38 mmol, 69%), respectively.

Reaction of 2,6-Dibromoanisole with *i*-PrMgCl. In a manner similar to that described above, 2,6-dibromoanisole (2.0 mmol) was treated with *i*-PrMgCl (2.5 equiv) in THF at 40 °C for 3 h. Hydrolysis and workup gave 2-bromoanisole in 95% yield (GLPC analysis).

Reaction of 2,4,6-Tribromoanisole with *i*-PrMgCl. In a manner similar to that described above, *i*-PrMgCl (4.0 mmol, 5.0 mL of a 1.2 N solution in THF) and a solution 2,4,6-tribromoanisole (1.03 g, 3.0 mmol) in THF (5 mL) were allowed to react at 40 °C for 1 h. Workup as described above and column chromatography gave 2,4-dibromoanisole (640 mg, 2.4 mmol; 80%) which contained a trace amount of 2,6-dibromoanisole (<3% by GLPC).

Preparation of 3,5-*cis*-Bis(2-bromophenoxy)-2-cyclopentene (12). To a suspension of NaH (50% dispersion in mineral oil, 2.78 g, 0.058 mol) and DME (20 mL) at 0 °C was slowly added

a solution of 2-bromophenol (6.67 mL, 0.058 mol) in DME (20 mL). After evolution of H_2 had ceased, the mixture was cooled to −30 °C, and a solution of 3,5-dibromocyclopentene[4] (6.24 g, 0.0267 mol) in DME (25 mL) was added. The mixture was warmed to rt and was stirred for 1 day. After evaporation of the solvent, the residue was dissolved in EtOAc (300 mL). The solution was washed with brine (20 mL × 2) and 1 N aqueous NaOH (20 mL). The solution was then dried (Na_2SO_4). Activated carbon (15 g) was added, and the mixture was warmed at 60 °C. The mixture was filtered. Concentration of the filtrate gave **12** (6.0 g, 0.015 mmol, 53%) as an almost pure white solid: mp 138–139 °C; ^{1}H NMR (100 MHz) δ 2.21 (dt, J = 5.0, 14.0 Hz, 1 H), 3.08 (q, J = 7.0, 14.0 Hz, 1 H), 5.20 (dd, J = 5.0, 7.0 Hz, 2 H), 6.30 (s, 2 H), 6.8–7.6 (m, 8 H); IR (KBr) 1585, 1473, 1440, 1272, 1165, 1130, 1050, 992, 790, 760, 750 cm^{-1}; MS m/e 239 (M^+ − 171, 171 = C_6H_4BrO), 237, 175, 172, 171, 158. Anal. Calcd for $C_{17}H_{14}Br_2O_2$: C, 49.66; H, 3.68. Found C, 49.66; H, 3.56.

Synthesis of 3a,8b-*cis*-Dihydro-3*H*-cyclopenta[*b*]benzofuran (14). To a stirred solution of 3,5-*cis*-bis(2-bromophenoxy)-2-cyclopentene (**12**) (6.0 g, 14.6 mmol) in THF (80 mL) at −50 °C was slowly added *n*-BuLi (2.0 N solution in hexane, 11 mL, 22 mmol). After 1 h, the solution was warmed to −10 °C and stirred for 3 h. Then brine (5 mL) was added. The mixture was concentrated. The residue was dissolved in Et_2O (300 mL). The solution washed with 1 N aqueous NaOH (20 mL) and brine (30 mL) and then was dried (Na_2SO_4) and concentrated. The residual oil was purified by column chromatography on silica gel (cyclohexane/EtOAc, 95:5) to give **14** as colorless oil (1.84 g, 11.7 mmol, 80%): ^{1}H NMR (100 MHz) δ 2.80 (dd, J = 0.5, 2.2 Hz, 1 H), 2.82 (dd, J = 0.5, 5.2 Hz, 1 H), 4.35 (d, J = 7.8 Hz, 1 H), 5.43 (m, 1 H), 5.71 (s, 2 H, olefinic), 6.7–7.6 (m, 4 H); ^{13}C (67.9 MHz) 40.58, 54.22, 86.33, 109.33, 120.19, 124.16, 128.02, 128.74, 128.94, 131.10, 159.49; IR (film) 1602, 1590, 1472, 1457, 1220, 1160, 1095, 900, 860, 827, 790, 750, 700 cm^{-1}; MS m/e 158 (M^+), 131, 115.

Preparation of 3,5-*cis*-Bis(2,6-dibromophenoxy)-2-cyclopentene (15). To a suspension of NaH (5.6 g, 0.117 mol) and DME (100 mL) at 0 °C was slowly added a solution of 2,6-dibromophenol[8] (29.4 g, 0.117 mol) in DME (159 mL). After the evolution of H_2 had ceased, 18-crown-6 (280 mg) and 3,5-dibromocyclopentene[5] (12.0 g, 0.053 mol) were added. The mixture warmed to rt and was stirred for 3 days. The white precipitate that formed was collected by filtration and were warmed (ca. 3 × 20 mL). Then it was dissolved in $CHCl_3$. The solution was dried ($MgSO_4$). Concentration gave almost pure **15** (22.6 g, 0.040 mol, 75%): mp 105–206 °C; ^{1}H NMR (100 MHz) δ 2.90 (dt, J = 8.0, 8.0, 16.0 Hz, 1 H), 3.12 (dt, J = 7.0, 7.0, 8.0 Hz, 1 H), 5.10 (dd, J = 7.0, 8.0 Hz, 1 H), 6.31 (s, 2 H, olefinic), 6.83 (t, J = 8.0 Hz, 1 H), 7.52 (d, J = 8.0, 8.0 Hz, 2 H); IR (KBr) 1550, 1430, 1375, 1235, 1068, 1015, 988, 960, 935, 895, 820, 760, 740, 715 cm^{-1}; MS m/e 572, 571, 570, 569, 568, 567, 566, 565, 564(M^+), 319, 317, 315. Anal. Calcd for $C_{17}H_{12}Br_4O_2$: C, 35.95; H, 2.13. Found: C, 35.86; H, 2.19.

Preparation of 3a,8b-*cis*-Dihydro-3*H*-5-bromocyclopenta[*b*]benzofuran (16). To a suspension of the tetrabromide **15** (87.1 g, 1.153 mol) in THF (300 mL) at 40 °C was added cyclohexylmagnesium bromide (140 mL of 2.18 M solution in THF). The mixture was stirred for 20 min, and then CuI (0.58 g) was added at room temperature. The mixture was stirred for 30 min and then was filtered. The filtrate was concentrated. The residue was dissolved in cyclohexane. The solution was washed with 5% aqueous NaOH, dried, and concentrated to give ca. 60 g of an oily material. This was distilled under reduced pressure (60–62 °C/10^{-3}) to afford 26.0 g (0.11 mol, 72%) of pure crystals of **16**: mp 38–39 °C; ^{1}H NMR (100 MHz) δ 2.90 (m, 2 H), 4.80 (d, J = 8.0 Hz, 1 H), 5.54 (dt, J = 4.0, 4.0, 8.0 Hz, 1 H), 5.66 (m, 2 H), 6.70 (t, J = 8.0, 8.0 Hz, 1 H), 7.20 (m, 2 H); ^{13}C (67.9 MHz) 40.61, 55.12, 87.05, 102.45, 121.69, 123.18, 129.57, 130.29, 130.55, 131.16, 156.84; IR (film) 3060, 2950, 1600, 1585, 1480, 1220, 1162, 1130, 1050, 945, 860, 832, 770, 750, 740, 710 cm^{-1}; MS m/e 238, 236 (M^+), 209, 211, 128. Anal. Calcd for $C_{11}H_9OBr$: C, 55.72; H, 3.83; Br, 33.80. Found: C, 55.46; H, 3.82; Br, 34.10.

Preparation of 3,5-*cis*-Bis(2,4,6-tribromophenoxy)cyclopentene (17). In a manner similar to that used to prepare **15**, **17** (131 g, 0.133 mol, 51%) was prepared from 2,4,6-tribromophenol (193 g, 0.509 mol) and 3,5-dibromocyclopentene (59 g, 0.26 mol). **17**: mp 253–254 °C; ^{1}H NMR (100 MHz) δ 2.73 (m, 1 H), 3.06 (m, 1 H), 5.05 (m, 2 H), 6.24 (s, 2 H), 7.68 (s, 4 H); IR (KBr) 1600, 1570, 1470, 805, 780 cm^{-1}; MS m/e 393 (M^+ − 327), 327.

Preparation of 3a,8b-*cis*-Dihydro-3*H*-5,7-dibromocyclopenta[*b*]benzofuran (18). To a stirred suspension of the hexabromide **17** (50 g, 0.069 mol) in THF (172 mL) at 40 °C was added cyclohexylmagnesium bromide (32 mL of a 2.1 M solution in THF). After 30 min of stirring, CuI (0.58 g) was added at rt. The mixture was stirred for 30 min and then was filtered. The residue was purified by column chromatography on silica gel (cyclohexane) to afford 20 g of crude product. Recrystallization (EtOAc/cyclohexane) gave **18** (15 g, 0.0457 mol, 69%): mp 110–112 °C; ^{1}H NMR (100 MHz) δ 2.90 (m, 2 H), 4.48 (m, 1 H), 5.60 (m, 1 H), 5.80 (m, 2 H), 7.25 (d, J = 2.0 Hz, 1 H), 7.40 (d, J = 2.0 Hz, 1 H); ^{13}C NMR (67.9 MHz) 40.59, 55.06, 87.74, 103.06, 112.10, 126.32, 130.00, 130.12, 132.02, 133.20, 156.38; IR (KBr) 3070, 2980, 2920, 1585, 1570, 865, 830, 740, 718 cm^{-1}. Anal. Calcd for $C_{11}H_8OBr_2$: C, 41.81; H, 2.55; Br, 50.58. Found: C, 41.67; H, 2.53; Br, 50.60.

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The Absolute Configuration of (*R*)-(−)-(4-Methylcyclohexylidene)acetic Acid[1]

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A recent paper by Salvadori et al.[3] concerning the lack of correspondence between the experimental and theoretical values for the circular dichroism (cd) spectra of the long wavelength $\pi-\pi^*$ for a number of chiral 1,3-dienes[4] prompts this report. Calculations using De Voe coupled oscillator theory or a semiempirical MO-SCF method (CND/S) yielded cd signs opposite to those found experimentally[4] for a series of s-trans chiral planar (cyclohexylidene)propenes **1**. The same result is obtained in using Weigang's amplified sector rule.[5] Although the absolute configurations of **1** had been confidently established by chemical correlations,[4a,6] because of Salvadori's findings it was thought desirable to confirm the absolute configurations of one of the key intermediates, Gerlach's

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