Samarium(II) Diiodide Mediated Coupling of Bis(bromomethyl)arenes. Facile Synthesis of [2^n]Cyclophanes without using High-Dilution Techniques

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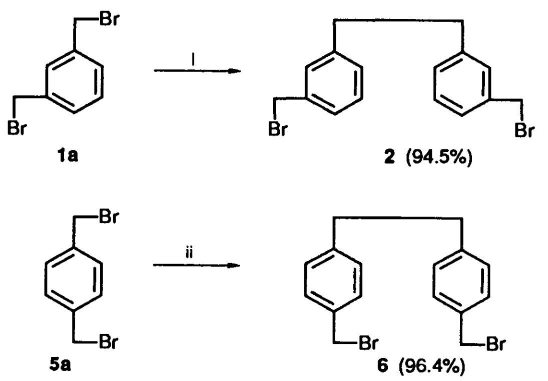
In the presence of samarium(II) diiodide (SmI_2), coupling of 1,3- and 1,4-bis(bromomethyl)benzenes proceeds smoothly to give their cyclic and acyclic oligomers. Use of 1.2 equiv of SmI_2 gives 1,2-bis(3- and 4-bromomethylphenyl)ethanes, respectively, in 95% yield, and the use of 5.0 equiv. of SmI_2 affords [2^n]metacyclophanes and [2^n]paracyclophanes ($n = 2$, 3 and 4), respectively, in satisfactory yields. By using 5.0 equiv. of SmI_2, 2-bromo- and 2-methoxy-1,4-bis(bromomethyl)benzenes and 1,4- and 2,6-bis(bromomethyl)naphthalenes each give only one of several expected isomeric [2.2]cyclophanes as the major cyclic oligomer.

All methods reported hitherto for the synthesis of [2.2]cyclophanes[1,2] utilize a time-consuming high-dilution technique for cyclization of open-chain starting materials to [2.2]cyclophanes or their cyclic precursors. Of these, the Wurtz reaction, the tetraphenylethylene-catalysed Wurtz reaction, and organolithium-mediated couplings of bis(halogenomethyl)arenes having no other active substituents are simple, useful methods when the starting dihalides are readily available.[1] The catalysed Wurtz reaction has also been used for the synthesis of higher members of [2^n]meta-[3] and [2^n]paracyclophanes.[4] In the hope of preparing [2^n]cyclophanes in satisfactory yields without using a high-dilution procedure, we have investigated the coupling of bis(halogenomethyl)arenes with low-valent lanthanoids, which is a direct application of Kagan's original work[5] on the samarium(II) diiodide-mediated coupling of benzyl bromide to 1,2-diphenylethane. Our preliminary report[6] indicated that, of the low-valent lanthanoid iodides used, iodized Misch metal (MmI_2) is the most effective reagent as far as obtaining [2.2]cyclophanes is concerned. During our continuing study, however, MmI_2 was found to be less useful for the synthesis of [2^n]cyclophanes, since yields of these cyclophanes were changed significantly depending not only on the composition of Misch metal used, but also on minor changes in procedure for the preparation of MmI_2. In contrast, samarium(II) diiodide (SmI_2) had no such faults and gave low, but satisfactory yields of [2.2]cyclophanes together with high yields of higher [2^n]cyclophanes as compared with those obtained using MmI_2. For this reason, our work was thereafter continued using SmI_2. We report here the results of the SmI_2-mediated coupling of bis(halogenomethyl)arenes, such as 1,3- and 1,4-bis(bromomethyl)benzenes, 2-bromo- and 2-methoxy-1,4-bis(bromomethyl)benzenes, 1,4- and 2,6-bis(bromomethyl)naphthalenes.

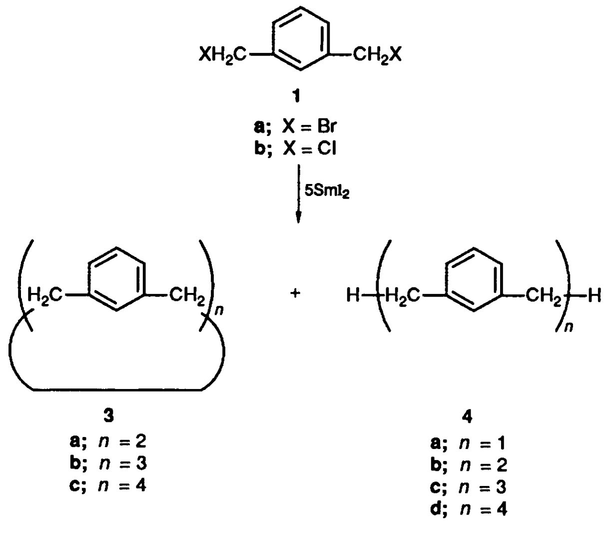
Results and Discussion

Coupling of 1,3- *and* 1,4-*Bis(bromomethyl)benzenes* **1a** *and* **5a**.—When **1a** and **5a** were each rapidly added to 1.2 equiv of SmI_2 in tetrahydrofuran (THF) at low temperature, a reaction smoothly took place, as monitored by the change of the initial deep-blue colour (Sm^{2+}) to orange (Sm^{3+}), and gave 1,2-bis(3- and 4-bromomethylphenyl)ethanes **2** and **6**, respectively, in *ca.* 95% yields, as shown in Scheme 1. Apparently, this synthetic method for **2** and **6** (intermediates used previously for the synthesis of [2.2]meta-[7] and [2.2]paracyclophanes[8]) has a greater advantage as to simplicity and yield than those starting from halogenobenzyl bromide[7] and 1,2-diphenylethane.[8]

In the hope of preparing [2^n]cyclophanes, next, **1a** and **5a** were each allowed to react with 3 equiv of SmI_2. It was found that, after the initial blue colour turned to orange, a considerable amount of the unchanged dibromide remained, a result which was brought about by competitive reduction of the bromomethyl group by 2 equiv of SmI_2[5]. The reaction was repeated using 5 equiv of SmI_2 for a period of time sufficient to allow complete consumption of the benzylic bromine atom. In this case, no colour change was observed. Under these conditions, **1a** smoothly reacted to give [2.2]metacyclophane **3a**, [2.2.2]metacyclophane **3b** and [2.2.2.2]metacyclophane **3c** in *ca.* 8, 11 and 8% yields, (see Table 1 and Scheme 2). The yields were almost constant and were independent of the type of



Scheme 1 *Reagents and Conditions:* i, 1.2 SmI_2, −20 °C, 0.5 h; ii, 1.2 SmI_2, −30 °C → room temp., 1 h



Scheme 2

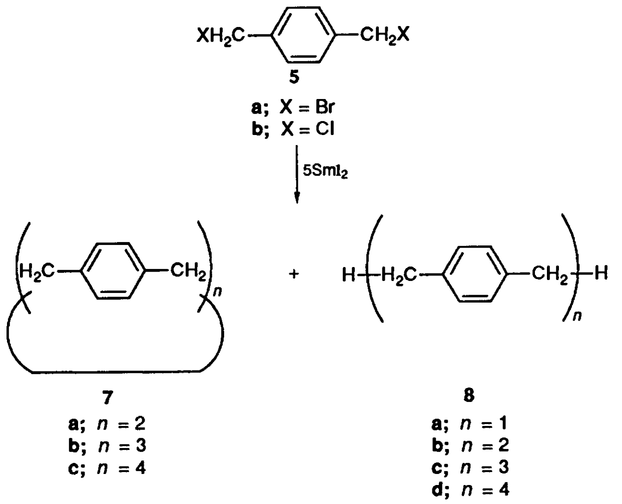
Table 1 Results of the coupling of 1,3-bis(halogenomethyl)benzenes with 5 equiv. of SmI_2

		Conditions			Isolated yields (%)						
Run	Substrate	t_1[a]	t_2[b]	T/°C	**3a**	**3b**	**3c**	**4a**	**4b**	**4c**	**4d**
1	**1a**	1 h	1 h	Room temp.	8.7	12.7	6.2	7.3	6.2	10.0	13.1
2	**1a**	0.5 h	2 h	0	7.3	10.1	9.2	4.5	13.6	16.4	14.6
3	**1a**	5 s	10 min	Room temp.	7.7	10.2	7.5	4.6	13.4	17.0	17.8
4	**1b**	1 h	4 h	Room temp.	1.1	7.3	8.6	10.1	12.9	14.6	10.7

[a] Time of addition of substrate to SmI_2 solution. [b] Time of reaction taken after t_1.

addition of substrate to SmI_2 *i.e.* rapid addition within 5 s or slow addition over 0.5 or 1 h. The yield of **3a** is much lower than that given by the catalysed Wurtz reaction,[3,9] and the yields of **3b** and **3c** are satisfactory compared with those (7.5 and 1.7%) given by the catalysed Wurtz reaction.[3d] Under similar conditions, 1,3-bis(chloromethyl)benzene **1b** slowly reacted to give a much lower yield (only 1.1%) of **3a** together with satisfactory yields of **3b** and **3c**. Apart from the cyclophanes, all reactions gave *m*-xylene **4a**, 1,2-bis(3-methylphenyl)ethane **4b**, 1,3-bis[2-(3-methylphenyl)ethyl]benzene **4c**, and 3,3′-bis[2-(3-methylphenyl)ethyl]dibenzyl **4d**.

Under the conditions described above, **5a** gave [2.2]paracyclophane **7a**, [2.2.2]paracyclophane **7b** and [2.2.2.2]paracyclophane **7c** in 7.5, 4.4 and 5.0% yields by using rapid addition, (see Table 2 and Scheme 3). With slow addition however, **7a** was not obtained, and **7b** and **7c** were isolated in satisfactory yields (13.9 and 11.3%) compared with those (11 and 6.2%) by the catalysed Wurtz reaction.[4a,b] In either case, *p*-xylene **8a** and three acyclic ologomers **8b**, **8c** and **8d** were also isolated.



Scheme 3

Coupling of compounds **2** *and* **6**.—Slow addition over 0.5 h of **2** or **6** to 5.0 equiv of SmI_2 in THF at room temperature caused intermolecular coupling to form **3c** or **7c** in preference to intramolecular coupling to form **3a** or **7a**, (see Scheme 4). The dibromide **6** underwent no significant intramolecular coupling. The yield of **7c** from **6** was satisfactory compared with those (7[4b] or 17%[4d]) attained by the catalysed Wurtz reaction of 1,2-bis(4-chloromethylphenyl)ethane[4b] or **6**,[4d] and the yield of **3c** was much lower than that by the catalysed Wurtz reaction of **2**.[7]

$\mathbf{2} \xrightarrow{5SmI_2,\ \text{room temp.}}$ **3a** + **3c** + **4b** + **4d**

t_1/h 0.5 t_2/h 2	10.1%	14.1%	7.2%	18.6%

$\mathbf{6} \xrightarrow{5SmI_2,\ \text{room temp.}}$ **7a** + **7c** + **8b** + **8d**

t_1/h 0.5 t_2/h 2	—	12.2%	7.0%	13.2%

Scheme 4

Coupling of Other Bis(bromomethyl)arenes.—Finally, coupling with 5.0 equiv of SmI_2 was performed for the four dibromides described below, each of which was expected to produce several isomeric [2.2]cyclophanes. Surprisingly, 2-bromo-1,4-bis(bromomethyl)benzene **9a** gave pseudo-*meta*-4,13-dibromo-[2.2]paracyclophane **10a** and 1,2-bis(2-bromo-4-methylphenyl)ethane **11a** as the major products (see Scheme 5). Their isomers and higher cyclic and acyclic oligomers were also formed in much smaller amounts, as detected by GLC. Under the same conditions, 2-methoxy-1,4-bis(bromomethyl)benzene **9b** gave pseudo-*meta*-4,13-dimethoxy[2.2]paracyclophane **10b** and 1-(2-methoxy-4-methylphenyl)-2-(3-methoxy-4-methylphenyl)ethane **12b** as the major products.

Coupling of 1,4-bis(bromomethyl)naphthalene **13** gave an 87% yield of *anti*-[2.2](1,4)naphthalenophane **14** together with a minor amount (5% yield) of 1,2-bis(4-methyl-1-naphthyl)ethane **15**. From 2,6-bis(bromomethyl)naphthalene **16**, the chiral, crossed form **17** of [2.2](2,6)naphthalenophane was obtained together with 1,2-bis(6-methyl-2-naphthyl)ethane **18**, (see Scheme 6).

Of the above four cyclophanes, only **10b** is new, the others being known. The cyclophane **10a** was obtained in 6% yield by direct bromination of **7a**.[10] The cyclophane **14** was prepared by the Hofmann degradation (3% yield) of the trimethylammonium hydroxide from 1-aminomethyl-4-methylnaphthalene,[11] by solvolysis (90%) of 1,4-bis(tosyloxymethyl)naphthalene[12] and by pyrolytic deselenation (75%) of 2,11-diselena[3.3](1,4)naphthalenophane;[2b] the cyclophane **17** was synthesized by pyrolytic desulphonation (38–48%) of the disulphone from 2,13-dithia[3.3](2,6)naphthalenophane.[13] The precursors used in the synthetic methods for **14** and **17** are available only with difficulty: for example, the dihetera-[3.3]naphthalenophanes were prepared starting from **13** and **16** by way of several reaction steps.[2b,13] Therefore, as compared with the earlier synthetic methods, the present method is greatly advantageous in terms of availability of precursor, ease of reaction procedure and product yields. The present method can also successfully use ring-halogenated bis(halogenomethyl)arenes, such as **9a**, which cannot be used in Wurtz and Wurtz-type reactions.

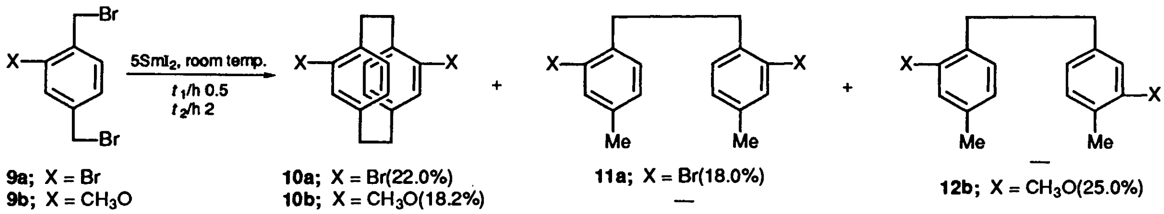
Experimental

General.—All m.p.s are uncorrected. GLC analyses were performed by using a Shimazu GC-4CM apparatus, equipped with a Shimazu Chromatopac C-R3A data processor, with a column of Silicone OV-17 (3%)-Chromosorb W (2.0 m) (N_2 as carrier gas). Preparative TLC separations were carried out on glass plates (20 × 20 cm) coated with Merck Kieselgel $60PF_{254}$ (1.5 mm). ^1H NMR spectra were measured for $CDCl_3$ solutions

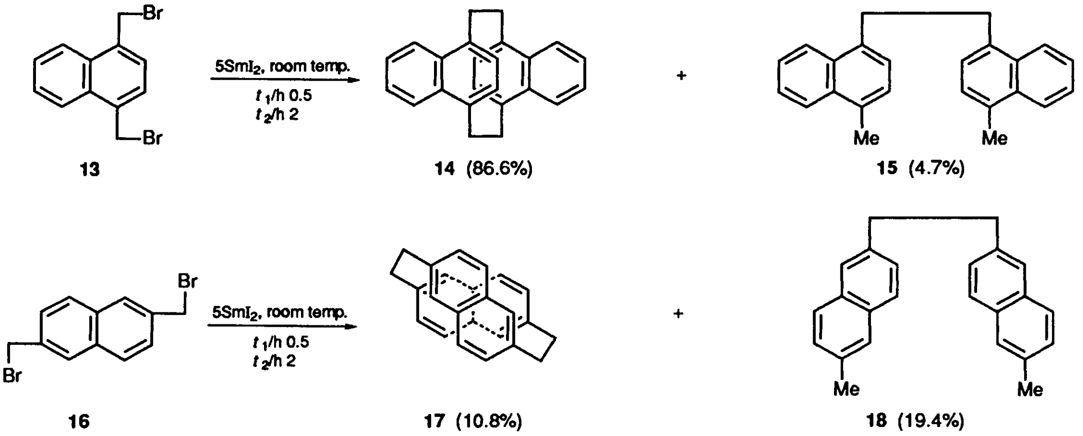
Table 2 Results of the coupling of 1,4-bis(halogenomethyl)benzenes with 5 equiv. of SmI_2

		Conditions			Isolated yields (%)						
Run	Substrate	t_1[a]	t_2[b]	T/°C	**7a**	**7b**	**7c**	**8a**	**8b**	**8c**	**8d**
1	**5a**	1 h	1 h	Room temp.	Trace	13.9	11.3	10.0	21.4	17.8	11.0
2	**5a**	5 s	10 min	Room temp.	7.5	4.4	5.0	9.2	33.6	16.2	4.7
3	**5b**	1 h	4 h	0	Trace	12.9	10.0	—	12.2	11.4	8.5

[a] Time of addition of substrate to SmI_2 solution. [b] Time of reaction taken after t_1.



Scheme 5



Scheme 6

containing tetramethylsilane (TMS) on a Hitachi R-24B spectrometer (60 MHz), J values are given in Hz. Mass spectra (EI) were measured on a Hitachi M-80 spectrometer equipped with an M-003 data processor. The structures of new compounds obtained were based upon spectroscopic characterization.

Preparation of SmI_2 *Solutions*.—Deep-blue 0.1 and 0.2 mol dm^{-3} SmI_2 solutions in THF were prepared from powdered samarium metal and 1,2-diiodoethane in anhydrous THF under an argon atmosphere.[5]

Coupling Reactions using 1.2 *Equiv of* SmI_2.—*Coupling of Compound* **1a**. A solution of **1a** (4.44 g, 16.8 mmol) in THF (46 cm^3) was rapidly added to the 0.1 mol dm^{-3} SmI_2 solution (200 cm^3) stirred at −20 °C under argon. The mixture was stirred at that temperature for 0.5 h until the initial blue colour turned to orange, and was then treated with dilute HCl and extracted with ether. The extract was washed successively with aq. $Na_2S_2O_3$, aq. $NaHCO_3$, brine and water, dried ($MgSO_4$) and evaporated. Crystallization of the resulting residue from hexane–CH_2Cl_2 gave 1,2-bis(3-bromomethylphenyl)ethane **2** as colourless needles (2.92 g, 94.5%): m.p. 90–91 °C (lit.,[7] 87–88 °C); δ 4.45 (8 H, s) and 7.20–7.43 (8 H, m).

Coupling of compound **5a**. A solution of **5a** (3.06 g, 11.6 mmol) in THF was rapidly added to the 0.2 equiv. SmI_2 solution (70 cm^3) stirred at −30 °C under argon. The mixture was allowed to warm to room temperature over 1 h, during which time the initial colour turned to orange. Work-up as above, followed by crystallization from hexane–CH_2Cl_2, gave 1,2-bis(4-bromomethylphenyl)ethane **6** (2.05 g, 96.4%) as colourless needles: m.p. 130–131 °C (lit.,[8] 129–131 °C); δ 4.41 (8 H, s) and 7.30 (8 H, s).

Coupling Reactions of Dibromides Using 5 *Equiv of* SmI_2.—*General Procedure*. A dibromide (3 mmol) in THF (15 cm^3) was added either rapidly within 5 s or dropwise slowly over 0.5 or 1 h to the 0.1 mol dm^{-3} SmI_2 solution (150 cm^3) stirred at 0 °C or room temperature under argon. The mixture was then stirred at that temperature for 10 min–2 h, during which time the initial blue colour became tinged slightly with green. The mixture was worked up and the resulting residue was then subjected to preparative TLC (PLC). The substances thus separated were further purified by PLC or crystallization. The results of typical examples of the coupling reaction with conditions shown are described below.

Coupling of compound **1a**. Coupling of **1a** (1.02 g, 3.87 mmol) gave the following six products as well as *m*-xylene **4a**, after preparative TLC with hexane and hexane–CH_2Cl_2 (50:1) and subsequent crystallization from hexane (Run 3 in Table 1).

[2.2]Metacyclophane **3a**. 31 mg (7.7%), m.p. 131–134 °C (lit.,[14] 133–134 °C); R_f 0.52 (hexane); δ 2.01–3.16 (8 H, m), 4.24 (2 H, s) and 6.98–7.30 (6 H, m).

1,2-Bis(3-methylphenyl)ethane **4b**. 54 mg (13.4%); oil; R_f 0.41 (hexane); δ 2.29 (6 H, s), 2.83 (4 H, s) and 6.89–7.10 (8 H, m).

1,3-Bis[2-(3-methylphenyl)ethyl]benzene **4c**. 69 mg (17.0%); m.p. 52–55 °C; R_f 0.38 (hexane–CH_2Cl_2, 50:1); δ 2.31 (6 H, s), 2.84 (8 H, s) and 6.80–7.14 (12 H, m).

[2.2.2]Metacyclophane **3b**. 41 mg (10.2%); m.p. 113–116 °C (lit.,[3d] 117–117.5 °C); R_f 0.31 (hexane–CH_2Cl_2, 50:1); δ 2.75 (12 H, s), 6.04 (3 H, s) and 6.77–7.15 (9 H, m).

3,3′-Bis[2-(3-methylphenyl)ethyl]dibenzyl **4d**. 72 mg (17.8%); m.p. 58–62 °C; R_f 0.20 (hexane); δ 2.28 (6 H, s), 2.83 (12 H, s) and 6.89–7.10 (12 H, m).

[2.2.2.2]Metacyclophane **3c**. 30 mg (7.5%); m.p. 129–131 °C (lit.,[3d] 132–133 °C); R_f 0.17 (hexane); δ 2.73 (16 H, s), 6.47 (4 H, s) and 6.82–7.14 (12 H, m).

Coupling of compound **5a**. Coupling of **5a** (0.81 g, 3.06 mmol) gave the following six products as well as *p*-xylene **8a**, after preparative TLC with hexane–CH_2Cl_2 (10:1) and subsequent crystallization from hexane (Run 2 in Table 2).

1,2-Bis(4-methylphenyl)ethane **8b**. 108 mg (33.6%), m.p. 80–82 °C (lit.,[8] 80–81 °C); R_f 0.63; δ 2.30 (6 H, s), 2.86 (4 H, s) and 7.07 (8 H, s).

1,4-Bis[2-(4-methylphenyl)ethyl]benzene **8c**. 52 mg (16.2%); m.p. 142–143 °C (lit.,[15] 140–141 °C); R_f 0.51; δ 2.28 (6 H, s), 2.82 (8 H, s) and 7.02 (12 H, s); *m/z* 314 (M^+, 25%), 209 (45), 105 (100), 104 (17), 77 (5) and 28 (14).

[2.2]Paracyclophane **7a**. 24 mg (7.5%); m.p. 284–286 °C (lit.,[8] 285–287 °C); R_f 0.48; δ 3.07 (8 H, s) and 6.43 (8 H, s).

[2.2.2]Paracyclophane **7b**. 14 mg (4.4%); m.p. 167–168 °C (lit.,[4a] 168 °C); R_f 0.43; δ 3.40 (12 H, s) and 6.42 (12 H, s).

4,4′-Bis[2-(4-methylphenyl)ethyl]dibenzyl **8d**. 15 mg (4.7%); m.p. 179–180 °C; R_f 0.35; δ 2.31 (6 H, s), 2.85 (12 H, s) and 7.09 (16 H, s); *m/z* 418 (M^+, 12%), 313 (8), 209 (24), 119 (8), 105 (100), 104 (22), 77 (4) and 28 (7).

[2.2.2.2]Paracyclophane **7c**. 16 mg (5.0%); m.p. 185–186 °C (lit.,[4a] 185 °C); R_f 0.27; δ 2.96 (16 H, s) and 6.56 (16 H, s).

Coupling of Compound **9a**. Coupling of **9a** (0.796 g, 2.32 mmol) gave **10a** and **11a** as the major products after preparative TLC treatment with hexane–CH_2Cl_2 (5:1), followed by crystallization from hexane.

pseudo-*m*-4,13-Dibromo-[2.2]paracyclophane **10a**. 93 mg (22.0%); m.p. 117–120 °C (lit.,[10] 123.5–125.5 °C); R_f 0.71; δ 2.68–3.30 (8 H, m), 6.42 (2 H, dd, *J* 2.0 and 8.0), 6.53 (2 H, d, *J* 2.0) and 7.13 (2 H, d, *J* 8.0). The NMR data agreed with those reported.[15]

1,2-Bis(2-bromo-4-methylphenyl)ethane **11a**. 77 mg (18.0%); m.p. 95–97 °C; R_f 0.82; δ 2.29 (6 H, s, CH_3), 2.96 (4 H, s), 7.02 (4 H, br s) and 7.35 (2 H, br s).

Coupling of compound **9b**. Coupling of **9b** (0.758 g, 2.58 mmol) gave **10b** and **12b** as the major products after preparative TLC treatment with hexane–CH_2Cl_2 (2:1), followed by crystallization from hexane–CH_2Cl_2.

pseudo-*m*-4,13-Dimethoxy[2.2]paracyclophane **10b**. 63 mg (18.2%); m.p. 175–177 °C; R_f 0.53; δ 2.43–3.60 (8 H, m), 3.68 (6 H, s), 5.65 (2 H, br s) and 6.30 (4 H, br s). The structure assignment was based upon a comparison of the data with those for the pseudo-*ortho*- and -*para*-isomers.[10,15]

1-(2-Methoxy-4-methylphenyl)-2-(3-methoxy-4-methylphenyl)ethane **12b**. 87 mg (25.0%); m.p. 92–94 °C; R_f 0.67; δ 2.21 (3 H, s, CH_3), 2.30 (3 H, s, CH_3), 2.80 (4 H, s), 3.71 (6 H, s, CH_3O), 6.60–6.90 (4 H, m) and 6.95–7.20 (2 H, br d, *J* 6.4).

Coupling of compound **13**. Coupling of **13** (303 mg, 0.96 mmol) gave **14** and **15**. In this case, the ether extract from the worked-up reaction mixture was first crystallized from hexane–CH_2Cl_2 to separate a great portion of **14** and the mother liquor was then subjected to preparative TLC with hexane–CH_2Cl_2 (2:1).

anti-[2.2](1,4)Naphthalenophane **14**. 128 mg (86.6%); m.p. 293–299 °C (lit.,[2b,11] 299–301 °C); δ 2.91–3.92 (8 H, m), 5.75 (4 H, s), 7.21–7.58 (4 H, m) and 7.60–7.90 (4 H, m); *m/z* 308 (M^+, 36%) and 154 (100).

1,2-Bis(4-methyl-1-naphthyl)ethane **15**. 7 mg (4.7%); m.p. 150–151.5 °C (lit., 154–155 °C[16] and 152–153 °C[17]); δ 2.67 (6 H, s), 3.47 (4 H, s), 7.24 (4 H, s), 7.35–7.64 (4 H, m) and 7.92–8.22 (4 H, m).

Coupling of compound **16**. Coupling of **16** (377 mg, 1.20 mmol) gave **17** and **18** as the major products after preparative TLC treatment with hexane–CH_2Cl_2 (5:1), followed by crystallization from benzene.

[2.2](2,6)Naphthalenophane **17**. 20 mg (10.8%); m.p. not measured (lit.,[13] 368–369 °C under nitrogen); $\delta(AsCl_3)$ 2.4–2.8 (4 H, m), 3.0–3.4 (4 H, m), 6.45 (4 H, s), 6.91 (4 H, A of AB pattern, *J* 8.0) and 7.25 (4 H, B of AB pattern, *J* 8.0).

1,2-Bis(6-methyl-2-naphthyl)ethane **18**. 36 mg (19.4%); m.p. 213–215 °C (lit.,[13] 218 °C); $\delta(AsCl_3)$ 2.50 (6 H, s), 3.0–3.25 (4 H, m), 7.40 (4 H, A of AB pattern, *J* 7.8), 7.70 (4 H, s) and 7.73 (4 H, B of AB pattern, *J*, 7.8).

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Paper 1/01405F
Received 25*th March* 1991
Accepted 30*th April* 1991