Formation of 1,3,5-Trilithiobenzene and Its Conversion to the Corresponding Magnesium, Mercury, and Tin Derivatives

Nicolette Rot and Friedrich Bickelhaupt*

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083,
1081 HV Amsterdam, The Netherlands

Received July 3, 1997[⊗]

Whereas the halogen−metal exchange approach from 1,3,5-tribromobenzene (**3**) to 1,3,5-trilithiobenzene (**1**) was unsuccessful, **1** was synthesized in high yield (about 80%) by reaction of **3** with LiDBB (lithium 4,4′-di-*tert*-butylbiphenyl). Compound **1** was used as the starting material for the preparation of other symmetrical trimetalated benzenes, 1,3,5-$C_6H_3(MgBr)_3$ (**20**), 1,3,5-$C_6H_3(SnMe_3)_3$ (**23**), and 1,3,5-$C_6H_3(HgBr)_3$ (**26**), by reaction with the corresponding metal halides.

Introduction

Polymetalated aromatic compounds with main group metal substituents bonded to the central ring are rare, in contrast to the mono- and dimetalated species. Only in metallocenes, are the rings susceptible to easy metalation. Thus, mixtures of polymetalated compounds were obtained in the reaction of ferrocene with potassium,[1] sodium,[2] and lithium[3,4] reagents. More well-defined products were formed by transmetalation of mercury compounds: perlithiated[5] and permagnesiated[6] ruthenocenes have been prepared.

Trilithiated benzenes were first reported from the ortho-metalation of trihalobenzenes by butyllithium.[7,8] Indications for the presence of 1,3,5-trilithio-2,4,6-trinitrobenzene in low yield (<18% yield) were obtained in the reaction of the corresponding tribromo compound with phenyllithium.[9] More drastic reaction conditions, such as the use of lithium vapor, seem necessary to achieve halogen−metal exchange of trichlorobenzene[10,11] or polymetalation of benzene or naphthalene.[11] Given these results, it is remarkable that the synthesis of hexalithiobenzene has been claimed to occur by conversion of hexachlorobenzene with a large excess of *tert*-butyllithium at extremely low temperature (−125 °C).[12] Several ab initio calculations concerning the structure of hexalithiobenzene have been reported.[13]

Table 1. Products and Yields Obtained in the Reaction of 3 with *t*-BuLi at −50 °C followed by Quenching with ICH_2CH_2I

			yield (%)			
entry	solvent	reagent	**8**	**9**	**10**	**11**
1	THF	*t*-BuLi	5	63	26	0
2	Et_2O	*t*-BuLi	4	95	1	0
3	Et_2O	*t*-BuLi/TMEDA	23	68	4	5

Grignard compounds of arenes with more than two metal functions are, to our knowledge, unknown, although an indication for the formation of a trimagnesiobenzene in very small amounts may be derived from the formation of 1,3,5-tris(dimesitylboryl)benzene (2% yield);[14] however, it is unclear whether this product results directly from a tri-Grignard reagent or from a stepwise substitution process, which in the presence of magnesium metal is conceivable (*cf.* the discussion of entry 3, Table 1). Finally, in this context, the *in situ* synthesis of 1,3,5-tris(dicyclopentadienylmethylzirconyl)benzene from triiodobenzene and $Cp_2Zr(CH_3)Cl$ in the presence of *tert*-butyllithium[15] should be mentioned.

Results and Discussion

Attempted Halogen−Lithium Exchange. Our first goal was the synthesis of 1,3,5-trilithiobenzene (**1**). This might be attempted in obvious analogy to the preparation of 1,3-dilithiobenzene (**2**), which we obtained by halogen−metal exchange from 1,3-dibromobenzene with *n*-butyllithium in refluxing hexane[16] or in ethereal solvent at low temperature from 1,3-diiodobenzene as a starting material.[17] Both methods proved to be unsuitable for the formation of **1**; only hydrogen- or butyl-substituted products were obtained from 1,3,5-tribromo- (**3**) and 1,3,5-triiodobenzene (**4**).

The reaction of **3** with *tert*-butyllithium in THF and diethyl ether was examined more closely. To a solution of 1,3,5-tribromobenzene (**3**) in an ethereal solvent (see Table 1), *tert*-butyllithium was added at −75 °C, after

---

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1997.

(1) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1978**, *162*, 79.

(2) Benkeser, R. A.; Nagai, Y.; Hooz, J. *J. Am. Chem. Soc.* **1964**, *86*, 3742.

(3) Halasa, A. F.; Tate, D. P. *J. Organomet. Chem.* **1970**, *24*, 769.

(4) Bednarik, L.; Neuse, E. *J. Organomet. Chem.* **1979**, *168*, C8−C12.

(5) Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1994**, *116*, 6468.

(6) Seneviratne, K. N.; Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1996**, *118*, 5506.

(7) Haiduc, I.; Gilman, H. *J. Organomet. Chem.* **1968**, *12*, 394.

(8) Howells, R. D.; Gilman, H. *Tetrahedron Lett.* **1974**, *14*, 1319.

(9) Buck, P.; Köbrich, G. *Chem. Ber.* **1970**, *103*, 1420.

(10) Shimp, L. A.; Chung, C.; Lagow, R. J. *Inorg. Chim. Acta* **1978**, *29*, 77.

(11) Massachusetts Institute of Technology, Brit. Patent 1,444,174; *Chem. Abstr.* **1977**, *86*, 106764t.

(12) (a) Baran, J. R., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 9415. (b) Baran, J. R., Jr.; Hendrickson, C.; Laude, D. A., Jr.; Lagow, R. J. *J. Org. Chem.* **1992**, *57*, 3759.

(13) (a) Xie, Y.; Schaefer, H. F., III *Chem. Phys. Lett.* **1991**, *179*, 563. (b) Smith, B. J. *Chem. Phys. Lett.* **1993**, *207*, 403 and references cited herein.

(14) Okada, K.; Sugawa, T.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1992**, 74.

(15) Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397.

(16) 1,3-Dilithiobenzene was synthesized in high yield by reaction of *n*-butyllithium and 1,3-dibromobenzene in refluxing hexane; Nijbacker, T. Unpublished results.

(17) Fossatelli, M.; den Besten, R.; Verkruijsse, H. D.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 527.

S0276-7333(97)00562-1 CCC: $14.00

Scheme 1

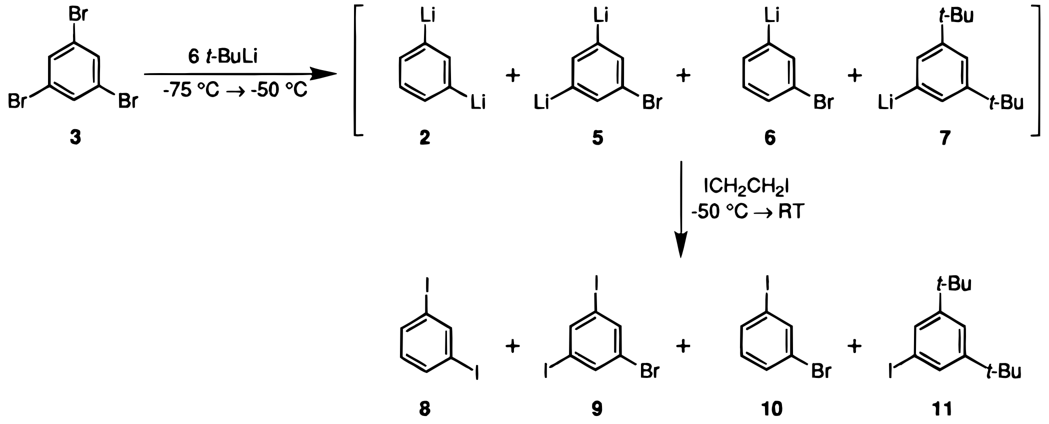


Table 2. Yields of 1, 2, and 12 Obtained in the Reaction of 3 with LiDBB As Determined from Quenching Reactions

entry	reaction temperature, °C	quenching reagent	yield (%) 1	2	12
1[a]	−75	ICH_2CH_2I	44	16	6
2[a]	−60	ICH_2CH_2I	57	12	7
3[a]	−50	ICH_2CH_2I	61	18	3
4[a]	−40	ICH_2CH_2I	79	13	7
5[a]	0	ICH_2CH_2I	21	28	4
6[b]	−40	CO_2	70	25	5
7[c]	−40	MeOD	74	6	10
8[a,d]	−40	$MgBr_2$	67	12	4
9[a]	−40	Me_3SnCl	69	15	4
10[e]	−40	$HgBr_2$	74	26	

[a] Yields were determined relative to hexamethylbenzene (internal standard) by GC. [b] Yields were calculated by weighing in combination with the ratio of the products (^{1}H NMR). [c] Relative yields (based on GC/MS, also 10% C_6H_6 present). [d] Yields based on the ratio of iodinated benzenes obtained after reaction with 1,2-diiodoethane. [e] Yields based on the ratio of brominated benzenes (^{1}H NMR) obtained after reaction with bromine.

which the reaction mixture was quickly warmed to −50 °C. Because the desired organolithium compounds are not stable at room temperature, the course of the reaction was followed by determination of the iodination products formed by quenching the reaction mixture at −50 °C with 1,2-diiodoethane. This derivatization is totally effective at low temperature; subsequent addition of MeOD followed by warming to room temperature showed no D-incorporation in the products. The iodinated products were identified by GC/MS analysis; the absolute yields were determined by GC using hexamethylbenzene as an internal standard.

In all experiments, three or four major products were obtained, **8**, **9**, **10**, and **11** (Table 1), which indicate the formation of the organolithium precursors **2**, **5**, **6**, and **7**, respectively (Scheme 1). The amount of the "hydrogenated" products **2** and **6** was substantial when the reaction was performed in THF (see Table 1, entry 1), presumbly due to proton abstraction from the solvent. We tried to suppress this side reaction by using the less reactive solvent diethyl ether. Although this was indeed effective (entry 2), in both experiments (entries 1 and 2) up to only two halogen atoms were exchanged, as indicated by the formation of **9**. The almost quantitative yield of **9** (entry 2) is remarkable and indicates that this procedure is attractive for the preparation of **5**. However, even the addition of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) did not result in the formation of 1,3,5-trilithiobenzene **1** (entry 3); only the amount of side products increased. In this last experiment, quenching was performed by pressing aliquots of the reaction mixture to 1,2-diiodoethane (inverse addition) to avoid variable results due to step-wise formation of products (sequential lithiation−derivatization−lithiation−derivatization etc.), which can occur if the quenching reaction is not fast enough so that the lithiating and the quenching reagent coexist in the reaction mixture. During the quenching process, the temperature of the reaction mixture was carefully maintained at the same low reaction temperature in order to avoid decomposition of the lithiated products.

The observation that more than two halogen−metal exchanges do not occur is remarkable. Possibly, the negative charge associated with the first two organolithium functions strongly counteracts the introduction of a third negative charge by bromine−lithium exchange.

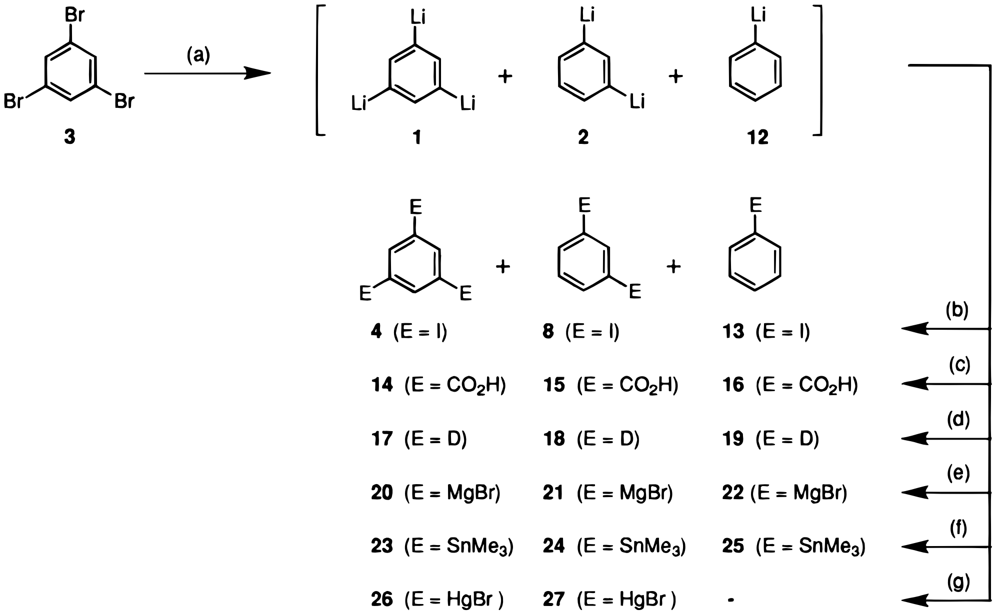
Reaction of 3 with LiDBB. Because the conditions mentioned above appeared to be too mild, we examined the reduction of **3** with lithium 4,4′-di-*tert*-butylbiphenyl (LiDBB).[18] The reaction was performed by adding 7 equiv of a solution of LiDBB in THF to **3** in diethyl ether at −75 °C. Subsequently, the temperature was increased to the final reaction temperatures indicated in Table 2. After 45 min, the reaction mixture was titrated with a solution of *tert*-butyl chloride in diethyl ether to remove the excess of LiDBB; this was indicated by a color change from blue-green (LiDBB) to red-brown (lithiated products). In this way, alternating lithiation and quenching during derivatization (as discussed above) is excluded. The quenching process at low temperature with the reagents indicated in Scheme 2 was complete, as evidenced by subsequent addition of MeOD which showed no D-incorporation in the products.

This approach to **1** was indeed successful. In all the experiments performed, **1** was formed as the main product, as indicated by the yield of the trisubstituted products obtained from the quenching reactions (Table 2). Small amounts of **2** and **12** were formed, too; this follows from the presence of minor amounts of 1,3-di- and monosubstitution products, respectively. The optimal reaction temperature proved to be −40 °C, where **1** can be obtained in about 80% yield (Table 2, entry 4). At lower temperatures, the reaction is too slow (entries 1−3), and at higher temperatures **1** seems to decompose (entry 5).

---

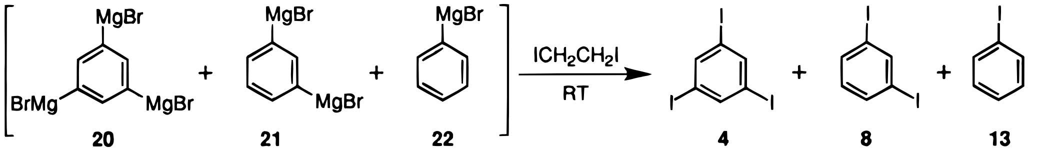
(18) (a) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924. (b) Freeman, P. K.; Hutchinson, L. L. *Tetrahedron Lett.* **1976**, *22*, 1849.

Scheme 2[a]

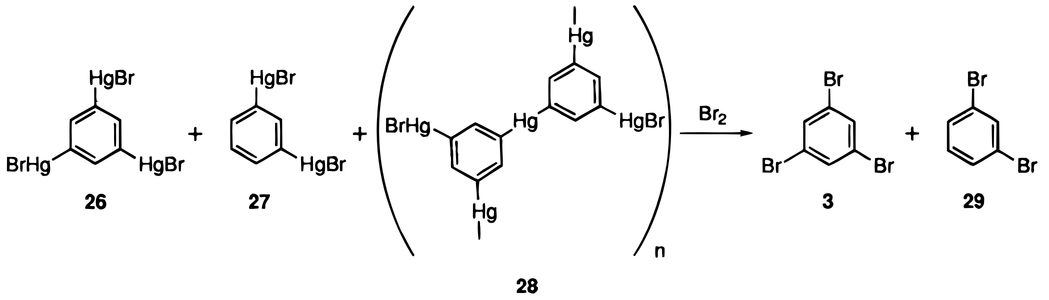


[a] Key: (a) 7 equiv of LiDBB. (b) ICH_2CH_2I. (c) CO_2. (d) MeOD. (e) $MgBr_2$. (f) Me_3SnCl. (g) $HgBr_2$; for the identity of the products, see text.

Scheme 3



Scheme 4



In order to verify the reliability of the 1,2-diiodoethane quenching reaction for the quantitative determination of the corresponding organolithium compounds, the lithiated products were reacted with other electrophiles (Table 2, entries 6−10). In all cases, the yields obtained were comparable. Bubbling gaseous CO_2 through the reaction mixture resulted in the formation of trimesic acid (**14**, 70%), isophthalic acid (**15**), and benzoic acid (**16**) (entry 6). These products could be separated from the large amount of DBB present after the reaction, which allowed determination of the yields by ^1H NMR spectroscopy; a symmetrical 1,3,5-substitution pattern was confirmed. Deuterolysis with MeOD (entry 7) gave a mixture of tri-, di-, and monodeuterobenzene (**17** (74%), **18**, **19**, respectively; GC/MS analysis).

The access to **1** allowed us to synthesize other, previously unknown, trimetalated benzenes in a straightforward fashion (Scheme 2, Table 2). The tri-Grignard reagent 1,3,5-tris(bromomagnesio)benzene (**20**) was obtained by addition of $MgBr_2$ to **1** (entry 8). Reactions of lithium compounds with metal salts are often fast, but in this case the conversion appeared to be rather slow. Even after 20 h, the reaction mixture was still red-colored, indicating the presence of organolithium compounds, while a white precipitate was formed. Quenching of the organomagnesium products that were formed with 1,2-diiodoethane at room temperature revealed the presence of **20**, the disubstituted derivate 1,3-bis(bromomagnesio)benzene **21**, and a minor amount of phenylmagnesium bromide **22**, as indicated by the products **4**, **8**, and **13** (Scheme 3). A separate quenching experiment showed that the precipitate consisted exclusively of a mixture of **20** and **21** (ratio 7.9:2.1), probably due to their diminished solubility compared to **22**. That these products are organomagnesium compounds and not unreacted organolithium compounds was established by the observation that **20** and **21** are stable for several days at room temperature in sharp contrast to **1** (*cf.* entry 5). Unfortunately, purification of this reaction mixture could not be achieved. Extraction of the solid with 2-MeTHF (in which **21** is

---

(19) Preparation of **21** from 1,3-dibromobenzene and Mg in 2-MeTHF did not lead to precipitation of this product.

soluble[19]) turned out to destroy **20**, as the amount of **4** in the product mixture after derivatization with 1,2-diiodoethane decreased while that of **8** increased.

1,3,5-Tris(trimethylstannyl)benzene (**23**) is formed as the main product (69% yield) in the reaction of **1** with Me$_3$SnCl. As side products, 1,3-bis(trimethylstannyl)-benzene (**24**) and trimethylstannylbenzene (**25**) were obtained (Scheme 2; Table 2, entry 9).

The relative yield of a benzene derivate carrying three mercurio substituents obtained by reaction of **1** with HgBr$_2$ was in line with expectations, as indicated by the yield of **3** (74%) after derivatization with bromine in DMSO (Scheme 4; Table 2, entry 10). However, the reaction mixture contained only a small amount of 1,3,5-tris(bromomercurio)benzene (**26**) (^{1}H NMR detectable, s, $\delta = 7.66$ ppm) and 1,3-bis(bromomercurio)benzene (**27**). The elemental analysis of the grey product mixture gave high percentages for mercury and low percentages for bromine, indicating the presence of mainly symmetrized products (**28**).

Experimental Section

General Comments. All reactions were carried out under an argon atmosphere. Glassware and syringes were dried in an oven at 120 °C for at least 24 h and extra flame-dried before use. The solvents Et$_2$O and THF were predried over NaOH and KOH, respectively, distilled from LiAlH$_4$, and kept over sodium-wire under nitrogen. 1,3,5-Tribromobenzene (**3**) was purchased from Janssen, recrystallized from methanol (mp 121 °C), and dried under vacuum prior to use. 1,2-Diiodoethane (Aldrich) was recrystallized from PE 40−60 and dried under vacuum (mp 81.5−82 °C). Lithium 4,4′-di-*tert*-butylbiphenyl (LiDBB) was obtained by reaction of lithium metal with DBB and prepared according to the literature.[18] DBB was purified by column chromatography using pentane as the eluent and recrystallized from MeOH (mp 125−126 °C).[20] ^{1}H NMR spectra were measured at 25 °C at 200 MHz on a Bruker AS 200 spectrometer; GC/MS measurements were performed on a HP 5890 GC/5970 MS combination (70 eV, Chrompack BP 1 (QSGE) 50 m × 0.25 mm column). The spectra of compounds **3**, **4**, **8**, **13**, **14**, **15**, **16**, **23**, **24**, **25**, and **29**, were identical with those of authentic samples, some of which have also been reported in the literature (*vide infra*). GC measurements were performed on an Intersmat gas chromatograph GC 120, equipped with a Chrompack column (2 m × 4 mm, 10% OV-101 Chromosorb WHP 80/100) and a thermal conductivity detector. Unless otherwise noted, separation of the product mixtures from DBB (*e.g.*, by crystallization) could not be achieved due to the large excess of DBB used (7 equiv per mol of **3**) and the small scale of the reaction. The yields of the products determined by GC using an internal standard are response-corrected unless otherwise noted (*vide infra*).

Reaction of 3 with *tert*-Butyllithium in THF. To a solution of **3** (0.0787 g, 0.25 mmol) in THF (10 mL) was added dropwise at −75 °C *tert*-butyllithium (1.1 mL, 1.50 M, 1.65 mmol, 6.6 equiv) in pentane. The reaction mixture had a dark yellow color. Subsequently, the bath temperature was raised to −45 °C, and after 50 min a solution of 1,2-diiodoethane in ether (2 mL, 0.855 M, 1.71 mmol) was added; the color changed to light yellow. After 15 min, MeOD (30 μL) was added and the reaction mixture was allowed to warm to room temperature. The internal standard hexamethylbenzene (0.0404 g, 0.25 mmol), water, and Et$_2$O were added, and the reaction mixture was extracted with Et$_2$O. The combined organic layers were washed with aqueous NaHSO$_3$, water, and brine and dried (MgSO$_4$). After filtration, the amount of solvent was reduced by pumping off *in vacuo*. The products were identified by GC/MS, and the yields were determined by GC relative to the internal standard; the responses for **9** and **10** with regard to the internal standard were assumed to be 1:1; the results are presented in Table 1. **8**: MS (EI, *m*/*z*, relative intensity) 330 (100, $M^{+\bullet}$), 203 (32, $[M - I]^+$), 127 (7), 76 (13, $[M - 2I]^+$), 50 (6).[21] **9**: MS (EI, *m*/*z*, relative intensity) 408/410 (100, $M^{+\bullet}$, Br pattern), 281/283 (37/39, $[M - I]^+$, Br pattern), 154/156 (26/27, $[M - 2I]^+$, Br pattern), 127 (15), 75 (58), 74 (44), 73 (11). **10**: MS (EI, *m*/*z*, relative intensity) 282/284 (95/100, $M^{+\bullet}$, Br pattern), 155/157 (15/16, $[M - I]^+$, Br pattern), 127 (5), 76 (5, $[M - I - Br]^+$), 75 (5), 74 (3), 50 (4).[21]

Reaction of 3 with *tert*-Butyllithium in Diethyl Ether. To a suspension of **3** (0.0784 g, 0.25 mmol) in Et$_2$O (10 mL) was added dropwise at −75 °C *tert*-butyllithium (1.1 mL, 1.50 M, 1.65 mmol, 6.6 equiv) in pentane. The reaction mixture became yellow. Subsequently, the bath temperature was raised to −45 °C, and after 50 min a solution of 1,2-diiodoethane in Et$_2$O (2 mL, 0.855 M, 1.71 mmol) was added. After 30 min, MeOD (30 μL) was added and the reaction mixture was allowed to warm to room temperature. The internal standard hexamethylbenzene (0.0407 g, 0.25 mmol), water, and diethyl ether were added, and the reaction mixture was worked up and analyzed as described above; the results are presented in Table 1.

Reaction of 3 with *tert*-Butyllithium/TMEDA in Diethyl Ether. The reaction was performed in a reaction vessel connected to five other vessels via glass capillaries. During the reaction, all vessels and capillaries were continuously immerged into the cooling liquid (pentane/liquid nitrogen). To a solution of **3** (0.1573 g, 0.50 mmol) and TMEDA (0.3424 g, 2.95 mmol) in Et$_2$O (20 mL; in the central vessel) was added dropwise at −75 °C *tert*-butyllithium in pentane (2 mL, 1.50 M, 3 mmol). The reaction mixture became dark yellow. After 15 min, the bath temperature was raised to −45 °C. At different times (45 min, 1.5 h, 2 h, 3 h, 4 h), samples of about 2 mL were pressed into one of the side vessels containing an excess of 1,2-diiodoethane; all samples decolorized immediately. After 15 min, MeOD (30 μL) was added. After the last sample was quenched, all vessels were allowed to warm to room temperature. The work-up and analysis were performed as described above; the response for **11** with regard to the internal standard was supposed to be 1:1; all aliquots showed the same composition; the results are presented in Table 1. **11**:[22] MS (EI, *m*/*z*, relative intensity) 316 (47, $M^{+\bullet}$), 301 (100), 57 (2.5).

Reaction of 3 with LiDBB; General Procedure. To a solution of **3** (0.0787 g, 0.25 mmol) in Et$_2$O (10 mL) was added dropwise at −75 °C a LiDBB solution in THF (3.5 mL, 0.48 M, 1.68 mmol, 7 equiv); the reaction mixture was brown and subsequently blue colored. Then the reaction mixture was warmed within 5 min to the reaction temperature, as indicated in Table 1. After 40 min, the reaction mixture was titrated with *t*-BuCl (0.25 M in Et$_2$O) until the blue-green color had changed to brownish. Several quenching reactions at the indicated reaction temperature were performed (*vide infra*).

Quenching with 1,2-Diiodoethane. The preparation of **1** was carried out according to the general procedure, using **3** (0.0787 g, 0.25 mmol) and LiDBB solution in THF (3.5 mL, 0.48 M, 1.68 mmol, 7 equiv). After the mixture was warmed and *t*-BuCl treatment (*vide supra*), an excess of 1,2-diiodoethane as a solution in Et$_2$O (0.8 M) was added dropwise to the reaction mixture. The solution decolorized immediately; after 15 min it was allowed to warm to room temperature, then MeOD (30 μL) was added. After the internal standard (hexamethylbenzene) and water were added, the reaction mixture was extracted with Et$_2$O, washed with aqueous NaHSO$_3$, water, and brine and dried (MgSO$_4$). After filtration, the amount of solvent was reduced by pumping off *in vacuo*. The products were identified by GC/MS, and the yields were

---

(20) Curtis, M. D.; Allred, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 2554.

(21) Heller, S. R.; Milne, G. W. A. *EPA/NIH Mass Spectral Data Base*; National Bureau of Standards: Washington, DC, 1978.

(22) Burgers, J.; van Hartingsveldt, W.; van Keulen, J.; Verkade, P. E.; Visser, H.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 1327.

determined by GC (see Table 1). **4**: MS (EI, *m*/*z*, relative intensity) 456 (100, $M^{+\bullet}$), 329 (43, $[M - I]^+$), 238 (7), 202 (16, $[M - 2I]^+$), 75 (16), 74 (11). **13**: MS (EI, *m*/*z*, relative intensity) 205 (7), 204 (100, $M^{+\bullet}$), 128 (1), 127 (13, $[M - C_6H_5]^+$), 78 (2), 77 (25, $[M - I]^+$), 76 (2), 75 (3), 74 (5), 73 (2), 51 (13), 50 (8).[21]

Quenching with Carbon Dioxide. The preparation of **1** was carried out according to the general procedure, using **3** (0.7869 g, 2.5 mmol) in Et_2O (100 mL) and a LiDBB solution in THF (35 mL, 0.52 M, 18.2 mmol). Then, a flask with solid CO_2 and P_2O_5 was equipped with a septum and connected via a capillary to the reaction vessel. On bubbling the CO_2 through the reaction mixture, a tough white precipitate was formed, which was acidified (2 M HCl) and extracted with Et_2O. The combined organic layers were extracted with aqueous NaOH; the water layer was neutralized with HCl, extracted with Et_2O, and dried ($MgSO_4$). Evaporation of the solvent and azeotropic distillation with benzene yielded 0.4976 g of a mixture of **14**:**15**:**16** (70:25:5) (^{1}H NMR). **14**: ^{1}H NMR (DMSO-d_6, ppm) δ 8.64 (s, C*H*). **15**: ^{1}H NMR (DMSO-d_6, ppm) δ 7.63 (t, 5-C*H*, $^3J = 7.73$ Hz), 8.17 (d, 4-C*H*, $^3J = 7.73$ Hz), 8.48 (s, 2-C*H*). **16**: ^{1}H NMR (DMSO-d_6, ppm) δ 7.46−7.62 (m, 2-C*H*, 3-C*H*), 7.92 (m, 1-C*H*).

Quenching with MeOD. The preparation of **1** was carried out according to the general procedure, using **3** (0.0779 g, 0.247 mmol) and a LiDBB solution in THF (3.5 mL, 0.48 M, 1.68 mmol). Subsequently, MeOD (40 μL, excess) was added to the reaction mixture, which was stirred for another 15 min (the solution decolorized fast) and warmed to room temperature. After the internal standard (hexamethylbenzene) and water were added, the reaction mixture was extracted with Et_2O, washed with water and a NaCl solution, and dried ($MgSO_4$). After filtration, the amount of ethereal solvent was diminished carefully by distillation at atmospheric pressure, using a long Vigreux column. The percentage of deuteration was determined by GC/MS of the residue (see Table 2). **17**, **18**, **19** (mixture): MS (EI, *m*/*z*, relative intensity) 82 (7), 81 (100), 80 (34), 79 (22), 78 (19, $M^{+\bullet}$), 77 (6), 76 (4), 75 (2).

Quenching with Magnesium Dibromide. The preparation of **1** was carried out according to the general procedure, using **3** (0.2516 g, 0.799 mmol) in Et_2O (20 mL) and a LiDBB solution in THF (7.2 mL, 0.80 M, 5.76 mmol). Subsequently, a solution of $MgBr_2$ (3.196 mmol) in THF (18.8 mL) was added dropwise. The solution decolorized very slowly to yield a faintly red solution with a white precipitate. After 20 h of stirring at −40 °C, 2 h at −30 °C, 2 h at −25 °C, 12 h at −15 °C, 12 h at −10 °C, 12 h at 0 °C, and 8 h at room temperature, an excess of 1,2-diiodoethane was added. Subsequently, the internal standard (hexamethylbenzene) and water were added, and the reaction mixture was extracted with Et_2O, washed with water and a NaCl solution, and dried ($MgSO_4$). After filtration, the ethereal solution showed the presence of **4**, **8**, and **13** (GC/MS). The yields were determined by GC (see Table 2). In a second identical experiment, the precipitate was filtered off under argon and washed with THF prior to quenching. This solid residue was suspended in Et_2O, and 1,2-diiodoethane was added; GC analysis indicated the presence of **4** and **8** exclusively in a ratio of 7.9:2.1. Extraction of the precipitate with 2-MeTHF (in which **21** is soluble) prior to reaction with 1,2-diiodoethane did not furnish the presence of pure **20**, the ratio of **4**:**8** had deteriorated to 5.5:4.5.

Quenching with Trimethylstannyl Chloride. The preparation of **1** was carried out according to the general procedure, using **3** (0.0786 g, 0.25 mmol) and a LiDBB solution in THF (3.5 mL, 0.48 M, 1.68 mmol). Subsequently, a solution of Me_3SnCl in THF (1 mL, 1.72 M, 1.72 mmol) was added. After the mixture was stirred for another 15 min, MeOD (30 μL) was added and the reaction mixture was allowed to warm to room temperature. After the internal standard (hexamethylbenzene) and water were added, the reaction mixture was extracted with Et_2O and the organic layer washed with water and brine and dried ($MgSO_4$). After filtration, the amount of solvent was reduced by pumping off *in vacuo*. The products were identified by GC/MS, and the yields were determined with GC (see Table 2). The responses for **23**, **24**, and **25** with regard to the internal standard were supposed to be 1:1. **23**:[23] MS (EI, *m*/*z*, relative intensity) 566 (1, $M^{+\bullet}$, Sn_3 pattern), 551 (100, $[M - CH_3]^+$, Sn_3 pattern), 521 (9, $[M - 3CH_3]^+$, Sn_3 pattern), 491 (6, $[M - 5CH_3]^+$, Sn_3 pattern), 389 (5.5, Sn_2 pattern), **24**:[24] MS (EI, *m*/*z*, relative intensity) 404 (1, $M^{+\bullet}$, Sn_2 pattern), 387 (100, $[M - CH_3]^+$, Sn_2 pattern), 359 (18, $[M - 3CH_3]^+$, Sn_2 pattern), 342 (4, $[M - 4CH_3]^+$, Sn_2 pattern), 329 (12, $[M - 4CH_3]^+$, Sn_2 pattern), 312 (5, $[M - 5CH_3]^+$, Sn_2 pattern), 240 (2, Sn pattern), 223 (2, Sn pattern), 209 (4, Sn pattern), 187 (5, Sn pattern), 165 (5, Sn pattern), 135 (8, Sn pattern), 120 (5, Sn pattern). **25**: MS (EI, *m*/*z*, relative intensity) 231 (18), 227 (100, $[M - CH_3]^+$, Sn pattern), 197 (35, $[M - 3CH_3]^+$, Sn pattern), 145 (5), 135 (11, $[CH_3Sn]^+$), 120 (17).[21,25]

Quenching with Mercury Dibromide. The preparation of **1** was carried out according to the general procedure, using **3** (0.3143 g, 1 mmol) in Et_2O (10 mL) and a LiDBB solution in THF (14.6 mL, 0.48 M, 7.0 mmol). Subsequently, $HgBr_2$ (in THF) (10 mL, 0.40 M, 4 mmol) was added dropwise to the reaction mixture. Instantly, a white precipitate formed, which turned grey on completion of the addition; the red supernatant decolorized simultaneously. After the reaction mixture was stirred for another 3 days at −40 °C, an excess of MeOD was added. The precipitate was filtered off and washed with water and MeOH to yield 0.3910 g of a grey powder. A ^{1}H NMR spectrum in DMSO-d_6 indicated the presence of **26**, as concluded from the signal at δ 7.66 ppm (s, C*H*). However, the main part of the precipitate was insoluble in DMSO and seemed to consist of symmetrized products. Elemental analysis of the grey precipitate confirmed this assumption: Found: C, 9.99; H, 0.73; Hg, 80.9; Br, 4.49. Anal. Calcd for a mixture of **26**:**27** (74:26; *vide infra*): C, 8.75; H, 0.41; Hg, 64.97; Br, 25.88. Anal. Calcd for **28** (a mixture of 74% $C_6H_3Hg_{1.5}$:26% C_6H_4Hg): C, 20.93; H, 0.97; Hg, 78.10.

The percentage of di- and trisubstituted products was determined by addition of bromine (in the dark) to an NMR tube containing a suspension of the precipitate in DMSO-d_6, which gave an immediate exothermic reaction. The clear solution contained exclusively **3** and **29** in a ratio of 74:26. **3**: ^{1}H NMR (DMSO-d_6, ppm) δ 7.69 (s, C*H*). **29**: ^{1}H NMR (DMSO-d_6, ppm) δ 7.19 (t, 5-C*H*), 7.45 (d, 4,6-C*H*), 7.67 (s, 2-C*H*).

In contrast, bromination in other solvents, such as pentane, were still incomplete after stirring for 1 day. However, GC/MS measurements of the supernatant (after washing with aqueous $NaHSO_3$, followed by drying on $MgSO_4$) showed the presence of **3** and **29** as well. **3**: MS (EI, *m*/*z*, relative intensity) 312/314/316/318 (34/100/97/32, $M^{+\bullet}$, Br_3 pattern), 233/235/237 (19/37/18, $[M - Br]^+$, Br_2 pattern), 154/156 (10/10, $[M - 2Br]^+$, Br pattern), 75 (20, $[M - 3Br]^+$), 74 (27).[25] **29**: MS (EI, *m*/*z*, relative intensity) 234/236/238 (51/100/50, $M^{+\bullet}$, Br_2 pattern), 155/157 (31/30, $[M - Br]^+$, Br pattern), 76 (12, $[M - 2Br]^+$), 75 (19), 74 (16), 50 (15).[21]

Determination of the absolute yields by addition of an internal standard to the brominated products in DMSO was unsuccessful due to insolubility (*e.g.*, hexamethylbenzene) and/or bromination (*e.g.*, CHI_3) of the standard.

Acknowledgment. This work was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

OM9705620

---

[23] The mass spectrum was identical with that of an authentic sample obtained via a different synthetic approach (from the reaction of **3** with trimethylstannyl sodium, paper to be published).

[24] The mass spectrum was identical with that of an authentic sample obtained from **2** and trimethylstannyl chloride.

[25] *Wiley Registry of Mass Spectral Data*; Palisade (6th edition), 1995.