

1,2-Di(silyl)benzene and 1,4-Dibromo-2,5-di(silyl)benzene

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Silanes, Silylbenzenes, Di(silyl)benzenes, Bromo(silyl)benzenes

1,2-Di(silyl)benzene (**3**), has been prepared in a three-step process starting with the reaction of 1,2-dibromobenzene and *p*-tolyl(chloro)silane with magnesium in tetrahydrofuran, which affords 1,2-bis(*p*-tolylsilyl)benzene (**1**) as a stable high-yield intermediate. Compound **1** has been converted into 1,2-bis(trifluoromethanesulfonatosilyl)benzene (**2**) with trifluoromethanesulfonic acid, and finally into **3** by reduction with lithiumaluminiumhydride, both again in high yields. – In an attempt to prepare 1,2,4,5-tetra(silyl)benzene in an analogous way, only the bis-silylated species could be obtained (from 1,2,4,5- $\text{C}_6\text{H}_2\text{Br}_4$, *p*- $\text{MeC}_6\text{H}_4\text{SiClH}_2$ and Mg powder: 1,4-dibromo-2,5-bis(*p*-tolylsilyl)benzene, **4**, and 1,4-dibromo-2,5-di(silyl)benzene, **6**, via 1,4-dibromo-2,5-bis(trifluoromethanesulfonatosilyl)benzene, **5**). The crystal structures of compounds **4** and **6** have been determined by X-ray diffraction. The results indicate no steric hindrance in these molecules and it is thus not obvious from the molecular structures why the silylation reaction does not proceed any further to give the tetrasilylated benzene derivatives. Electronic effects have to be invoked to rationalize the experimental findings.

Poly(silylated) aromatic hydrocarbons are important starting materials for the preparation of arene-bridged polysilanes through dehydrogenative coupling reactions. Depending on the substitution pattern of the monomers, different kinds of cross-linking are to be expected, which are leading to simple oligomers, rings, chains, or polydimensional networks [1]. Simple poly(silyl)-arenes bearing *solely hydrogen* at the silicon substituents were largely unknown until some very recent studies, which have shown the way to at least a few of the possible poly(silyl)benzenes and their isomers [2].

Following our own work on poly(silyl)alkanes [3–7], -alkenes [8–10], -alkynes [11, 12], and -arenes [12], including hexa(silyl)benzene [13] and 1,8-di(silyl)naphthalene [14], we now report the first synthesis of the title compounds, the silicon analogue of *o*-xylene and one of its brominated derivatives.

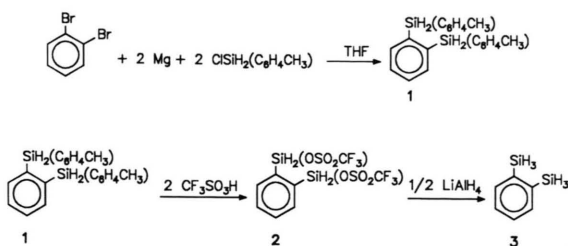
The synthetic strategy followed here is the same as that used for the above analogues. The results are surprising, however, as the tetra-silylation proved to be extremely difficult and lead only to

partially substituted (brominated) precursors. These products could be isolated in a pure state and fully characterized. Their structures have been determined by X-ray diffraction in order to get a clue as to the reasons of the unexpected inertness towards further substitution (silylation).

Synthesis and Properties of the Poly(silyl)benzenes

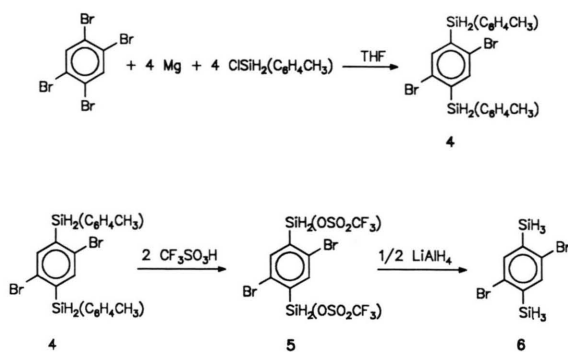
The reaction of 1,2-dibromobenzene with a little more than two equivalents of *p*-tolyl(chloro)silane [15] and magnesium metal (powder) in boiling tetrahydrofuran for 8 h gave – after an aqueous work-up – a 60% isolated yield of 1,2-bis(*p*-tolylsilyl)benzene (**1**, b.p. 180 °C/0.1 Torr). Treatment of this product with exactly two equivalents of trifluoromethanesulfonic acid (triflic acid) at low temperature gave the corresponding 1,2-bis(trifluoromethanesulfonatosilyl)benzene (**2**) in quantitative yields. This intermediate has not been isolated, but converted directly into 1,2-di(silyl)benzene (**3**) by the reaction with lithiumaluminiumhydride in diethyl ether (eq. (1)). Compound **3** is obtained as a stable, clear, distillable liquid, b.p. 95 °C/70 Torr, which is miscible with most common organic solvents, and readily identified by its spectroscopic data (Exp. Section). It

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was the last of the di-sila-xylenes still missing in the literature, after the 1,3- and 1,4-isomers had been obtained [2].

Analogous experiments carried out with 1,2,4,5-tetra-bromobenzene were oriented towards the preparation of 1,2,4,5-tetra(silyl)benzene, another missing sila-analogue (of durol). Very surprisingly, these efforts met only with limited success. Even with prolonged reaction times and an excess of chlorosilane reagent, only the products of the double-silylation (instead of the expected tetra-silylation) could be obtained. As formulated in Eq. (2), 1,4-dibromo-2,5-bis(*p*-tolylsilyl)benzene



(**4**) was the only product of the Merker-Scott reaction [16] to be isolated in acceptable yields. This precursors could readily be converted into the bis-triflate (**5**) with triflic acid, and finally into the hydride (**6**) with LiAlH_4 . Compounds **4** and **6** were obtained in the crystalline state and their composition and structure could be unambiguously confirmed by analytical, spectroscopic, and diffraction methods (Exp. Section).

Crystal and Molecular Structures of Compounds **4** and **6**

Both compounds crystallize in the monoclinic space group $P2_1/c$ with two molecules in the unit cell (Table I). The crystal packing shows no anomalies regarding intermolecular contacts. The molecules have a crystallographic center of inversion (Figs. 1 and 2). The bond distances and angles are in the normal range established for arylsilanes and bromoarenes. It is noteworthy that the *conformation* at the silicon atoms is roughly the same in both compounds: The two hydrogen atoms at each silicon atom are “embracing” the neighbouring bromine atom, which puts the axis of the *p*-tolyl group (in **4**) or the remaining Si-bound hydrogen atom (in **6**) into the plane of the central benzene ring. Thus none of the molecules is showing significant steric hindrance. The space around the bromine atoms appears to be sufficiently open for any nucleophilic attack to occur at the neighbouring carbon atom. It is therefore not clear from the structural data as to why the silylation reaction is not proceeding beyond the second step (above).

Table I. Crystallographic data for the compounds **4** and **6**.

	4	6
Empirical formula	$\text{C}_{20}\text{H}_{20}\text{Br}_2\text{Si}_2$	$\text{C}_6\text{H}_8\text{Si}_2\text{Br}_2$
Formula weight [g/mol]	476.36	296.11
Crystal system	monoclinic	monoclinic
Space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)
<i>a</i> [Å]	12.356(1)	6.307(1)
<i>b</i> [Å]	10.428(1)	7.424(1)
<i>c</i> [Å]	8.179(1)	11.052(1)
α [°]	90	90
β [°]	104.82(1)	100.48(1)
γ [°]	90	90
ρ_{calc} [g cm ⁻³]	1.553	1.618
<i>Z</i>	2	2
<i>F</i> (000) [e]	476	284
μ (Mo—K α) [cm ⁻¹]	40.96	67.43
<i>T</i> [°C]	+22	−62
<i>hkl</i> -range	−15/+13/±10	+8/+9/±14
Measured reflections	2377	1288
Unique reflections	2215	1031
Observed reflections	1944	878
<i>R</i> _{int}	0.0160	0.0281
<i>F</i> >	4 σ (<i>F</i>)	4 σ (<i>F</i>)
Refined parameters	146	54
Weighting parameters <i>a/b</i>	0.0695/0.2248	—
Weighting parameters <i>l/k</i>	—	1.00/1.42890
H-atoms (found/calcd.)	20/0	2/2
<i>wR</i> 2/ <i>R</i> _{based on <i>F</i>} (OMIT4)	0.1006/0.0343	—
<i>R/R</i> _w	—	0.0279/0.0297
ρ_{fin} (max/min) [e Å ⁻³]	+0.294/−0.526	+0.512/−0.666

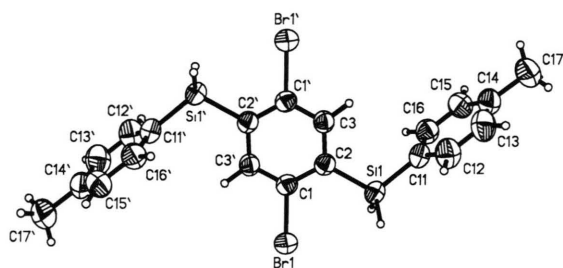


Fig. 1. Molecular structure of 1,4-dibromo-2,5-bis-(*p*-tolylsilyl)benzene (**4**) as projected on to the benzene plane. The molecule has a crystallographic center of inversion. (ORTEP, 50% probability ellipsoids for non hydrogen atoms; arbitrary radii for hydrogen atoms.) Selected distances [Å] and angles [°]: Br 1–C1 1.908(2), Si1–C2 1.882(2), Si1–C11 1.864(3), C1–C2 1.397(3), C2–C3 1.392(4), C1–C3' 1.385(3); C11–Si1–C2 111.21(12), C1–C2–Si1 122.4(2), C3–C2–Si1 121.4(2), C2–C1–Br1 118.9(2), C3'–C1–Br1 117.8(2).

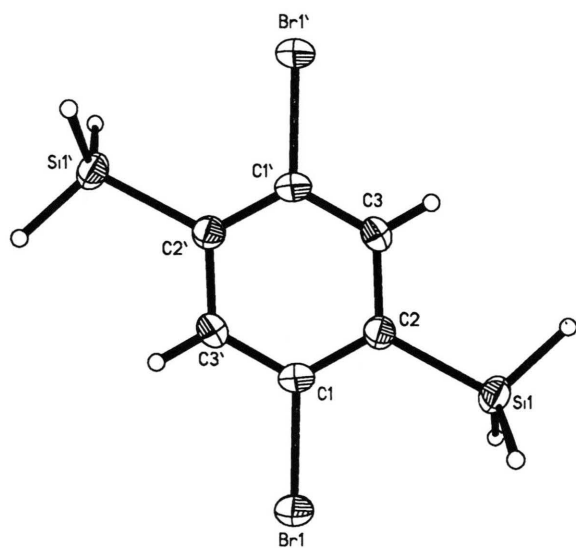


Fig. 2. Molecular structure of 1,4-dibromo-2,5-di(silyl)benzene (**6**). The molecule has a crystallographic center of inversion. (ORTEP, 50% probability ellipsoids for non hydrogen atoms; arbitrary radii for hydrogen atoms.) Selected distances [Å] and angles [°]: Br 1–C1 1.904(4), Si1–C2 1.875(4), C1–C2 1.390(5), C2–C3 1.395(5), C1–C3' 1.390(6), Si–H (average) 1.42; C1–C2–Si1 123.9(3), C3–C2–Si1 119.7(3), C2–C1–Br1 119.5(3), C3'–C1–Br1 117.4(3), H–Si–H (average) 109.0.

Discussion

The preparative work on two prototypes of ortho-disilylated benzenes, di-sila-xylene and tetra-sila-durene, has only been successful with the former. 1,2-Di(silyl)benzene could be obtained for the first time in good yields in a convenient three-

Table II. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for **4**.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
Br 1	3176(1)	1925(1)	967(1)	62(1)
Si 1	5759(1)	1764(1)	3471(1)	54(1)
C 1	4250(2)	795(2)	431(3)	48(1)
C 2	5330(2)	758(2)	1501(3)	48(1)
C 3	6083(2)	−64(2)	1024(3)	49(1)
C 11	7236(2)	1432(3)	4645(3)	56(1)
C 12	8091(3)	2265(4)	4563(5)	74(1)
C 13	9187(3)	2033(4)	5483(5)	82(1)
C 14	9460(3)	975(4)	6504(4)	73(1)
C 15	8612(3)	142(4)	6595(4)	73(1)
C 16	7513(3)	371(3)	5690(4)	64(1)
C 17	10656(4)	759(7)	7500(7)	104(2)

step synthesis following established methods. All attempts to obtain 1,2,4,5-tetra(silyl)benzene gave only the disilylated species with two of the four halogen atoms of the starting material remaining in the product. This result is surprising since the structural situation appears to be very similar for each substitution step in 1,2-dibromo- and in 1,2,4,5-tetrabromo-benzene, and also since even complete substitution was possible in hexachlorobenzene (to give hexa(silyl)benzene) [13]. The structural data for **4** and **6** give no indication of any steric congestion, which could make steric effects responsible for the failure of the synthetic work. The orientation of the tolyl groups is also such that no covering of the reaction center is expected. We are therefore suggesting electronic effects to be the origin of the disactivation. It is difficult to sort out individual contributions from a para-bromo-, and from an ortho- and a meta-silyl substituent to the electronic situation at the carbon center bearing a bromine atom to be replaced in **4** (Fig. 1). Apparently a combined influence of these contributions is rendering the molecule inert towards the attack of active species present in the Merker-Scott reaction mixture (halo-arene, chlo-

Table III. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for **6**.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
Br 1	7700(1)	1740(1)	9007(1)	39(1)
Si 1	1850(2)	4003(2)	11989(1)	29(1)
C 1	6126(6)	3664(5)	9561(3)	24(1)
C 3	4806(6)	3250(5)	10402(3)	25(1)
C 2	3639(6)	4599(5)	10866(3)	24(1)

rosilane, magnesium). Since the mechanism of the reaction has never been fully elucidated, any more detailed assignment is not possible at this time.

Compounds **3** and **6** are promising substrates for dehydrogenative or oxydative coupling reaction, which can lead to arene-bridged polysilanes and siloxanes of different structures as other poly(silyl)arenes are co-coupled/-oxidized. With **6**, halogen-rich products are expected which could be useful in their own right.

Experimental Part

All experiments were carried out under pure and dry nitrogen. Solvents were purified, dried and kept under nitrogen. C_6D_6 and $CDCl_3$ were used as solvents for NMR spectroscopy, tetramethylsilane was employed as the reference compound. (NMR: Jeol GX 270, GX 400, Bruker WT 100 SY spectrometers. GC/MS: Hewlett Packard, model 5890 series II, mass selective detector HP MS 5970 B (EI-MS 70 eV). MS: Varian MAT 311 A, MAT 112 S).

1,2-Bis(p-tolylsilyl)benzene (1): A solution of 1,2-dibromobenzene (49.6 g, 0.21 mol) in THF (180 ml) was slowly added to a slurry of magnesium turnings (11.2 g, 0.46 mol) in a boiling solution of *p*-tolyl(chloro)silane (72.4 g, 0.46 mol) in THF (600 ml) at such a rate, that the mixture continued to reflux with reduced heating. After complete addition and further refluxing for 8 h the mixture was cooled to room temperature. Pentane (300 ml) was added and the magnesium salts were filtered off. The filtrate was poured onto crushed ice and neutralized with Na_2CO_3 . The organic layer was separated, washed three times with 200 ml of water, and the collected aqueous layers washed three times with 100 ml of pentane. The combined organic extracts were dried with $MgSO_4$ and the solvent was evaporated to leave a yellow oil. A vacuum distillation gave compound **1** (41.0 g, 61% yield, b.p. 160 °C/0.1 Torr).

1H NMR (C_6D_6): δ = 2.24 (s, 6H, CH_3), 5.45 (s, $^1J(SiH)$ = 200 Hz, 4H, SiH_2), 7.11 and 7.60 (d each, $^3J(HCCH)$ = 7.5 Hz, 8H, *p*-Tol), 7.30 and 7.80 (m each, 4H, C_6H_4). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 21.5 (CH_3), 128.2, 129.2, 136.2, 139.8 (*p*-Tol), 129.5 ($C_{4/5}$), 136.4 ($C_{1/2}$), 137.6 ($C_{3/6}$ of benzene). – ^{29}Si NMR (C_6D_6): δ = –35.7 (t^*q^*m , $^1J(SiH)$ = 200, $^3J(SiCCH)$ = 7 Hz). – MS (EI, 70 eV): m/z = 317 [$M^+ - H$], 227 [$M^+ - C_6H_4CH_3$], 195 [$M^+ - 2H - SiH_2(C_6H_4CH_3)$].

1,2-Bis(trifluoromethanesulfonatosilyl)benzene (2): A solution of **1** (8.0 g, 0.025 mol) in toluene

(80 ml) was cooled to –40 °C and triflic acid (7.5 g, 0.05 mol) was slowly added with stirring. After 1 h the mixture was warmed to room temperature and used at once for reduction.

1,2-Di(silyl)benzene (3): The solution of **2** (above) was slowly added to a suspension of $LiAlH_4$ (0.52 g, 0.014 mol) in diethyl ether (150 ml). After complete addition the mixture was first heated to reflux temperature for 2 h and then poured onto crushed ice mixed with $NaHCO_3$ for neutralization. The organic layer was separated and washed three times with 50 ml of water. The collected aqueous residue was washed once with pentane (100 ml). The organic extracts were dried over $MgSO_4$ and concentrated in a vacuum. Distillation of the residual oil gave 1,2-di(silyl)benzene (**3**) (3.00 g, 87% yield, b.p. 95 °C/70 Torr).

1H NMR (C_6D_6): δ = 4.31 (s, $^1J(SiH)$ = 200 Hz, 6H, SiH_3), 7.02 (d*d, $^3J(HCCH)$ = 5.4, $^4J(HCCCH)$ = 3.4 Hz, 2H, $C_{3/6}H$), 7.39 (d*d, $^3J(HCCH)$ = 5.4, $^4J(HCCCH)$ = 3.4 Hz, 2H, $C_{4/5}H$). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 129.6 ($C_{4/5}$), 136.5 ($C_{1/2}$), 137.5 ($C_{3/6}$). – ^{29}Si NMR (C_6D_6): δ = –61.7 (broad q^*d , $^1J(SiH)$ = 200, $^3J(SiCCH)$ = 7 Hz). – MS (EI, 70 eV): m/z = 138 [M^+], 107 [$M^+ - SiH_3$].

1,4-Dibromo-2,5-bis(p-tolylsilyl)benzene (4): To a boiling solution of *p*-tolyl(chloro)silane (70.0 g, 0.44 mol) in THF (250 ml) containing magnesium turnings (12.0 g, 0.5 mol) was added 1,2,4,5-tetrabromobenzene (44.0 g, 0.11 mol), dissolved in 450 ml warm THF at such a rate, that the solution continued to reflux with reduced heating. After additional refluxing for 8 h the solution was cooled to room temperature and filtered. Chloroform (400 ml) was added, and the mixture was poured onto crushed ice mixed with Na_2CO_3 . The organic layer was separated and washed three times with 200 ml of water. The aqueous extracts were washed with 100 ml of diethyl ether, and the collected organic phase was dried over $MgSO_4$. The solvent was evaporated to leave a brown oil, from which the product crystallized upon the addition of pentane (300 ml). Recrystallization from chloroform gave colourless crystals. (**4**, 7.50 g, 15% yield, m.p. 168–170 °C).

1H NMR ($CDCl_3$): δ = 2.35 (s, 6H, CH_3), 4.93 (s, $^1J(SiH)$ = 204 Hz, 4H, SiH_2), 7.19 and 7.50 (d each, $^3J(HCCH)$ = 8 Hz, 8H, *p*-Tol), 7.59 (s, 2H, C_6H_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.6 (CH_3), 125.7, 129.1, 135.9, 141.1 (*p*-Tol), 129.8 (C_1), 140.2 (C_2), 140.4 (C_3 of benzene). – ^{29}Si NMR ($CDCl_3$): δ = –32.8 (broad t^*q , $^1J(SiH)$ = 207, $^3J(SiCCH)$ = 6 Hz). – MS (CI): m/z = 475.4 [$M^+ - H$], 395.4 [$M^+ - H - Br$], 385.3 [$M^+ - C_6H_4CH_3$],

355.3 [$M^+ - SiH_2(C_6H_4CH_3)$], 275.2 [$M^+ - SiH_2(C_6H_4CH_3) - Br$], 196.3 [$M^+ - SiH_2(C_6H_4CH_3) - 2 \times Br$], 139.2 [$M^+ - 2 \times C_6H_4CH_3 - 2 \times Br$].

$C_{20}H_{20}Br_2Si_2$ (476.4)

Calcd C 50.43 H 4.23 Br 33.55 Si 11.79%,
Found C 50.06 H 4.27 Br 33.16 Si 13.00%.

1,4-Dibromo-2,5-bis(trifluoromethanesulfonato-silyl)benzene (5): Compound **4** (5.00 g, 0.011 mol) was dissolved in toluene (25 ml) and cooled to $-40^\circ C$ and treated slowly with triflic acid (3.30 g, 0.022 mol). After 1 h the clear solution was allowed to warm to room temperature and used at once for reduction.

1,4-Dibromo-2,5-di(silyl)benzene (6): The solution of **5** (above) was slowly added to a suspension of $LiAlH_4$ (0.27 g, 7 mmol) in 30 ml of diethyl ether. The mixture was then heated to reflux for 2 h, and finally poured onto crushed ice mixed with $NaHCO_3$ for neutralization. The organic layer was separated, and washed three times with 20 ml of water. The aqueous residue phase was washed once with 20 ml of diethyl ether, and the organic extracts were dried over $MgSO_4$ and the solvent removed. The yellow residue was recrystallized from chloroform to give colourless crystals (**6**, 1.80 g, 58% yield, m.p. $78-80^\circ C$).

1H NMR ($CDCl_3$): $\delta = 4.24$ (s, $^1J(SiH) = 204$ Hz, 6H, SiH_3), 7.71 (s, 2H, C_6H_2). – $^{13}C\{^1H\}$ NMR

($CDCl_3$): $\delta = 129.8$ (C_1), 137.9 (C_2), 140.6 (C_3). – ^{29}Si NMR ($CDCl_3$): $\delta = -57.0$ (broad q*d, $^1J(SiH) = 204$, $^3J(SiCCH) = 6$ Hz). – MS (EI, 70 eV): $m/z = 296$ [M^+], 265 [$M^+ - SiH_3$], 215 [$M^+ - Br$], 185 [$M^+ - SiH_3 - Br$], 138 [$M^+ - 2 \times Br$], 107 [$M^+ - 2 \times Br - SiH_3$].

$C_6H_8Br_2Si_2$ (296.1)

Calcd C 24.31 H 2.72 Br 53.90 Si 19.07%,
Found C 23.97 H 2.66 Br 54.78 Si 18.92%.

X-ray structure determinations of the compounds 4 and 6

Single crystals of the compounds were mounted in glass capillaries and examined on an Enraf-Nonius CAD4 diffractometer. Graphite-monochromated $Mo-K_\alpha$ -radiation was used. The structures were solved by Direct Methods (SHELXTL [17]). All heavy atoms were refined with anisotropic displacement parameters (compound **4**: SHELXTL-93 [18], compound **6**: SHELXTL-PLUS [17]). Hydrogen atoms, which could not be refined isotropically, were placed in calculated positions (XANADU [19]). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD 58290, the names of the authors and the journal citation.

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