Convergent Synthesis and Characterization of Organotin Dendrimers $Sn\{(CH_2)_nSn[(CH_2)_4SnPh_3]_3\}_4$ (n = 3, 4)

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The reaction of the ω-haloalkyltin trihalides $Br(CH_2)_3SnBr_3$ and $Br(CH_2)_4SnBr_3$ with 3 equiv of but-3-enylmagnesium bromide yielded $Br(CH_2)_3Sn(CH_2CH_2CH{=}CH_2)_3$ (**3**) and $Br(CH_2)_4Sn(CH_2CH_2CH{=}CH_2)_3$ (**4**). Both dendritic branches can be converted into their corresponding Grignard reagents, whose consequent treatment with 0.25 M amounts of $SnCl_4$ resulted in the formation of the dendrimers $Sn[(CH_2)_3Sn(CH_2CH_2CH{=}CH_2)_3]_4$ (**5**) and $Sn[(CH_2)_4Sn(CH_2CH_2CH{=}CH_2)_3]_4$ (**6**), respectively. The subsequent hydrostannation of **5** and **6** delivered $Sn\{(CH_2)_3Sn[(CH_2)_4SnPh_3]_3\}_4$ (**7**) and $Sn\{(CH_2)_4Sn[(CH_2)_4SnPh_3]_3\}_4$ (**8**) as dendrimers of the second generation. All compounds were characterized by elemental analysis, ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy, and MALDI-TOF mass spectrometry.

Introduction

An increasing expectance for materials with new properties focused interest on polymer research, from the traditional linear polymers to the more promising hyperbranched and dendritic polymers.[1−6] Such fascinating macromolecules found rapidly widespread applications in many fields of modern chemistry.[7] Although most of the first dendrimers were prepared by the divergent route, the concept of convergent synthesis occupied in a short time an important place in the development of new dendritic macromolecules.[8] The attractiveness of this method is based on the ability to prepare pure dendrimers free of any imperfectly built architectures.[9,10] The convergent approach is based on the synthesis of dendritic arms (dendrons) and the subsequent condensation of them with a multifunctional core unit.[11] Due to the multiple reactive sites of the dendrons, it is essential to develop a strategy that leads to no damage of those intermediate compounds during their gradual synthesis and the final linkage with the nuclei.[12−15]

In contrast to pure organic dendrimers, the number of metallodendrimers, especially those consisting of covalently bonded metal−carbon moieties, is very limited, mainly due to the lack of suitable reagents and synthetic methods.[16−18] Only a very few main group metal based dendrimers have been described so far.[19,20] Recently we have been successful in the synthesis of organotin dendrimers[21] analogous to the well-known organosilicon[22] and organogermanium[23] dendrimers. On the basis of the results of our previous work[24,25] in this area, we

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focused our intention on developing a method to prepare organotin dendrimers by the convergent way. In this paper, we report the preparation of dendritic organotin dendrons and their utilization for the convergent synthesis of organotin dendrimers.

Experimental Section

General Comments. All manipulations involving air-sensitive compounds were carried out in dry, oxygen-free solvents under an inert atmosphere of nitrogen using standard Schlenk techniques. Melting points were measured in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O 2400 analyzer. The NMR spectra were recorded on Bruker ARX 200 (^{1}H, 200.13 MHz; ^{13}C, 50.32 MHz) and ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz; ^{119}Sn, 149.21 MHz) spectrometers at ambient temperature. Chemical shifts are reported in ppm and referenced to the ^{1}H and ^{13}C residues of the deuterated solvents. Chemical shifts for ^{119}Sn are given relative to $(CH_3)_4Sn$. IR spectra were obtained on a Nicolet Magna System 750 spectrometer. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing isotopes of the highest abundance are listed. Relative intensities are given in parentheses.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed in the reflection mode of an Applied Biosystems Voyager-Elite mass spectrometer equipped with a nitrogen laser emitting at 337 nm. Acceleration voltage was set to 20 and 25 kV, respectively, with positive or negative ionization. The mass spectrometers were externally calibrated with a mix of three synthesized peptides. *trans*-Indoleacrylic acid (IAA) was used as a MALDI matrix at concentrations of 0.2 M and 10 mM in THF/CH_3CN (3:1), respectively. Sample solutions were prepared with an approximate concentration of 1mM in THF or CH_2Cl_2. Solutions containing 2 mM CH_3COONa, KCl, or AgI were used as ionization agents. Sonification was applied to speed up mixing. One μL of the sample was mixed with 1 μL of the matrix solution, and 1 μL of the resulting mixture was deposited on a stainless steel flat plate and allowed to dry at room temperature.

trans-Indoleacrylic acid, α-cyano-4-hydroxycinnamic acid, $BrCH_2CH_2CH{=}CH_2$, $Br(CH_2)_3Br$, $Br(CH_2)_4Br$, $SnBr_2$, Ph_3SnCl, Sb_2O_3, and $AlEt_3$ were used as purchased. $SnCl_4$ was distilled prior to use. Ph_3SnH[26] and $SbEt_3$[27] were prepared according to published procedures.

$Br_3SnC^aH_2C^bH_2C^cH_2Br$ (1).[28] Anhydrous $SnBr_2$ (24.6 g, 88 mmol), 1,3-dibromopropane (89.2 g, 442 mmol), and $SbEt_3$ (1.2 g, 5.7 mmol) were placed in a 100 mL three-necked flask equipped with a reflux condenser and an addition funnel. The suspension was warmed slowly to 155 °C within 45 min and stirred for 5 h at this temperature. After complete conversion of $SnBr_2$, the remaining 1,3-dibromopropane was removed under vacuum (10^{-2} mbar) and the crude product was distilled, leaving **1** as a light orange oil (35.5 g, 84%). Bp: 94−95 °C/0.2 mbar (111−112 °C/0.1 mmHg[28]). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.54 (m, $|^2J(^1H^{117/119}Sn)| = 73.07/76.51$ Hz, 2H, H^a), 2.28 (m, 2H, H^b), 3.54 (m, 2H, H^c). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 32.39 (C^a, $|^1J(^{13}C^{117/119}Sn)| = 577.65/604.36$ Hz), 33.93 (C^b, $|^2J(^{13}C^{119}Sn)| = 45.78$ Hz), 27.80 (C^c, $|^3J(^{13}C^{117/119}Sn)| = 137.60/143.60$ Hz). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −152.33. MS (100 °C; *m*/*z* (%)): 438 (0.05) [M − C_3H_6]$^+$, 401 (9) [M − Br]$^+$, 359 (19) [M − Br − C_3H_6]$^+$, 280 (3) [$SnBr_2$]$^+$, 199 (11) [M − 3Br − C_3H_6]$^+$, 120 (2) [Sn]$^+$, 80 (1) [Br]$^+$. Anal. Calcd for $C_3H_6Br_4Sn$ (480.39): C, 7.50; H, 1.26. Found: C, 7.39; H, 1.19.

$Br_3SnC^aH_2C^bH_2C^cH_2C^dH_2Br$ (2).[28] In analogy with the synthesis of **1**, a mixture of anhydrous $SnBr_2$ (25.4 g, 91 mmol), 1,4-dibromobutane (98.3 g, 455 mmol), and $SbEt_3$ (1.2 g, 5.7 mmol) was stirred for 5 h at 150−160 °C. After complete conversion of $SnBr_2$, the remaining 1,4-dibromobutane was removed under vacuum (10^{-2} mbar) and the crude product was distilled, leaving **2** as a light brown oil (32.3 g, 72%). Bp: 112−113 °C/0.3 mbar (123−124°C/0.1 mmHg[28]). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 2.47 (m, $|^2J(^1H^{117/119}Sn)| = 73.07/76.29$ Hz, 2H, H^a), 2.03 (m, 4H, $H^{b,c}$), 3.46 (m, 2H, H^d). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 33.11 (C^a, $|^1J(^{13}C^{117/119}Sn)| = 558.31/584.19$ Hz), 24.13 (C^b, $|^2J(^{13}C^{117/119}Sn)| = 49.59/51.50$ Hz), 33.79 (C^c, $|^3J(^{13}C^{117/119}Sn)| = 120.44/125.89$ Hz), 31.99 (C^d, $|^4J(^{13}C^{119}Sn)| = 8.17$ Hz. $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −151.93. MS (100 °C, *m*/*z* (%)): 438 (19) [M − C_4H_8]$^+$, 415 (9) [M − Br]$^+$, 360 (58) [M − Br − C_4H_8]$^+$, 335 (5) [M − 2Br]$^+$, 281 (5) [$SnBr_2$]$^+$, 200 (5) [SnBr]$^+$, 120 (6) [Sn]$^+$, 80 (6) [Br]$^+$. Anal. Calcd for $C_4H_8Br_4Sn$ (494.41): C, 9.72; H, 1.63. Found: C, 9.59; H, 1.48.

$(C^gH_2{=}C^fHC^eH_2C^dH_2)_3SnC^aH_2C^bH_2C^cH_2Br$ (3). A solution of **1** (11.6 g, 24 mmol) in THF (50 mL) was placed in a 250 mL three-necked flask equipped with a reflux condenser and an addition funnel. Then 77 mL (96 mmol) of a 1.25 M (but-3-enyl)magnesium bromide solution in THF was added slowly at 0 °C. After stirring for 4 h at room temperature, the reaction was cooled again to 0 °C and hydrolyzed cautiously with water. The organic fraction was extracted with diethyl ether, washed several times with saturated NH_4Cl solution, and dried over Na_2SO_4. After the removal of all volatiles, **3** was obtained as a light yellow oil (9.35 g, 96%). Bp: 55−56 °C/0.1 mbar. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.90 (m, $|^2J(^1H^{117/119}Sn)| = 48.14/50.29$ Hz, 2H, H^a,), 2.07 (m, 2H, H^b), 3.41 (m, 2H, H^c), 1.03 (m, $|^2J(^1H^{117/119}Sn)| = 47.07/49.00$ Hz, 6H, H^d,), 2.34 (m, 6H, H^e), 5.91 (m, 3H, H^f), 5.02 (m, 6H, H^g). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 7.89 (C^a, $|^1J(^{13}C^{117/119}Sn)| = 282.83/295.91$ Hz), 30.55 (C^b, $|^2J(^{13}C^{119}Sn)| = 14.17$ Hz), 37.06 (C^c, $|^3J(^{13}C^{117/119}Sn)| = 75.20/78.20$ Hz), 8.36 (C^d, $|^1J(^{13}C^{117/119}Sn)| = 305.18/319.35$ Hz), 30.62 (C^e, $|^2J(^{13}C^{119}Sn)| = 18.53$ Hz), 141.43 (C^f, $|^3J(^{13}C^{117/119}Sn)| = 46.89/49.05$ Hz), 113.13 (C^g). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −5.77. MS (100 °C, *m*/*z* (%)): 405 (0.3) [M] $^+$, 351 (28) [M − C_4H_7]$^+$, 309 (100) [M − C_4H_7 − C_3H_6]$^+$, 255 (5) [M − 2C_4H_7 − C_3H_6]$^+$, 199 (15) [M − 3C_4H_7 − C_3H_6]$^+$, 120 (6) [Sn]$^+$, 80 (1) [Br]$^+$. Anal. Calcd for $C_{15}H_{27}BrSn$ (405.97): C, 44.38; H, 6.70. Found: C, 44.14; H, 6.58.

$(C^hH_2{=}C^gHC^fH_2C^eH_2)_3SnC^aH_2C^bH_2C^cH_2C^dH_2Br$ (4). In analogy with the synthesis of **3**, a solution of **2** (13.5 g, 27 mmol) in THF (50 mL) was treated at 0 °C with 73 mL (90 mmol) of a 1.25 M (but-3-enyl)magnesium bromide solution in THF. Appropriate workup gave **4** as a light yellow oil (11.11 g, 98%). Bp: 66−67 °C/0.1 mbar. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 0.86 (m, $|^2J(^1H^{117/119}Sn)| = 48.63/50.86$ Hz, 2H, H^a), 1.64 (m, 2H, H^b), 2.86 (m, 2H, H^c), 3.43 (m, 2H, H^d), 0.94 (m, $|^2J(^1H^{117/119}Sn)| = 46.58/48.73$ Hz, 6H, H^e), 2.27 (m, 6H, H^f), 5.85 (m, 3H, H^g), 4.98 (m, 6H, H^h). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 8.11 (C^a, $|^1J(^{13}C^{117/119}Sn)| = 298.40/312.38$ Hz), 25.29 (C^b, $|^2J(^{13}C^{119}Sn)| = 17.74$ Hz), 37.01 (C^c, $|^3J(^{13}C^{117/119}Sn)| = 55.51/58.07$ Hz), 33.28 (C^d), 8.25 (C^e, $|^1J(^{13}C^{117/119}Sn)| = 301.09/315.07$ Hz), 30.73 (C^f, $|^2J(^{13}C^{119}Sn)| = 18.28$ Hz), 141.78 (C^g, $|^3J(^{13}C^{119}Sn)| = 48.93$ Hz), 113.08 (C^h). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −6.75. MS (100 °C, *m*/*z* (%)): 419 (0.6) [M]$^+$, 365 (86) [M − C_4H_7]$^+$, 309 (100) [M − 2C_4H_7]$^+$, 285 (72) [M − Br − C_4H_7]$^+$, 255 (7) [M − 3C_4H_7]$^+$, 175 (57) [M − Br − 3C_4H_7]$^+$, 120 (4) [Sn]$^+$, 81 (0.6) [Br]$^+$. Anal. Calcd for $C_{16}H_{29}BrSn$ (420.00): C, 45.76; H, 6.96. Found: C, 45.57; H, 6.68.

$Sn^z[C^cH_2C^bH_2C^aH_2Sn^p(C^dH_2C^eH_2C^fH{=}C^gH_2)_3]_4$ (5). The Grignard reagent **3a** was prepared from **3** (15.2 g, 37.4 mmol) and magnesium turnings (1.8 g, 73.9 mmol) in THF (75 mL) in the presence of 1,2-dibromoethane (1.0 g, 5.3 mmol). After treatment of the vigorously stirred solution with ultrasound for 0.5 h and

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subsequently boiling for 5 h, the reaction mixture was cooled to room temperature and was stirred further overnight. The unreacted Mg was separated, and the filtrate was cooled to 0 °C. Then freshly distilled $SnCl_4$ (1.66 g, 6.37 mmol) was dropped in cautiously, and the reaction mixture was warmed to room temperature and stirred for 5 h. The solution was then hydrolyzed with water at 0 °C, and the residue was extracted with diethyl ether. The resulting organic phase was washed, dried with Na_2SO_4, filtered, and concentrated under vacuum (10^{-2} mbar). The crude product was purified by column chromatography over silica gel (eluent hexane). **5** was obtained as a viscous light yellow oil (6.43 g, 71%). IR (KBr/film): ν(C═C) 1639 cm^{-1} (s). ^1H NMR (200.13 MHz, $CDCl_3$): δ 0.83−0.97 (m, 16H, $H^{a,c}$), 1.56−1.89 (m, 8 H, H^b), 0.94 (m, $|^2J(^1H^{117/119}Sn)|$ = 46.42/48.14 Hz, 8H, H^d), 2.19−2.36 (m, 8H, H^e), 5.75−5.98 (m, 4H, H^f), 4.86−5.08 (m, 8H, H^g). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 12.15 (C^a, $|^1J(^{13}C^{117/119}Sn^p)|$ = 309.81/325.61 Hz), 18.94 (C^b, $|^2J(^{13}C^{117/119}Sn^{z,p})|$ = 53.77/56.24 Hz), 8.48 (C^c, $|^1J(^{13}C^{117/119}Sn^z)|$ = 294.82/308.38 Hz), 8.33 (C^d, $|^1J(^{13}C^{117/119}Sn^z)|$ = 296.46/310.08 Hz), 30.86 (C^e, $|^2J(^{13}C^{119}Sn^z)|$ = 17.71 Hz), 141.95 (C^f, $|^3J(^{13}C^{119}Sn^z)|$ = 48.50/50.68 Hz), 113.90 (C^g). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −10.84 (Sn^z), −7.60 (Sn^p). MS-MALDI-TOF (matrix IAA): *m*/*z* 1425.68 $[M]^+$ (calcd 1424.40). Anal. Calcd for $C_{60}H_{108}Sn_5$ (1422.97): C, 50.64; H, 7.65. Found: C, 50.47; H, 7.51.

$Sn^z[C^dH_2C^cH_2C^bH_2C^aH_2Sn^p(C^eH_2C^fH_2C^gH{=}C^hH_2)_3]_4$ (6). The Grignard reagent **4a** was prepared by a procedure analogous to that described for **3a** from magnesium turnings (1.8 g, 73.9 mmol), 1,2-dibromoethane (1 g, 5.3 mmol), and **4** in THF (75 mL). To this solution was added dropwise freshly distilled $SnCl_4$ (1.58 g, 6.07 mmol) at 0 °C. The reaction mixture was stirred for 5 h at room temperature and then hydrolyzed slowly with water at 0 °C. Appropriate workup with water and purification by column chromatography in an inert atmosphere over dried silica gel and hexane as eluent gave **6** as a viscous light yellow oil (6.55 g, 73%). IR (KBr/film): ν(C═C) 1639 cm^{-1} (s). ^1H NMR (200.13 MHz, $CDCl_3$): δ 0.70−0.90 (m, 16H, $H^{a,d}$), 1.32−1.74 (m, 16H, $H^{b,c}$), 0.94 (m, $|^2J(^1H^{117/119}Sn^p)|$ = 46.42/48.34 Hz, 24H, H^e), 2.19−2.36 (m, 24H, H^f), 5.75−6.00 (m, 12H, H^g), 4.85−5.10 (m, 24H, H^h). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 9.12 (C^a, $|^1J(^{13}C^{117/119}Sn^z)|$ = 306.54/321.52 Hz), 31.85 (C^b, $|^3J(^{13}C^{117/119}Sn^z)|$ = 52.32/54.50 Hz, $|^2J(^{13}C^{119}Sn^p)|$ = 20.16 Hz), 31.98 (C^c, $|^3J(^{13}C^{117/119}Sn^p)$ = 53.95/56.13 Hz, $|^2J(^{13}C^{119}Sn^z)|$ = 19.35 Hz), 8.75 (C^d, $|^1J(^{13}C^{117/119}Sn^p)|$ = 295.91/309.81 Hz), 8.33 (C^e, $|^1J(^{13}C^{117/119}Sn^p)|$ = 296.18/309.81 Hz), 30.86 (C^f, $|^2J(^{13}C^{119}Sn^p)|$ = 17.71 Hz), 141.90 (C^g, $|^3J(^{13}C^{119}Sn^p)|$ = 48.23/50.41 Hz), 112.94 (C^h). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −11.32 (Sn^z), −6.98 (Sn^p). MS-MALDI-TOF (matrix IAA): *m*/*z* 1479.20 $[M]^+$ (calcd 1480.40). Anal. Calcd for $C_{64}H_{116}Sn_5$ (1479.08): C, 51.97; H, 7.91. Found: C, 50.72; H, 7.75.

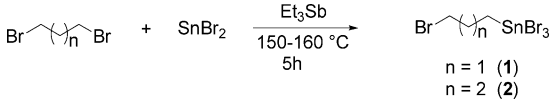
$Sn^z\{C^cH_2C^bH_2C^aH_2Sn^m[C^dH_2C^eH_2C^fH_2C^gH_2Sn^p(C_6H_5)_3]_3\}_4$ (7). A mixture of Ph_3SnH (11.1 g, 31.6 mmol) and AIBN (0.26 g, 1.6 mmol, 5 mol %) was stirred at room temperature for 0.5 h. To this mixture was dropped slowly **5** (2.5 g, 1.76 mmol), and the solution was stirred until after 48 h the signals corresponding to ethylenic protons in the IR and NMR spectra of the solution disappeared. After addition of pentane (25 mL) to the reaction mixture, a pasty-white precipitate was formed. Repeated purification by washing of the crude product with a mixture of pentane/diethyl ether (1:1) several times yielded pure **7** as a viscous white oil (7.66 g, 77%). ^1H NMR (200.13 MHz, $CDCl_3$): δ 0.75−1.35 (m, 40H, $H^{a,c,d}$), 1.86−2.17 (m, 24H, H^g), 1.53−1.86 (m, 56H, $H^{b,e,f}$), 7.85−7.89 (m, 72H, Ph-H^{ortho}), 7.48−7.65 (m, 108H, Ph-$H^{meta/para}$). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 8.47 ($C^{a,c,d}$, $|^1J(^{13}C^{117/119}Sn)|$ = 292.37/307.90 Hz), 24.89 (C^b), 31.84 (C^e, $|^3J(^{13}C^{119}Sn^p)|$ = 63.76 Hz, $|^2J(^{13}C^{119}Sn^m)|$ = 18.53 Hz), 31.38 (C^f, $|^3J(^{13}C^{119}Sn^m)|$ = 54.77 Hz, $|^2J(^{13}C^{119}Sn^p)|$ = 21.53 Hz), 10.66 (C^g, $|^1J(^{13}C^{117/119}Sn^p)|$ = 375.75/395.37 Hz), 138.98 (Ph-C^{ipso}, $|^1J(^{13}C^{119}Sn)|$ = 458.85/ 480.11 Hz), 136.94 (Ph-C^{ortho}, $|^2J(^{13}C^{119}Sn^p)|$ = 34.88 Hz), 128.39 (Ph-C^{meta}, $|^3J(^{13}C^{119}Sn^p)|$ = 47.14 Hz), 128.73 (Ph-C^{para}, $|^4J(^{13}C^{119}Sn^p)|$ = 13.08 Hz). $^{119}Sn^p\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −13.30 (Sn^z), −14.93 (Sn^m), −98.98 (Sn^p). MS-MALDI-TOF (matrix IAA): *m*/*z* 5659.40 $[M + Na]^+$ (calcd 5658.40). Anal. Calcd for $C_{276}H_{300}Sn_{17}$ (5635.15): C, 58.83; H, 5.37. Found: C, 58.41; H, 5.03.

$Sn^z\{C^dH_2C^cH_2C^bH_2C^aH_2Sn^m[C^eH_2C^fH_2C^gH_2C^hH_2Sn^p(C_6H_5)_3]_3\}_4$ (8). 8 was prepared by a procedure analogous with that described for **7** with Ph_3SnH (10.2 g, 29.1 mmol), AIBN (0.24 g, 1.5 mmol, 5 mol %), and **6** (2.3 g, 1.56 mmol). The product was obtained as a viscous white oil (6.37 g, 72%). ^1H NMR (200.13 MHz, $CDCl_3$): δ 0.85−1.15 (m, 24H, H^e), 1.58−1.97 (m, 72H, $H^{f,g,h}$), 1.15−1.31 (m, 16H, $H^{a,d}$), 1.97−2.22 (m, 16H, $H^{b,c}$), 7.85−7.98 (m, 72H, Ph-H^{ortho}), 7.56−7.75 (m, 108H, Ph-$H^{meta/para}$). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 8.40 ($C^{a,d,e}$, $|^1J(^{13}C^{117/119}Sn)|$ = 294.82/308.17 Hz), 32.14 ($C^{b,c}$), 31.79 (C^f, $|^3J(^{13}C^{119}Sn^p)|$ = 63.49 Hz, $|^2J(^{13}C^{119}Sn^m)|$ = 19.07 Hz), 31.37 (C^g, $|^3J(^{13}C^{119}Sn^m)|$ = 55.04 Hz, $|^2J(^{13}C^{119}Sn^p)|$ = 22.34 Hz), 10.70 (C^h, $|^1J(^{13}C^{117/119}Sn^p)|$ = 376.29/393.73 Hz), 139.01 (Ph-C^{ipso}, $|^1J(^{13}C^{119}Sn^p)|$ = 458.58/479.83 Hz), 136.95 (Ph-C^{ortho}, $|^2J(^{13}C^{119}Sn^p)|$ = 35.15 Hz), 128.40 (Ph-C^{meta}, $|^3J(^{13}C^{119}Sn^p)|$ = 47.96 Hz), 128.73 (Ph-C^{para}, $|^4J(^{13}C^{119}Sn^p)|$ = 13.08 Hz). $^{119}Sn^p\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −11.89 (Sn^z), −11.42 (Sn^m), −98.88 (Sn^p). MS-MALDI-TOF (matrix IAA): *m*/*z* 5714.60 $[M + Na]^+$ (calcd 5714.5), 5783.71 $[M + 4Na]^+$ (calcd 5783.50), 5823.70 $[M + Na + Ag]^+$ (calcd 5823.50). Anal. Calcd for $C_{280}H_{308}Sn_{17}$ (5691.26): C, 59.09; H, 5.45. Found: C, 58.73; H, 5.23.

Results and Discussion

The simplest method of a convergent preparation of organotin dendrimers consists of condensation of the well-established haloalkyltin compounds $R_3Sn(CH_2)_nX$[29] with tin tetrachloride, but our first attempt to synthesize a dendrimer using this procedure resulted in no isolable products.[30] However, ω-haloalkyltin trihalides, first reported by Bulten,[28] are suitable reagents for the synthesis of a variety of ω-haloalkyltin compounds. They are excellent reactive key intermediates for the convergent preparation of organotin dendrimers. Such ω-haloalkyltin trihalides are readily accessible by the reaction of the corresponding haloalkyls with stannous halides.[28] Thus, the treatment of stannous bromide with an excess of 1,3-dibromopropane and 1,4-dibromobutane in the presence of triethylantimony at 150−160 °C resulted in the formation of the appropriate (3-bromopropyl)tribromostannane (**1**) and (4-bromobutyl)tribromostannane (**2**), respectively (Scheme 1).

Scheme 1



The air- and moisture-sensitive compounds **1** and **2** are soluble in chlorinated hydrocarbons and tetrahydrofuran, but insoluble in diethyl ether, alkanes, and aromatic solvents. Although ^1H NMR and some physical data have already been reported for both compounds,[28] no spectroscopic details (^{13}C and $^{119}Sn\{^1H\}$ NMR, mass spectral data) were given. Compounds **1** and **2** show the C−$SnBr_3$ resonances in the $^{13}C\{^1H\}$ NMR spectra, recorded in $CDCl_3$, at 32.39 (C^a) and 33.11 ppm (C^a), respectively. The $^{119}Sn\{^1H\}$ NMR chemical shifts of

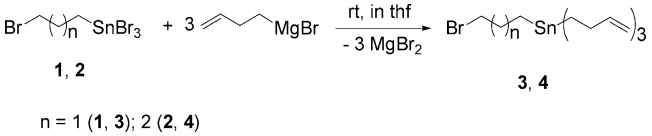
(29) Gielen, M.; Topart, J. *Bull. Soc. Chim. Belg.* **1971**, *80*, 655.
(30) Aksu, Y. Ph.D. Thesis, Technische Universität Berlin, Berlin, Germany, 2005.

−152.33 and −151.93 ppm, as well as the corresponding coupling constants of $|^1J(^{13}C^{117/119}Sn)| = 577.65/604.36$ Hz and 558.31/584.19 Hz, respectively, are very representative for organotin trihalides[31] and indicate the tin atom in both compounds to be tetracoordinated. However, the $^{13}C\{^1H\}$ NMR chemical shifts of **1**, measured in THF-d_8, differ slightly from the respective values obtained in $CDCl_3$. In contrast, the drastic enlarged coupling constant of $|^1J(^{13}C^{117/119}Sn)| = 719.89/753.13$ Hz and the strong upfield shifted $^{119}Sn\{^1H\}$ resonance at −306.88 ppm suggest a higher coordination at the tin atom.[32,33] The Lewis acidity of the metal center, due certainly to the presence of the electronegative bromine atoms, seems to be sufficient for a coordination with donor ligands, like tetrahydrofuran.

With their very reactive $SnBr_3$ units, **1** and **2** are suitable starting materials for the synthesis of a variety of novel types of functionally substituted organotin compounds by reaction with Grignard or organolithium reagents. On the other hand, the C−Br bond of the alkyl chain is inert enough toward such reagents, so it is needless to protect it. It remains intact during the reaction and could serve in turn for further activation and functionalization of those compounds. In a previous paper, we reported the synthesis of the first *all*-tin dendrimer and investigated its synthetic potential for the preparation of new derivatives.[21] During our research we realized, that vinylic and allylic derivatives of tin are very sensitive toward electrophilic reagents. Redistribution reactions caused the formation of unexpected products. Therefore, we chose the γ-butenyl chain as building blocks for dendrons, which seem to be chemically more stable.

Compounds **1** and **2** react with 3 molar equiv of (but-3-enyl)-magnesium bromide in tetrahydrofuran after 0 °C and at completion of the reaction at room temperature for 4 h to give (3-bromopropyl)tribut-3-enylstannane (**3**) and (4-bromobutyl)-tribut-3-enylstannane (**4**), respectively, as light yellow liquids in excellent yield (Scheme 2). In contrast to their parent compounds, **3** and **4** are fairly air and moisture stable. They are soluble in all common organic solvents.

Scheme 2

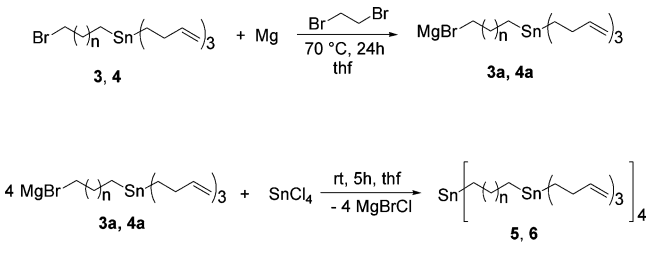


The ^1H NMR spectra of **3** and **4** show distinguishable and good separated signals for all groups of protons. The relative intensities of the butenyl substituents are stronger than those of the butyl or propyl chain, allowing a simple location of the signals. The resonances attributed to the $-C^aH_2Sn$ fragments appear at 0.90 and 0.86 ppm, respectively, upfield of the corresponding signals observed for the parent compounds **1** and **2**, confirming the complete substitution of all bromine atoms by the butenyl groups. The $^{13}C\{^1H\}$ NMR spectra reflect the ^1H NMR results. However, it must be noted that the intensity difference between the signals of the butenyl and the butyl or propyl substituent is more distinguishable in the $^{13}C\{^1H\}$ NMR spectra. According to $|^1J| > |^3J| > |^2J| > |^4J|$, the assignment of the signals can be established without difficulties. The $-C^aH_2$-Sn carbon signals appear at 7.89 (**3**) and 8.11 ppm (**4**), respectively, significantly upfield of the parent complexes and in the expected region observable for comparable substituted organotin compounds.[31] The corresponding coupling constants $|^1J(^{13}C^{a117/119}Sn)| = 282.83/295.91$ Hz (**3**) and 298.40/312.38 Hz (**4**), which feature a decrease by an average of about 284 Hz in comparison with **1** and **2**, evidence the diminished Lewis acidity at the metal center with loss of the electron-rich bromine atoms and fall into the range of those reported for tetracoordinated organotin analogues.[34] The butenyl groups deshield the ^{119}Sn resonances by 146 to −5.77 ppm (**3**) and by 145 to −6.75 ppm (**4**) as compared with those found for **1** and **2**, corroborating the deshielding of the ^{119}Sn resonances as halogen atoms are replaced with alkene or alkyl groups.[34]

In contrast to **1** and **2**, the dendrons **3** and **4** are sufficiently thermostable, allowing characterization by mass spectrometry. The appropriate molecular ion peaks were observed at *m*/*z* 405 and 419, respectively.

The following transformation of **3** and **4** to their corresponding Grignard reagents **3a** and **4a** by usual treatment with excess magnesium turnings afforded only poor yields. The process seems to be very slow and inefficacious, probably because of the insufficient polarity of the C−Br bond, which prevents a satisfactory conversion to the Grignard reagent. However, after activation with 1,2-dibromoethane, treating with ultrasound for 0.5 h, and subsequent refluxing in tetrahydrofuran for 5 h, the reaction of **3** and **4** with a surplus of magnesium produced rapidly the desired Grignard reagents **3a** and **4a** in good yields (Scheme 3). Dropwise addition of tin tetrachloride to 4 molar equiv of solutions of **3a** and **4a** in tetrahydrofuran at 0 °C, followed by stirring at ambient temperature for 5 h, resulted rapidly in the formation of the corresponding dendrimers tetrakis[4-(tribut-3-enylstannyl)propyl]stannane (**5**) and tetrakis-[3-(tribut-3-enylstannyl)butyl]stannane (**6**), respectively (Scheme 3). The crude products, slightly contaminated with unreacted **3** and **4**, could be purified by column chromatography in an inert atmosphere with dried silica gel and hexane as eluent to give **5** and **6** as yellowish oils, which are moderately air sensitive and soluble in polar solvents such as tetrahydrofuran and diethyl ether, as well as in alkanes and aromatic solvents.

Scheme 3



Due to the symmetry of the molecules, **5** and **6** show in their NMR spectra only one signal for each of the different carbon atoms in the four inner and 12 outer branches of the dendrimers, confirming a complete conversion. The ^{13}C NMR chemical shift values of C^c (**3**) and C^d (**4**) especially reflect the successful condensation of the dendrons with the tin nuclei. The linkage of the dendritic branches to the metal center results in a shielding of these carbon atoms: The upfield shift of their resonances at 37.06 and 33.28 ppm as compared to **5** (8.48 ppm) and **6** (8.75

(31) Mitchell, T. N. *J. Organomet. Chem.* **1973**, *59*, 189.
(32) Al-Allaf, T. A. K. *J. Organomet. Chem.* **1986**, *306*, 337.
(33) (a) Holecek, J.; Nadvornik, M.; Handlir, K. *J. Organomet. Chem.* **1983**, *241*, 177. (b) Holecek, J.; Nadvornik, M.; Handlir, K. *J. Organomet. Chem.* **1984**, *275*, 43.
(34) (a) Mitchell, T. N.; Walter, G. *J. Organomet. Chem.* **1976**, *121*, 177. (b) Mitchell, T. N.; Amamria, A.; Fabisch, B. *J. Organomet. Chem.* **1983**, *259*, 157.

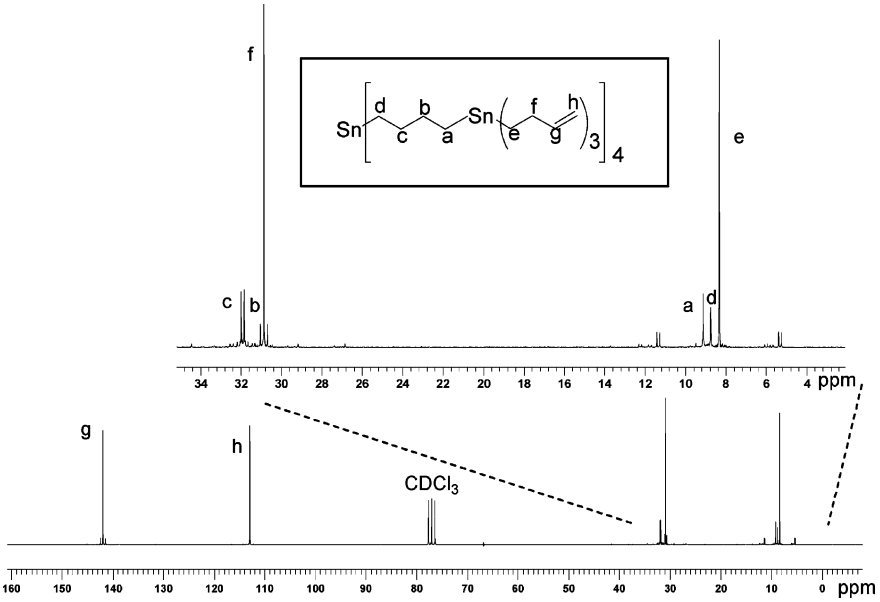


Figure 1. ^{13}C NMR spectrum of $Sn[(CH_2)_4Sn(CH_2CH_2CH{=}CH_2)_3]_4$ (**6**) in $CDCl_3$.

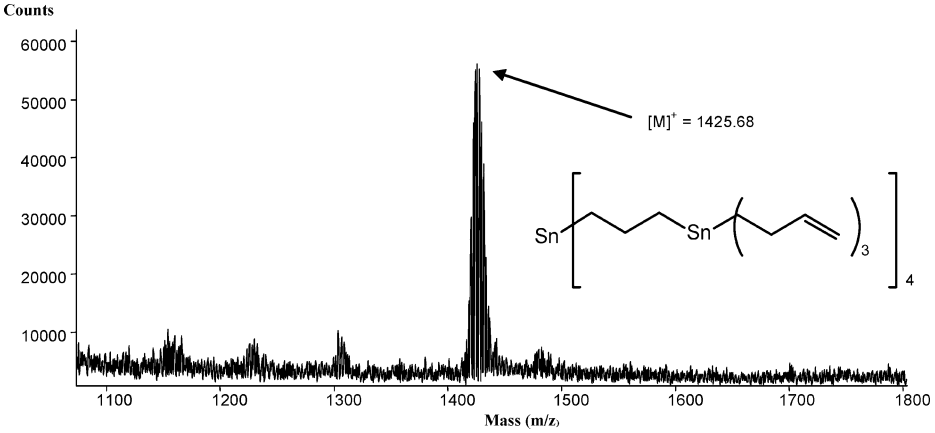


Figure 2. MALDI-TOF mass spectrum of $Sn[(CH_2)_3Sn(CH_2CH_2CH{=}CH_2)_3]_4$ (**5**).

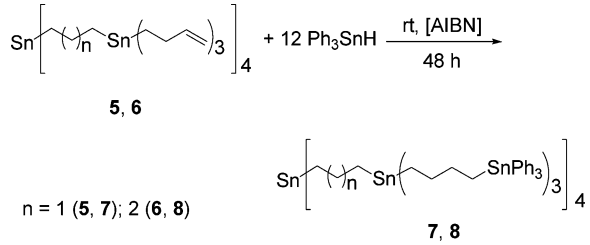
ppm) establishes the formation of the new compounds (Figure 1). The corresponding coupling constants $|^1J(^{13}C^{117/119}Sn)|$ = 294.82/308.38 Hz (**5**) and 295.91/309.81 Hz (**6**) evidence tetracoordination of the tin atoms.

The ^{119}Sn NMR spectra of **5** and **6** reveal two signals each at −10.84 (Sn^z), −7.60 ppm (Sn^p) for **5** and −11.32 (Sn^z), −6.98 ppm (Sn^p) for **6** with different intensities. The number of signals indicates the absence of any byproducts and confirms the equivalence of the branches of the dendrimers, which is in agreement with the ^1H and $^{13}C\{^1H\}$ NMR results.

Due to their high molecular weights, **5** and **6** could not be investigated with the classical ionization methods. As discussed in previous papers,[21,25] MALDI-TOF mass spectrometry is more suitable for the analysis of such macromolecules. Both dendrimers were characterized with their corresponding molecular ion peaks, which were detected at *m*/*z* 1425.68 (**5**) and 1479.20 (**6**), respectively (Figure 2). These values were obtained with the appropriate isotopic resolution and are in very close agreement with the simulated ones (see Experimental Section). The absence of lower mass peaks or those assignable to dendrimers with missing dendrons as well as other impurities further proves the proposed structure of the compounds.

Reaction of **5** and **6** each with 12 molar equiv of triphenyltin hydride in the presence of 5 mol % of AIBN at room temperature gave the second-generation dendrimers tetrakis{3-[tris(4-triphenylstannylbutyl)stannyl]propyl}stannane (**7**) and tetrakis{4-[tris(4-triphenylstannylbutyl)stannyl]butyl}stannane (**8**), respectively (Scheme 4). Compounds **7** and **8** were isolated from the reaction medium as very viscous white oils in moderate yields, by repeatedly washing with a mixture of pentane/diethyl ether (1:1). The air- and moisture-stable dendrimers are soluble in tetrahydrofuran, chlorinated alkanes, and aromatic solvents such as toluene, but almost insoluble in diethyl ether and alkanes.

Scheme 4



The most characteristic feature of the ^1H and ^{13}C NMR spectra is the lack of the low-field signals of the olefin groups, confirming that the hydrostannation of all butenyl groups had taken place completely. With the achievement of the second-generation dendrimers, some NMR signals, especially those of

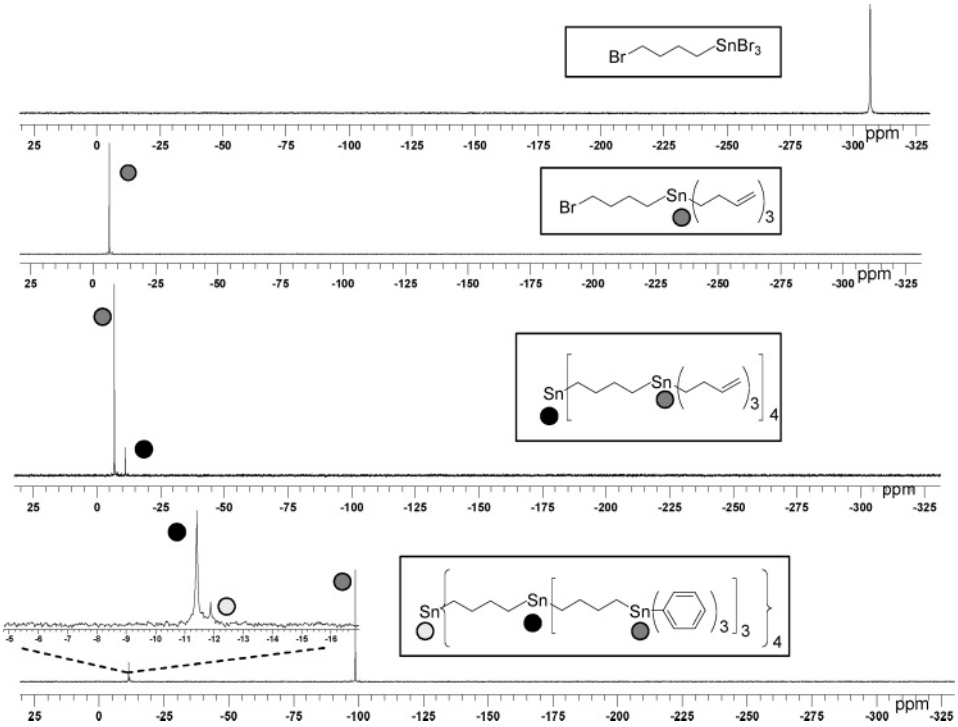


Figure 3. ^{119}Sn NMR spectra (149.21 MHz) of **2** in THF-d_8; **4**, **6**, and **8** in $CDCl_3$.

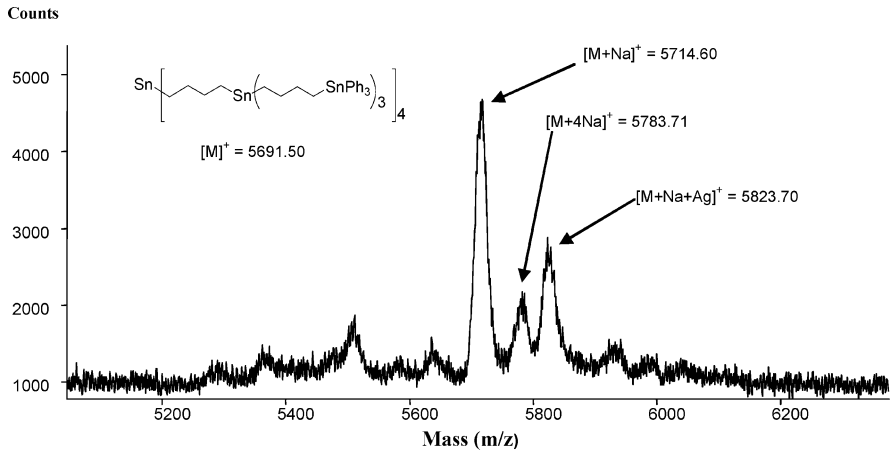


Figure 4. MALDI-TOF mass spectrum of tetrakis{4-[tris(4-triphenylstannylbutyl)stannyl]butyl}stannane (**8**).

the inner atoms, become magnetically indistinguishable and appear therefore at the same chemical shifts, due to the high symmetrical structures of the new dendritic molecules. This manifests itself in the occurrence of only one resonance for the three carbon atoms bound to the internal tin atoms Sn^z and Sn^m, at 8.47 ppm, $|^1J(^{13}C^{117/119}Sn)| = 292.37/307.90$ Hz (**7**) and 8.40 ppm, $|^1J(^{13}C^{117/119}Sn)| = 294.82/308.17$ Hz (**8**). The carbon atoms bound to the phenyl-substituted peripheral tin atoms were shifted downfield at 10.66 (**7**) and 10.70 ppm (**8**), as reflected by their coupling constants $|^1J(^{13}C^{117/119}Sn^p)| = 375.75/395.37$ and 376.29/393.73 Hz, respectively, with values clearly larger than those estimated for the carbon atoms mentioned above.

The ^{119}Sn NMR spectra of compounds **7** and **8** (Figure 3 shows a comparison of the ^{119}Sn NMR spectra of **2**, **4**, **6**, and **8**) exhibit exactly three resonances each for the three tin atoms present in the molecules, indicating the equivalence of the dendrons, thus corroborating the results found in the ^{1}H and ^{13}C NMR spectra. The downfield shifted signals belong to the internal tin atoms and are assigned by their different intensities at −13.30 ppm (Sn^z) and −14.93 ppm (Sn^m) for **7** as well as at −11.89 ppm (Sn^z) and −11.42 ppm (Sn^m) for **8**, whereas the upfield shifted signals belong to the phenyl-substituted peripheral metal atoms at −98.98 ppm (Sn^p) and −98.88 ppm (Sn^p), respectively.

The positive ion MALDI-TOF mass spectra of compounds **7** and **8** also indicate the completeness of the synthetic route with isotopic multiplets centered at *m*/*z* 5659.40 and *m*/*z* 5714.60, respectively, corresponding to the sodium ion adducts (Figure 4). The well-resolved isotopic cluster patterns of high intensity bear a close resemblance to the simulated isotopic distribution. Signals attributable to incompletely hydrostannated byproducts, dendrimers with missing dendrons, or end groups were not observed.

Attempts to grow dendrimers **7** and **8** via functionalization of the outer 12 tin atoms have failed until now. Substitution of one, two, or all three phenyl ligands at all tin atoms e.g., by bromine, did not result in isolable compounds.

Conclusion

Novel organotin dendrimers of the first generation carrying peripheral butenyl groups have been prepared by a convergent

method and used as starting materials for the construction of the second-generation dendrimers **7** and **8**. ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopic as well as MALDI-TOF mass spectrometric investigations evidenced that all synthetic steps proceeded efficiently without steric hindrance and competitive reactions. ω-Haloalkyltin trihalides are easily accessible synthons for the preparation of suitable dendrons, providing a convenient entry into dendritic macromolecules. The ability to synthesize a variety of dendritic branches in two steps starting from the corresponding dihaloalkanes and stannous bromide represents an efficient route for the production of functionally substituted organotin dendrimers.

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