Pergamon

Tetrahedron Letters, Vol. 38, No. 34, pp. 6043-6046, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)01356-7

An Organosilicon Dendrimer Composed of 16 Thiophene Rings

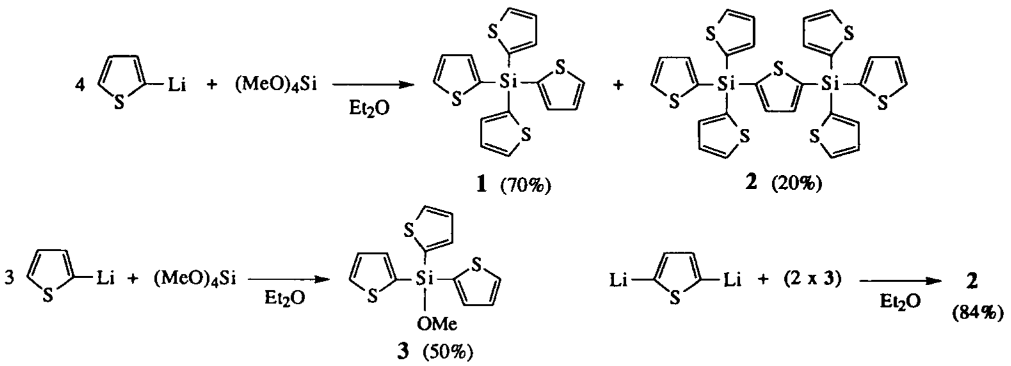
Juzo Nakayama* and Jin-Song Lin
Department of Chemistry, Faculty of Science, Saitama University,
Urawa, Saitama 338, Japan

Abstract: An organosilicon dendrimer composed of 16 thiophene rings, $C_{64}H_{44}S_{16}Si_5$, was prepared by tetralithiation of tetra-2-thienylsilane followed by reaction with 3 molar amounts of methyl tri-2-thienylsilyl ether.

Dendrimers, polymers with a regularly and highly branched, three-dimensional, tree-like structure, are the subject of recent extensive investigation. Particularly, dendrimers containing silicon atoms have attracted keen interest very recently because of their potential functionalities.[1-3] Meanwhile, numerous reports have also appeared on the syntheses and properties of thiophene oligomers because they serve as building blocks for a variety of molecular devices.[4] In this connection, we have become interested in the preparation of dendrimers containing both silicon atoms and thiophene rings. Here we report the first synthesis of such a dendrimer with 16 thiophene rings and a molecular formula of $C_{64}H_{44}S_{16}Si_5$ (molecular weight, 1466.5).

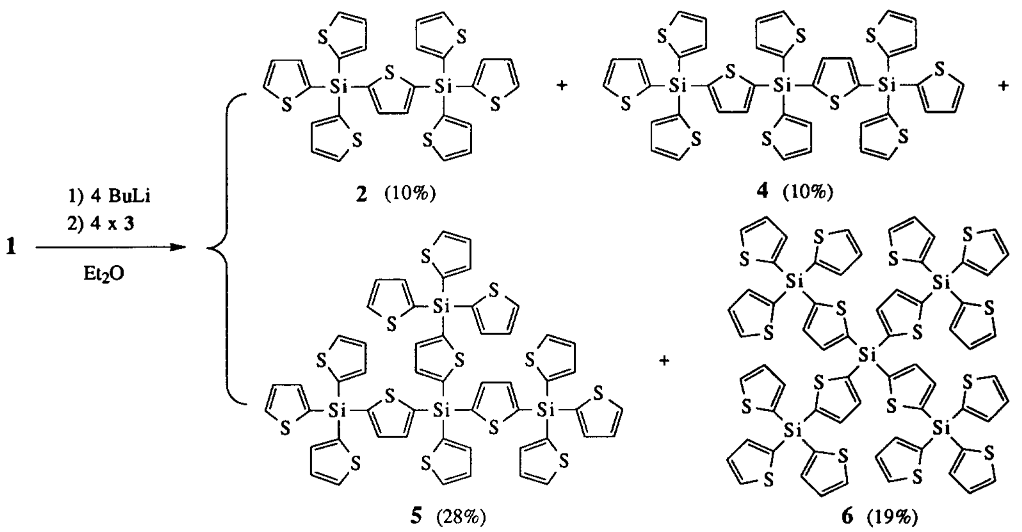
The zeroth generation dendrimer, tetra-2-thienylsilane (**1**), was previously prepared in less than 10% yields by reactions of 2-thienyllithium or 2-thienylmagnesium bromide with tetrachlorosilane or tetraethoxysilane.[5,6] Combination of these reagents persistently afforded polymeric materials as the principal product which are insoluble in common organic solvents. After some effort we have found that treatment of tetramethoxysilane with 4 molar amounts of 2-thienyllithium (1.0 *M* solution in THF, Aldrich) affords **1** in 70% yield along with 2,5-bis[tri(2-thienyl)silyl]thiophene (**2**)[7] in 20% yield.

Methyl tri-2-thienylsilyl ether (**3**),[7] which is required as the building block for the preparation of higher generation dendrimers, was prepared by treatment of tetramethoxysilane with 3 molar amounts of 2-thienyllithium in THF in more than 50% yield.



The formation of **2** in the foregoing reaction will be explained as the result of hydrogen-lithium exchange between **1** and 2-thienyllithium, followed by reaction of the lithiated **1** with **3** produced from 2-thienyllithium and tetramethoxysilane. Alternatively, compound **2** could be most effectively synthesized in 84% yield by reaction of two molar amounts of **3** with 2,5-dilithiothiophene, prepared from 2,5-dibromothiophene and *tert*-BuLi.

Treatment of **1** with 4 molar amounts of BuLi in ether and quenching of the mixture with D_2O revealed that the α-position of each thiophene ring was lithiated in more than 80% efficiency. Thus, **1** was lithiated with 4 molar amounts of BuLi and then treated with 4 molar amounts of **3** in ether. Purification of the resulting mixture with silica-gel column chromatography and HPLC gave the expected first-generation dendrimer 5,5',5'',5'''-tetrakis[tri-2-thienylsilyl(tetra-2-thienyl)]silane (**6**)[7] in 19% yield along with **2** (10%), 5,5'-bis[tri-2-thienylsilyl(tetra-2-thienyl)]silane (**4**)[7] (22%), and 5,5',5''-tris[tri-2-thienylsilyl(tetra-2-thienyl)silane (**5**)[7] (28%) with 10% recovery of **1**.[8] Relative yield of the products depends on reaction conditions (solvent, temperature, reaction time, lithiation reagents and concentration and relative amounts of the substrates). The yield of **6** given above is obtained under optimized conditions.

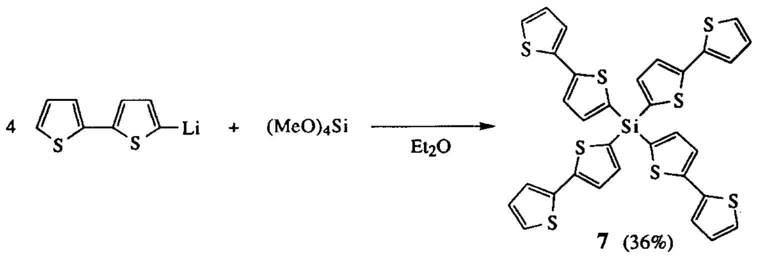


2 (10%)

4 (10%)

5 (28%)

6 (19%)



7 (36%)

Structures of **2**-**6** were determined based on spectroscopic data and elemental analyses; ^{13}C NMR analyses[7] are particularly useful for their regularly branched structures.

It is noteworthy that the dendrimer **6** forms inclusion complexes with CCl_4, CH_2Cl_2, benzene, and acetone, when crystallized from these solvents or mixtures of these solvents and hexane. Combination of ^1H NMR and elemental analyses revealed that the complex with CCl_4 contains one molecule of CCl_4 per one molecule of **6**, while those with CH_2Cl_2, benzene, and acetone contain 1/3 molecule of these solvents, even after drying under vacuum for 24 h at room temperature.[7] Curiously enough, no inclusion complex formed with $CHCl_3$. The solvent-free crystal obtained from this mixed solvent showed a higher melting point than those of any inclusion complexes.[7]

Treatment of compound **2** with 6 molar amounts of BuLi in ether and quenching of the mixture with D_2O revealed that hexalithiation of **2** took place in about 80% efficiency. However, an attempted reaction of the hexalithiated **2** with 6 molar amounts of **3** gave a complex mixture containing compounds **3-6** and failed to give the expected dendrimer with 25 thiophene rings. This is due to the poor solubility of the lithiated **2**, which impedes the reaction with **3**. The use of THF as the solvent of lithiation resulted in the cleavage of the silicon-thiophene ring bond to give **1** in 52% yield.

The reaction of tetramethoxysilane with 4 molar amounts of 5-lithio-2,2'-bithiophene, prepared from 5-bromo-2,2'-bithiophene and *tert*-BuLi, gave another zeroth generation dendrimer **7** in 36% yield.[9]

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1. Polysiloxane dendrimers. (a) E. A. Rebrov, A. M. Muzafarov, V. S. Papkov, and A. A. Zhadnov, *Dokl. Akad. Nauk SSSR.*, 1989, **309**, 376; (b) H. Uchida, Y. Kabe, K. Yoshino, A. Kawamata, T. Tsumuraya, and S. Masamune, *J. Am. Chem. Soc.*, 1990, **112**, 7077; (c) L. J. Mathias and T. W. Carothers, *J. Am. Chem. Soc.*, 1991, **113**, 4043; (d) A. Morikawa, M. Kakimoto, and Y. Imai, *Macromolecules,* 1991, **24**, 3469.

2. Carbosilane dendrimers. (a) A. W. van der Made and P. W. N. M. van Leeuwen, *J. Chem. Soc., Chem. Commun.*, 1992, 1400; (b) L.-L. Zhou and J. Roovers, *Macromolecules,* 1993, **26**, 963; (c) J. Roovers, L.-L. Zhou, P. M. Toporowski, M. van der Zwan, H. Iatrou, and N. Hadjichristidis, *Macromolecules,* 1993, **26**, 4324; (d) D. Seyferth, D. Y. Son, A. L. Rheingold, and R. L. Ostrander, *Organometallics,* 1994, **13**, 2682; (e) J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leuuwen, P. Wijkens, D. M. Grove, and G. van Koten, *Nature,* 1994, **372**, 659.

3. Polysilane dendrimers. (a) J. B. Lambert, J. L. Pflug, and C. L. Stern, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 98; (b) H. Suzuki, Y. Kimata, S. Sato and A. Kuriyama, *Chem. Lett.*, 1995, 293; (c) A. Sekiguchi, M. Nanjo, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, 1995, **117**, 4195.

4. Only representative examples are given below. α-Thiophene oligomers: (a) J. Nakayama, T. Konishi, and M. Hoshino, *Heterocycles*, 1990, **27**, 1731; (b) W. ten Hoeve, H. Wynberg, E. E. Havinga, and E. W. Meijer, *J. Am. Chem. Soc.*, 1991, **113**, 5887 and references cited therein. Thiophene-pyrrole cooligomers: (c) B. A. Merrill and E. LeGoff, *J. Org. Chem.*, 1990, **55**, 2904; (d) M. R. Johnson, D. C. Miller, K. Bush, J. J. Becker, and J. A. Ibers, *J. Org. Chem.*, 1992, **57**, 4414. Thiophene-derived macrocycles: (e) Z. Hu and M. P. Cava, *Tetrahedron Lett.*, 1994, **35**, 3493. Orthogonally-fused thiophene oligomers: (f) J. Nakayama and T. Fujimori, *J. Chem. Soc., Chem. Commun.*, 1991, 1614; (g) J. Guay, A. Diaz, R. Wu, and J. M. Tour, *J. Am. Chem. Soc.*, 1993, **115**, 1869 and references cited therein. Cofacially-oriented thiophene oligomers: (h) K. Kuroda, J. Nakayama, M. Hoshino, N. Furusho, and S. Ohba, *Tetrahedron Lett.*, 1994, **35**, 3957 and references cited therein. Thiophene-silole

cooligomers: (i) K. Tamao, S. Yamaguchi, M. Shiozaki, Y. Nakagawa, and Y. Ito, *J. Am. Chem. Soc.*, 1992, **114**, 5867.

5. E. Lukevics, O. A. Pudova, J. Popelis, and N. P. Erchak, *Zh. Obsch. Khim.*, 1981, **51**, 115.

6. For electropolymerization of **1**: A. Guy, M. Lemaire, R. Garreau, and H. A. Hoa, *J. Electroanal. Chem.*, 1991, **312**, 277. For ruthenium complexes of **1**: M.-H. Woo and M.-G. Choi, 4th International Conference on Heteroatom Chemistry, Seoul, Korea, Abst. No. PA-40.

7. Selected physical data for **2-7** and elemental analyses for **6** and its inclusion complexes (other new substances also gave correct elemental analyses). **2**: mp 142.5-143.5 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 4.4, 3.2 Hz, 6H), 7.49 (d, *J* = 3.2 Hz, 6H), 7.58 (s, 2H), 7.74 (d, *J* = 4.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.43, 133.13, 133.22, 138.51, 139.32, 141.91; MS (70 eV); m/z 636 (M^+); UV (CH_2Cl_2) λ_{max} (ε) 244.4 nm (41600). **3**: mp 64.5-65 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.67 (s, 3H), 7.25 (dd, *J* = 4.8, 3.4 Hz, 3H), 7.51 (dd, *J* = 3.4, 0.7 Hz, 3H), 7.73 (dd, *J* = 4.8, 0.7 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 51.75, 128.32, 132.81, 132.92, 138.02; MS (70 eV); m/z 308 (M^+). **4**: mp 152-153.5 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 4.8, 3.8 Hz, 8H), 7.48 (dd, *J* = 3.8, 0.8 Hz, 8H), 7.56 (s, 4H), 7.74 (dd, *J* = 4.8, 0.8 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.44, 128.46, 132.95, 133.12, 133.22, 133.31, 138.52, 138.62, 139.33, 139.41, 141.74, 141.96; MS (70 eV) m/z 912 (M^+); UV (CH_2Cl_2) λ_{max} (ε) 245.8 nm (73200). **5**: mp 148-152 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.0, 3.7 Hz, 10H), 7.47 (dd, *J* = 3.7, 0.8 Hz, 10H), 7.55 (d, *J* = 3.2 Hz, 3H), 7.56 (d, *J* = 3.2 Hz, 3H), 7.72 (dd, *J* = 5.0, 0.8 Hz, 10H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.43, 128.47, 132.57, 133.11, 133.20, 133.39, 138.50, 138.70, 139.32, 139.47, 141.54, 142.05; UV (CH_2Cl_2) λ_{max} (ε) 246.0 nm (95600). Anal. Calcd for $C_{52}H_{36}S_{13}Si_4$: C, 52.48; H, 3.04. Found: C, 52.65; H, 3.16. **6**: mp 218-219 °C (chloroform/hexane); colorless needles; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 4.5, 3.2 Hz, 12H), 7.47 (d, *J* = 3.2 Hz, 12H), 7.54 (d, *J* = 3.3 Hz, 4H), 7.56 (d, *J* = 3.5 Hz, 4H), 7.72 (d, *J* = 4.5 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.43, 133.10, 133.20, 138.51, 139.32, 139.54, 141.28, 142.10; UV (CH_2Cl_2) λ_{max} (ε) 245.4 nm (140000). Anal. Calcd for $C_{64}H_{44}S_{16}Si_5$: C, 52.41; H, 3.02. Found: C, 52.17; H, 3.00. **6** crystallized from a mixture of CCl_4 and hexane: mp 200-201 °C. Anal. Calcd for $C_{64}H_{44}S_{16}Si_5 \cdot CCl_4$: C, 48.18; H, 2.73. Found: C, 47.90; H, 2.68. **6** crystallized from a mixture of C_6H_6 and hexane: mp 205-206 °C. Anal. Calcd for $C_{64}H_{44}S_{16}Si_5 \cdot 1/3C_6H_6$: C, 53.11; H, 3.11. Found: 53.37; H, 3.22. **6** crystallized from acetone: mp 205-206 °C. Anal. Calcd for $C_{64}H_{44}S_{16}Si_5 \cdot 1/3C_3H_6O$: C, 52.54; H, 3.12. Found: C, 52.71; H, 3.08. **6** crystallized from a mixture of CH_2Cl_2 and hexane: mp 206.5-207 °C. Anal. Calcd for $C_{64}H_{44}S_{16}Si_5 \cdot 1/3CH_2Cl_2$: C, 51.69; H, 3.01. Found: C, 51.94; H, 2.94. **7**: mp 154-154.5 °C (C_6H_6/hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 5.2, 3.8 Hz, 4H), 7.22 (d, *J* = 5.2 Hz, 4H), 7.23 (d, *J* = 3.8 Hz, 4H), 7.30 (d, *J* = 3.5 Hz, 4H), 7.43 (d, *J* = 3.5 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 124.59, 125.08, 125.26, 127.90, 131.73, 136.82, 139.35, 145.56; MS (70 eV) m/z 688 (M^+); UV/Vis; λ_{max} (ε) 327.5 nm (88900).

8. A 1.65 M hexane solution of BuLi (4 ml, 6.6 mmol) was added to a solution of **1** (540 mg, 1.5 mmol) in ether (15 ml) at –18 °C under argon. The mixture was stirred for 1 h. A solution of **3** (2.03 g, 6.6 mmol) in ether (10 ml) was added to the above mixture, and the resulting mixture was warmed to room temperature and stirred for 12 h. The reaction was quenched by adding ice-water and then CH_2Cl_2 (150 ml) was added and the organic layer was washed with water, dried, and evaporated. The residue was placed on a column of silica gel and eluted with a mixture of CH_2Cl_2/hexane (1/3) to give 55 mg (10%) of **1**, 92 mg (10%) of **2**, 309 mg (22%) of **4**, 500 mg (28%) of **5**, and 446 mg (19%) of **6** (separation of **4-6** by column chromatography is incomplete; these were separated by HPLC on a column of JAIGEL-2H (Japan Analytical Industry Co.) to give them in the yields given above).

9. For tetrakis(2,2':5',2"-terthiophene-2-yl)silane, see J. Roncali, C. Thobie-Gautier, H. Brisset, J.-F. Favart, and A. Guy, *J. Electroanal. Chem.*, 1995, **381**, 257.

(*Received in Japan* 12 *May* 1997; *revised* 27 *June* 1997; *accepted* 3 *July* 1997)