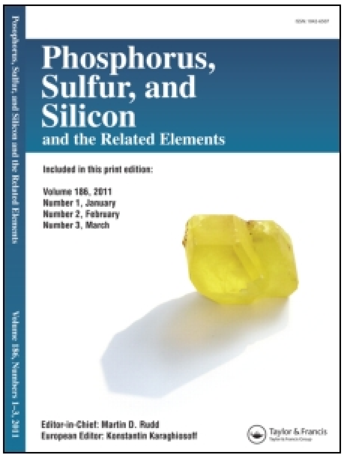

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SYNTHESIS AND CHARACTERIZATION OF A POLY(BENZYL ETHER) DENDRON SULFENYL IODIDE

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A poly(benzyl ether) dendron with a sulfenyl iodide group at the focal point was synthesized and well characterized. Although the molecule showed high stability to chemical reactions, the corresponding dendrimer disulfide was obtained upon photoirradiation quantitatively.

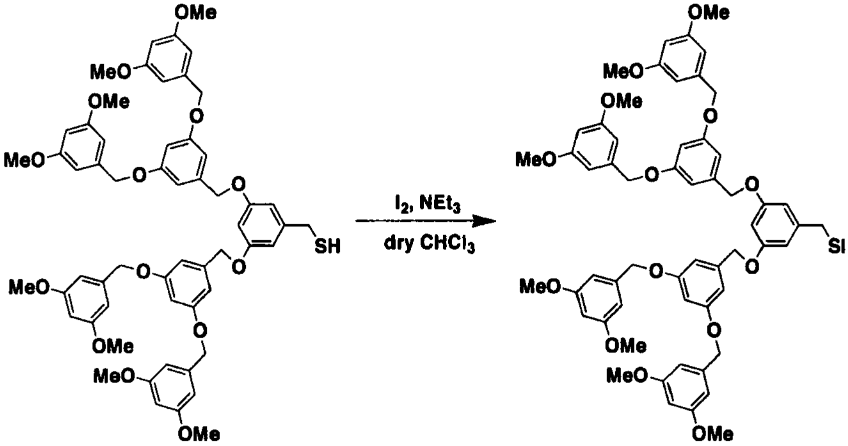
Keywords: Dendrimer; dendron; sulfenyl iodide; photoreaction

INTRODUCTION

A new kind of well-defined regularly branched macromolecules of nanoscopic size, called dendrimers, have widely attracted scientific attention. In particular, dendrimers with specific functionalities at the core are of current interest in the viewpoint of site isolation. In this regard, several groups have reported the covalent incorporation of highly unstable subunits at the core of dendrimer as isolable active-site mimics for enzymes.[1] However, the site isolation properties of dendrons have not been well explored.[2,3] Meanwhile, it is well known that sulfenyl iodides (RSI) are key intermediates in the iodination reaction in the human thyroid gland,[4–6] as well as in iodine oxidation of thiols.[7] However, because of their instability, the investigation of such compounds has been obstructed.[8–10] Recently, Goto et al. have reported on several isolable arenesulfenyl iodides and alkylsulfenyl iodide which were stabilized by covalent fixation in the interior of molecular bowls.[11–14] Dendritic systems containing a sulfenyl iodide at the focal point are especially attractive targets because they should possess site isolation properties and could be obtained as a stable compound. During our studies on the reactivities of dendrimers containing chalcogen atoms,[15] we found that dendritic branch efficiently stabilized highly-reactive chalcogen species. This article describes the synthesis and characterization of a poly(benzyl ether) dendron sulfenyl iodide (**1**), although an isolable sulfenyl iodide having dendritic substituent is without precedent. Photoreactivity of dendron sulfenyl iodide **1** is also discussed.

RESULT AND DISCUSSIONS

Dendron sulfenyl iodide (**1**) was synthesized as shown in Scheme 1. A dendritic thiol (**2**) was selected as the starting material, which was synthesized by the method we previously reported.[15] The dendron **2** was allowed to react with iodine in the presence of triethylamine (1 equivalent) in chloroform under a nitrogen atmosphere at room temperature for 20 h in the dark to give the aryl ether dendron sulfenyl iodide **1** in 70% yield. It is notable that a stable sulfenyl iodide synthesized by iodine oxidation of a thiol is quite rare.[11–14]



2 **1**

SCHEME 1

The structure of **1** was confirmed by the ^1H and ^{13}C NMR spectroscopies, elemental analysis, and MALDI-TOF mass spectrometry. A methylene proton signal [δ 3.65 (d, 2H)] of the focal point of dendron thiol **2** disappeared and a new singlet peak appeared at δ 4.61. The marked downfield shift is consistent with the sulfenyl iodide structure, whereas the dendrimer disulfide **3** shows a singlet peak at 3.53 ppm. The MALDI-TOF-MS spectrum of **2** showed clearly the parent peak at *m/z* 1128.04, which is consistent with the molecular weight of the dendron sulfenyl iodide ($[M+H]^+$, calcd 1128.06), together with a peak at *m/z* 1001.06 ($[MH-I]^+$) derived from elimination of an iodine

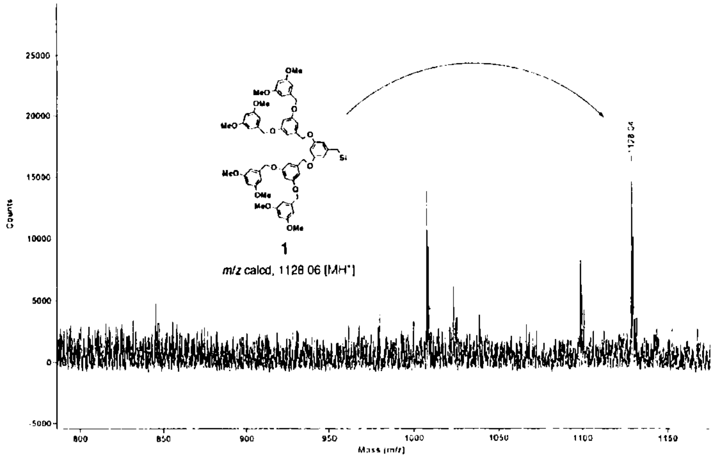
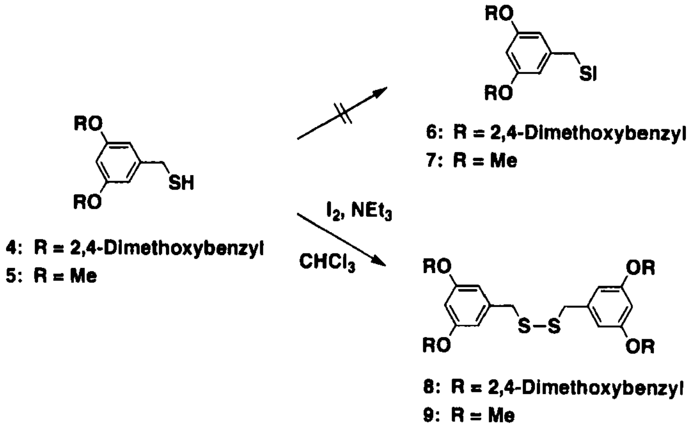


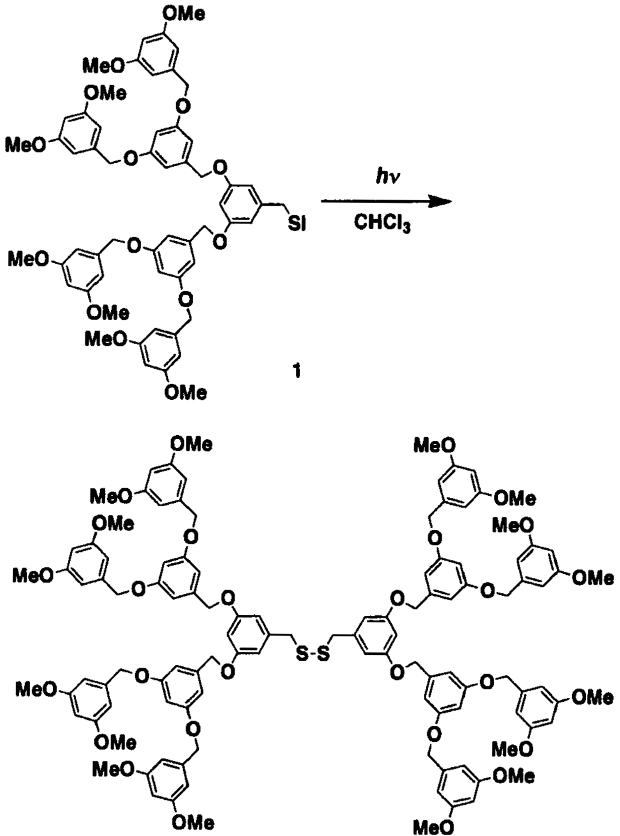
FIGURE 1 MALDI-TOF-MS of compound 1.

atom (Figure 1). This assignment is also supported by the appearance of a single peak corresponding to dendron **2** in the size-exclusion chromatography (SEC) traces. The SEC retention volume (164 ml) of the dendron sulfenyl iodide **1** was an intermediate value between that of dendron thiol **2** (168 ml) and dendrimer disulfide **3** (154 ml). On the other hand, the reactions of lower generation dendron thiols (**4**) and (**5**) with iodine in the presence of triethylamine did not give dendron sulfenyl iodide (**6**) and (**7**) but afforded dendrimer disulfides (**8**) and (**9**), respectively (Scheme 2).



SCHEME 2

The reactivity of the dendron sulfenyl iodide **1** was examined as follows. As with the bowl-type sulfenyl iodide reported by Goto et al.,[11,12] compound **1** was unreactive toward the thiol **2** bearing the same substituent. Furthermore, **1** was found to be extremely stable to nucleophiles, that is, butane-1-thiol (10 equiv.) in the presence of triethylamine, benzylamine (10 equiv.), and butane-1-amine (10 equiv.) in marked contrast with Goto's sulfenyl iodide.[11,12] On the other hand, dendron **1** was converted to a dendrimer disulfide (**3**) in 8% yield when it had been allowed to stand for two months in the dark as the oil. It is likely that the bulky dendritic wedges can stabilize the sulfur-iodine bond of monomeric or the polymeric structure of the sulfenyl iodide via van der Waals interactions, similarly to hydrogen bonds at the dendritic core reported by Aida et al.[16]



1

3

SCHEME 3

It is well-known that sulfenyl iodide decompose upon irradiation.[8-10] Thus, chloroform solutions of the dendron **1** (ca. 0.14 M) was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 2 h to give dendrimer disulfide **3** in 100% yield (Scheme 3).

The results described herein show the isolation of sulfenyl iodide as a stable compound by the use of site isolation of the dendritic system. Although photoreactivity of sulfenyl iodide have not been well explored, the dendron sulfenyl iodide **1** was transformed into the corresponding dendrimer disulfide **3** in quantitative yield upon irradiation. Further work is in progress to explore the applications and advantages of the site isolation effect of the dendrimer to stabilize the highly reactive species containing sulfur atoms.

EXPERIMENTAL SECTION

NMR spectra were measured on a Bruker AVANCE400 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a Voyager Elite mass spectrometer using dithranol as a matrix. Elemental analysis was carried out on a Perkin-Elmer 2400 CHN elemental analyzer. GPC experiments were performed on a Japan Analytical Industry Co. model LC-918V with JAIGEL 1H, 2.5H columns, and chloroform was used as the eluting solvent. Photoirradiation was carried out in a Pyrex reactor. Prior to irradiation, the samples were deaerated by nitrogen bubbling for 15 min. A 500 W high-pressure mercury lamp was used as the light source. The reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., and Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Preparation of the Aryl Ether Dendron Sulfenyl Iodide 1

A solution of dendron thiol **2** (160 mg, 0.16 mmol) in dry chloroform (5.0 ml) and a solution of iodine (40 mg, 0.16 mmol) in dry chloroform (5.0 ml) were added dropwise to a solution of triethylamine (16 mg, 0.16 mmol) in dry chloroform (5.0 ml) under a nitrogen atmosphere. The entire mixture was stirred at room temperature for 20 h in the dark. After the usual work-up, the residue was purified by GPC to afford the aryl ether dendron sulfenyl iodide **1** (127 mg, 0.112 mmol) as a thick oil in 70% yield: ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 24H), 4.61 (s, 2H), 4.97 (s, 12H), 6.40–6.66 (m, 21H); ^{13}C NMR ($CDCl_3$) δ 55.4, 65.3, 69.9, 70.1, 100.0, 101.3, 101.7, 105.3, 105.8, 106.4, 139.2, 139.4, 143.6, 160.11, 160.14, 161.0; MALDI-TOF-MASS for $C_{57}H_{59}O_{14}SI$: m/z calcd, 1128.06 [MH^+]; found, 1128.04. Anal. Calcd for $C_{57}H_{59}O_{14}SI$: C, 60.74; H, 5.28. Found: C, 60.52; H, 5.68.

Under the same condition, the reactions of dendron thiols **4** and **5** with iodine gave dendrimer disulfides **8** (100%) and **9** (100%), respectively. Dendrimer **8**: ^1H NMR ($CDCl_3$) δ 3.56 (s, 4H), 3.75 (s, 12H), 6.36 (s, 2H), 6.40 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 43.5, 55.1, 99.4, 107.1, 139.4, 160.6. Anal. Calcd for $C_{18}H_{22}O_4S_2$: C, 58.99; H, 6.05. Found: C, 59.23; H, 6.05. Dendrimer **9**: ^1H NMR ($CDCl_3$) δ 3.58 (s, 4H,), 3.75 (s, 24H), 4.95 (s, 8H), 6.41–6.60 (m, 18H); ^{13}C NMR ($CDCl_3$) δ 41.5, 53.2, 67.9, 97.8, 99.5, 103.2, 106.5, 137.2, 137.7, 157.9, 159.0. Anal. Calcd for $C_{50}H_{54}O_{12}S_2$: C, 65.91; H, 5.97. Found: C, 66.11; H, 5.68.

Photoirradiation of Dendron Sulfenyl Iodide 1

A solution of dendron **1** (80 mg, 0.071 mmol) in chloroform (0.5 ml) was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 2 h. After removal of the solvent, the residue was purified by GPC to afford the aryl ether dendrimer disulfide **3** (71 mg, 0.036 mmol) as a thick oil in 100% yield. The structure of **3** was confirmed by direct comparison with an authentic sample prepared independently.[15]

ACKNOWLEDGMENTS

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