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Preparation of 1-Alkynyl 2-(Trimethylsilyl)ethyl Sulfides as Thiolate Anion Precursors for Self-Assembled Monolayers

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Abstract: Syntheses of 1-alkynyl 2-(trimethylsilyl)ethyl sulfides are reported. Deprotection of 2-(trimethylsilyl)ethyl groups using fluoride ions permits the formation of thiolate anions which are trapped by *in situ* alkylation with methyl iodide and can be used to produce self-assembled monolayers on gold.

Recently composite materials containing metal particles and π-conjugated organic compounds are attracting much attention because of their special linear or nonlinear optical properties. In particular, an electromagnetic resonance effect in metal particles called the surface-plasmon resonance is expected to greatly enhance the optical nonlinearities of organic π-electron systems.[1] We anticipated that the self-assembled monolayers (SAMs) of organomercaptans on gold surface could produce composite materials consisting of the π-conjugated systems adjacent to the gold surface. However there have been no previous reports concerning SAMs of organomercaptans which contain alkynyl or alkenyl groups adjoining sulfur atoms. These SAMs could result in composite materials described above by polymerization of unsaturated functionalities.[2] This is because 1-alkynethiols and 1-alkynyl disulfides are too unstable for their use in the preparation of SAMs as reported by Senning et al.[3]

Meanwhile we have investigated the solid-state polymerization of various types of diacetylene compounds as third-order nonlinear optical materials, especially diacetylenes having sulfur atoms directly bound to the *sp*-carbons.[4] Based upon the results of our work, we started to develop the stable precursors which can release 1-alkynethiolate anions under mild conditions. These compounds can be also used as reactants of [2+2][5] and [4+2][6] reaction to afford alkenyl sulfide derivatives that would be precursors of 1-alkenethiolate anions. As a prelude to the design of such systems, we believe that the 2-(trimethysilyl)ethyl group might serve as a promising protecting group for thiols because 2-(trimethylsilyl)ethyl sulfide is easily converted into the corresponding thiolate anion, ethylene, and trimethylsilyl fluoride by treatment with tetrabutylammonium fluoride (TBAF).[7] In this paper we discuss a general synthesis of 1-alkynyl 2-(trimethylsilyl)ethyl sulfides and confirmed the generation of the corresponding thiolate anions from them. In the second paper in this series we demonstrate that these molecules self-assemble onto gold surface by *in situ* deprotection as illustrated in Scheme 1.

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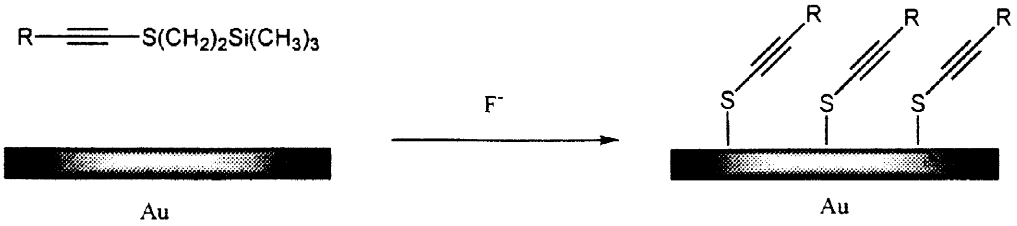
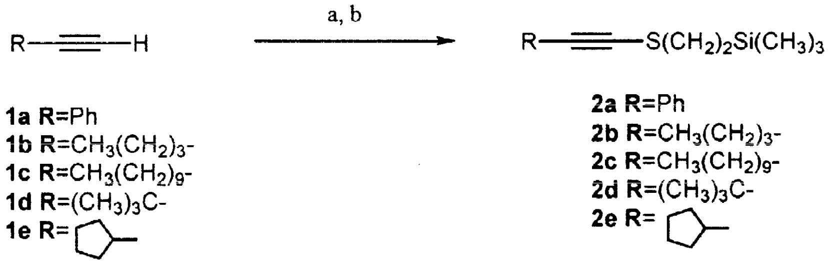


Scheme 1.

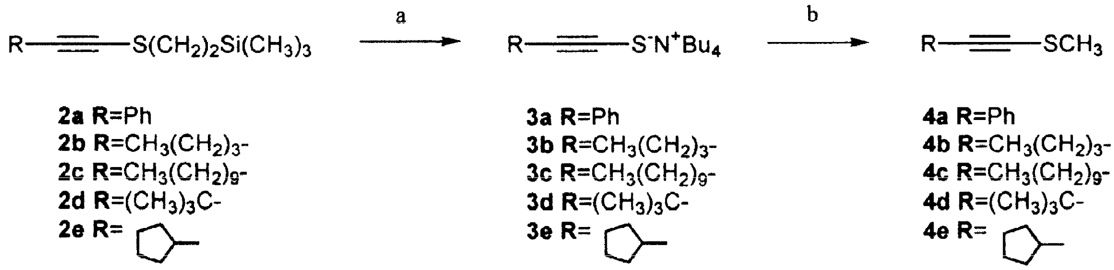
The syntheses of 1-alkynyl 2-(trimethylsilyl)ethyl sulfides **2a-e** are shown in Scheme 2. *n*-Butyl lithium in *n*-hexane was introduced into a THF solution of acetylenes **1a-e** at -78°C. After 1hour, addition of a THF solution of 2-(trimethylsilyl)ethylsufenyl chloride[8] to the mixture gave the sulfides **2a-e** in poor yield (<5%). However, the sulfenylation reaction proceeded more smoothly to give **2a-e** as yellow oil in 64, 86, 57, 79, and 72%, respectively, when *S*-2-(trimethylsilyl)ethyl *p*-toluenethiosulfonate[9] was used. All of the 1-alkynyl 2-(trimethylsilyl)ethyl sulfides **2a-e** are fairly stable and can be isolated even by reduced-pressure distillation.[10]



Scheme 2. *Reagents and conditions*; a. BuLi, THF, -78°C; b. $TsS(CH_2)_2Si(CH_3)_3$, THF, -78°C.

We tried to confirm the generation of thiolate anion **3a** from the compound **2a**. (Scheme 3) Since 1-alkynyl thiols are unstable and spontaneously converted to thioketenes via [1,3]-sigmatropic rearrangement,[3] the released thiolate anion **3a** should be trapped by methyl iodide as a stable 1-alkynyl methyl sulfide. A THF solution of TBAF (1.0 M) was added to a THF solution of compound **2a** and methyl iodide at -78°C. As a result, methyl phenylethynyl sulfide **4a** was obtained as a yellow oil in 63% yield.[11] Concerning the compounds **2b-e**, we verified the formation of **4b-e** under the same condition as used for **2a** by a gas chromatograph-mass spectrometer.

For comparison, we also synthesized $CH_3(CH_2)_5S(CH_2)_2Si(CH_3)_3$ (**5**) from hexyl bromide and 2-(trimetylsilyl)ethanethiol by a method similar to those reported by Fuchs et al.[12] Compound **5** was stable and the formation of methyl sulfide was not observed at all under the above conditions. Under aprotic conditions, obtained with molecular sieves 4A,[7, 13] the deprotection reaction proceeded very slowly even at room temperature. From these results, we concluded that deprotection of compound **2a-e** proceeds more smoothly than that of alkyl 2-(trimetylsilyl)ethyl sulfide to afford the corresponding thiolate anion **3a-e**.



Scheme 3. *Reagents and conditions*; a. 2 equiv of Bu_4NF, THF, -78°C; b. CH_3I, THF, -78°C-rt.

In summary, we have successfully synthesized 1-alkynethiol precursors protected by 2-(trimethylsilyl)ethyl groups. The formation of 1-alkynethiolates from them with TBAF was confirmed by a trapping experiment with methyl iodide. Moreover, the compounds **2a-c** yield close-packed self-assembled monolayers on an Au surface through *in situ* deprotection of 2-(trimethylsilyl)ethyl group with TBAF. We are currently working to investigate the SAMs in detail.

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10. Analytical data of **2a**: ^{1}H-NMR ($CDCl_3$) δ: 0.00 (s, 9H), 0.99-1.06 (m, 2H), 2.80-2.86 (m, 2H), 7.22-7.24

(m, 3H), 7.34-7.38 (m, 2H), ^{13}C-NMR (CDCl$_3$) δ: -1.80, 17.57, 32.51, 79.93, 93.68, 123.64, 127.88, 128.24, 131.39, IR (KBr, cm^{-1}) 690, 753, 840, 858, 888, 1015, 1162, 1249, 1442, 1487, 1595, 2166, 2954, HRMS Calcd. for $C_{13}H_{18}SSi$: 234.090. Found: 234.090. Anal. Calcd. for $C_{13}H_{18}SSi$: C, 66.61; H, 7.74; S, 13.68. Found: C, 67.55; H, 8.09; S, 13.25. **2b**: ^{1}H-NMR (CDCl$_3$) δ: 0.00 (s, 9H), 0.88 (t, 3H, *J*= 7.0), 0.93-1.00 (m, 2H), 1.37-1.51 (m, 4H), 2.29 (t, 2H, *J*= 6.8), 2.68-2.74 (m, 2H), ^{13}C-NMR (CDCl$_3$) δ: -1.85, 13.53, 17.39, 19.81, 21.87, 30.88, 31.93, 68.54, 95.01, IR (KBr, cm^{-1}) 840, 859, 889, 1015, 1107, 1162, 1249, 1260, 1455, 1465, 2873, 2933, 2956, HRMS Calcd. for $C_{11}H_{22}SSi$: 214.121. Found: 214.121. **2c**: ^{1}H-NMR (CDCl$_3$) δ: 0.00 (s, 9H), 0.84 (t, 3H, *J*= 6.1), 0.93-0.99 (m, 2H), 1.23-1.53 (m, 16H), 2.27 (t, 2H, *J*= 6.9), 2.67-2.74 (m, 2H), ^{13}C-NMR (CDCl$_3$) δ: -1.81, 14.09, 17.42, 20.16, 22.67, 28.83, 28.85, 29.14, 29.31, 29.54, 29.58, 31.89, 31.96, 68.54, 95.13, IR (KBr, cm^{-1}) 840, 858, 888, 1015, 1162, 1249, 1259, 1421, 1467, 2854, 2925, 2954, HRMS Calcd. for $C_{17}H_{34}SSi$: 298.215. Found: 298.215. **2d**: ^{1}H-NMR (CDCl$_3$) δ: 0.01 (s, 9H), 0.93-0.99 (m, 2H), 1.20 (s, 9H), 2.67-2.74 (m, 2H), ^{13}C-NMR (CDCl$_3$) δ: -1.66, 17.23, 28.83, 31.13, 32.13, 67.34, 102.89, IR (KBr, cm^{-1}) 840, 859, 888, 1015, 1163, 1202, 1250, 1361, 2866, 2899, 2955, 2968 cm^{-1}, HRMS Calcd. for $C_{11}H_{22}SSi$: 214.121. Found: 214.119. Anal. Calcd. for $C_{11}H_{22}SSi$: C, 61.61; H, 10.34; S, 14.95. Found: C,62.40; H, 10.26; S, 15.26. **2e**: ^{1}H-NMR (CDCl$_3$) δ: 0.01 (s, 9H), 0.93-0.99 (m, 2H), 1.40-1.70 (m, 6H), 1.85-1.90 (m, 2H), 2.65-2.75 (m, 3H), ^{13}C-NMR (CDCl$_3$) δ: -1.69, 17.33, 24.96, 31.59, 32.10, 33.97, 68.11, 99.02, IR (KBr, cm^{-1}) 840, 858, 889, 1015, 1162, 1249, 1416, 1452, 2871, 2917, 2955, HRMS Calcd. for $C_{12}H_{22}SSi$: 226.121. Found: 226.124. Anal. Calcd. for $C_{12}H_{22}SSi$: C, 63.65; H, 9.79; S, 14.16. Found: C,62.88; H, 9.59; S, 14.48.

11. Analytical data of **4a**: ^{1}H-NMR (CDCl$_3$) δ: 2.48 (s, 3H), 7.28-7.31 (m, 3H), 7.40-7.43 (m, 2H), ^{13}C-NMR (CDCl$_3$) δ: 19.37, 80.89, 91.83, 123.37, 128.03, 128.26, 131.43, IR (KBr, cm^{-1}) 689, 755, 977, 1070, 1142, 1313, 1441, 1487, 1595, 2167, 2927, HRMS Calcd. for C_9H_8S: 148.035. Found: 148.033.
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