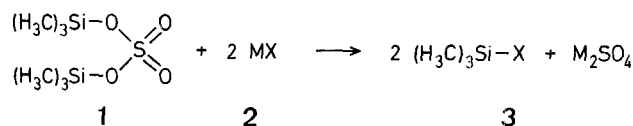


## Bis[trimethylsilyl] Sulfate as an Organosilicon Synthon

M. G. VORONKOV\*, V. K. ROMAN, E. A. MALETINA

Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, 664033 Irkutsk, USSR

Recently, a convenient synthetic route to cyanotrimethylsilane, isocyanatotrimethylsilane, and isothiocyantotrimethylsilane from the reaction of bis[trimethylsilyl] sulfate (**1**) with potassium cyanide, potassium isocyanate, and potassium isothiocyante, respectively, in *N*-methylpyrrolidone was reported<sup>1</sup>. It was not mentioned here, however, that the reactions of **1** with inorganic and organic acid salts **2**, including the above-mentioned, were described by the present authors as long as 5 years ago and offered as preparative methods for the synthesis of not only the above esters of cyanic, isocyanic, and isothiocyanic acids but also of the esters of hydrofluoric, hydrochloric, hydrobromic, nitric, acetic, and trifluoroacetic acids as well<sup>2-5</sup>. These reactions occur smoothly without any solvent (Scheme A) and give the products **3** in yields of 60–100% (Table 1). Use of solvents (including *N*-methylpyrrolidone) is not necessary and only makes the purification of the product **3** more difficult.

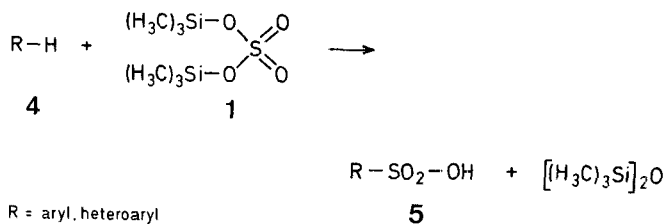


M = Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>

X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, NCS<sup>-</sup>, <sup>-</sup>O-CO-CH<sub>3</sub>, <sup>-</sup>O-CO-CF<sub>3</sub>

### Scheme A

It was also reported recently that **1** may be used for sulfuration of organic compounds<sup>6</sup>. However, this possible application of **1** had been reported by us two years earlier<sup>7</sup>. Compound **1** was shown by us to react with aromatic and heterocyclic compounds **4** according to Scheme B to give the sulfonic acids **5** (Table 2).



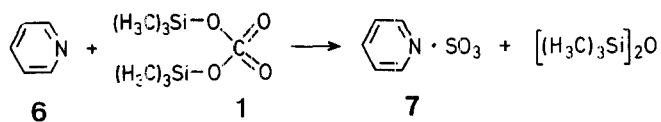
R = aryl, heteroaryl

### Scheme B

Thus, when heated with anisole, **1** affords 4-methoxybenzenesulfonic acid in 78% yield. The reaction of **1** with aniline and dimethylaniline leads to 4-aminobenzenesulfonic acid (65%)

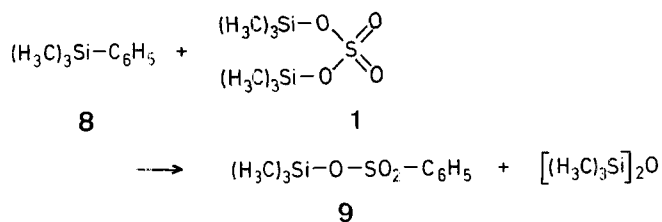
and 4-(*N,N*-dimethylamino)-benzenesulfonic acid (85%), respectively. *p*-Toluenesulfonic acid is formed from toluene and **1** in 23% yield. Benzene, bromobenzene, and nitrobenzene are not converted to the sulfonic acids by **1** even under rather drastic conditions (200–210 °C).

Heating of **1** with pyridine (**6**) gives pyridine·sulfur trioxide (**7**) in 72% yield (Scheme C). Thiophene can also be converted by excess **1** to thiophenesulfonic acid (77%, Table 2).



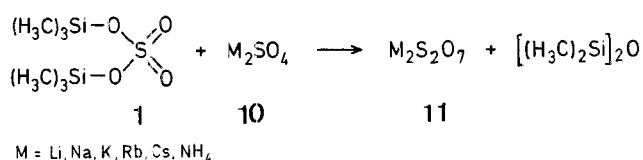
Scheme C

The reaction of **1** with phenyltrimethylsilane (**8**) leads to trimethylsilyl benzenesulfonate (**9**; 42% yield, Scheme D).



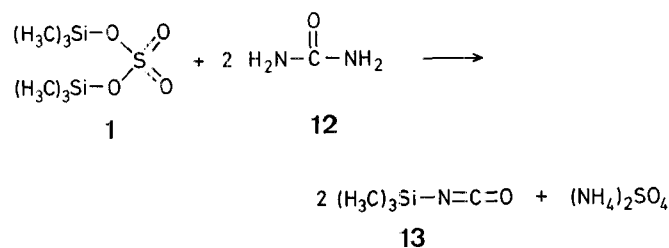
Scheme D

Bis(trimethylsilyl) sulfate (**1**) reacts as the sulfurating agent with alkali and ammonium sulfates **10** to convert the latter to pyrosulfates **11** (Scheme E).



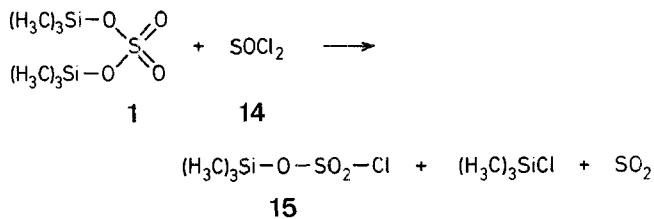
Scheme E

Although isocyanatotrimethylsilane (**13**) is formed by the reaction of **1** with potassium isocyanate<sup>17</sup>, it is more convenient to use for this purpose the reaction of **1** with the cheaper and more readily available urea<sup>18</sup> (**12**, Scheme F).



Scheme F

The reaction of **1** with thionyl chloride (**14**) leads smoothly to trimethylsilyl chlorosulfate<sup>19</sup> (**15**), which is also successfully used as an organosilicon synthon<sup>20,21</sup> (Scheme G).



Scheme G

Bis(trimethylsilyl) sulfate (**1**) was obtained in 92% yield by the reaction of trimethylchlorosilane with 100% sulfuric acid<sup>22</sup> and purified by vacuum distillation; b.p. 100–101 °C/7 torr (Lit.<sup>22</sup>, b.p. 87–90 °C/4 torr).

#### Cyanotrimethylsilane (**3**; X = —CN):

A mixture of **1** (18.65 g, 0.077 mol) and anhydrous potassium cyanide (10.0 g, 0.154 mol) is placed into a flask equipped with a Vigreux column and a condenser, and heated to 170–200 °C whereby cyanotrimethylsilane is distilled off; yield: 13.56 g (89%); b.p. 117.2 °C/738 torr; *n*<sub>D</sub><sup>20</sup>: 1.3912 (Lit.<sup>12</sup>, b.p. 117.8 °C; *n*<sub>D</sub><sup>23</sup>: 1.3891).

I.R. (neat): *ν* = 2195 cm<sup>−1</sup> (C≡N).

The reactions of **1** with other salts **2** of inorganic and organic acids are carried out in an analogous manner (Table 1).

#### 4-Methoxybenzenesulfonic Acid (**5**; R = 4-H<sub>3</sub>CO—C<sub>6</sub>H<sub>4</sub>):

In the flask described above, a mixture of **1** (8.5 g, 0.035 mol) with anisole (3.8 g, 0.035 mol) is placed and heated for 2 h at 125–170 °C whereby hexamethyldisiloxane is distilled off (yield: 4.0 g, 70%). The cooled, dark brown residue is poured into aqueous barium carbonate suspension (7.9 g, 0.04 mol) in water (10 ml). From the filtrate, the barium salt of 4-methoxybenzenesulfonic acid is isolated; yield: 7.0 g (78%).

C <sub>14</sub> H <sub>14</sub> BaO <sub>8</sub> S <sub>2</sub>	calc.	C 32.87	H 2.74
(431.7)	found	32.47	2.55

4-Aminobenzenesulfonic acid and 4-(*N,N*-dimethylamino)-benzenesulfonic acid were prepared similarly (Table 2).

#### Thiophenesulfonic Acid (**5**; R = 2-thienyl):

A mixture of **1** (10.9 g, 0.045 mol) and thiophene (1.3 g, 0.015 mol) is heated in a sealed tube for 10 h at 200–220 °C. The cooled mixture is poured into the same volume of water, and aqueous barium carbonate suspension is added in small portions (3.4 g, 0.017 mol). The mixture is heated in a water bath and filtered. The filtrate is evaporated and the residue is dried at 130 °C; yield of barium salt of **5**: 2.7 g (77%).

C <sub>8</sub> H <sub>6</sub> BaO <sub>6</sub> S <sub>4</sub>	calc.	C 20.73	H 1.30
(463.7)	found	21.33	1.59

*p*-Toluenesulfonic acid was prepared similarly (Table 2).

#### Pyridine·Sulfur Trioxide (**7**):

To dry pyridine (**6**; 3.2 g, 0.04 mol) placed in a flask fitted with a reflux condenser, compound **1** (7.9 g, 0.033 mol) is added and heated for 1 h at 100–120 °C. The residue is separated by filtration, washed with benzene, and dried at 125–150 °C; yield: 3.7 g (72%); m.p. 162 °C (Lit.<sup>25</sup>, m.p. 155 °C, Lit.<sup>26</sup>, m.p. 175 °C).

C <sub>5</sub> H <sub>5</sub> NO <sub>3</sub> S	calc.	C 37.73	H 3.14	S 20.12
(159.2)	found	37.53	3.06	19.79

Hexamethyldisiloxane was isolated from the liquid residue; yield: 1.15 g (22%).

#### Trimethylsilyl Benzenesulfonate (**9**):

A mixture of **1** (7.2 g, 0.03 mol) and phenyltrimethylsilane (**8**; 5.0 g, 0.033 mol) is heated in a flask equipped with a Vigreux column and a condenser at reduced pressure (400 torr) to 135–170 °C (bath temperature) until hexamethyldisiloxane ceases to be liberated (yield: 3.3 g 68%). Trimethylsilyl benzenesulfonate (**9**) is isolated by vacuum distillation of the residue; yield: 2.9 g (42%); b.p. 135 °C/3 torr (Lit.<sup>27</sup>, b.p. 155 °C/18 torr).

#### Potassium Pyrosulfate (**11**; M = K):

A mixture of dry, finely ground potassium sulfate (5.8 g, 0.033 mol with **1** (7.9 g, 0.033 mol) is heated for 3 h at 250 °C. During this proce

**Table 1.** Reaction of Bis[trimethylsilyl] Sulfate (**1**) and Bis[triethylsilyl] Sulfate with Inorganic Salts **2** (Scheme A)

Product <b>3</b>	Salt <b>2</b>	Yield [%] of <b>3</b>	b.p. [°C]/torr		n <sub>D</sub> <sup>20</sup>		d <sub>4</sub> <sup>20</sup>	
			found	reported	found	reported	found	reported
(H <sub>3</sub> C) <sub>3</sub> Si—F <sup>8</sup>	NaF	75	16°/728	16–17°/760	1.3320 <sup>b</sup>	—	—	—
(H <sub>3</sub> C) <sub>3</sub> Si—F <sup>8</sup>	Na <sub>2</sub> SiF <sub>6</sub>	82	16°/728	16–17°/760	1.3316 <sup>b</sup>	—	—	—
(H <sub>3</sub> C) <sub>3</sub> Si—F <sup>8</sup>	NH <sub>4</sub> BF <sub>4</sub>	100	16.5°/740	16–17°/760	1.3310 <sup>b</sup>	—	0.7152	—
(H <sub>3</sub> C) <sub>3</sub> Si—Cl <sup>9</sup>	NaCl	67	56–57°/73 <sup>8</sup>	58°/760	—	1.3885	0.846	0.8580
(H <sub>3</sub> C) <sub>3</sub> Si—Br <sup>10</sup>	KBr	45	78–79°/740	79.9°/753	1.4210	1.4211	1.182	1.188
(H <sub>3</sub> C) <sub>3</sub> Si—O—NO <sub>2</sub> <sup>11</sup>	KNO <sub>3</sub>	85	119°/740	56–58°/80	1.4060	1.4062	0.9755	—
(H <sub>3</sub> C) <sub>3</sub> Si—NCS <sup>9</sup>	KNCS	85	141°/730	141.8–142°/760	1.4810	1.4809	—	0.9308
(H <sub>3</sub> C) <sub>3</sub> Si—NCS <sup>9</sup>	NH <sub>4</sub> NCS	85	141°/725	141.8–142°/760	1.4810	1.4809	0.9291	0.9308
(H <sub>3</sub> C) <sub>3</sub> Si—CN <sup>12</sup>	KCN	89	117.2°/738	117.8°/760	1.3912	1.3891	—	—
(H <sub>3</sub> C) <sub>3</sub> Si—O—CO—CH <sub>3</sub> <sup>13</sup>	NaO—CO—CH <sub>3</sub>	70	100°/735	103–104°/760	1.3880	1.3875	0.8890	0.8914
(H <sub>3</sub> C) <sub>3</sub> Si—O—CO—CF <sub>3</sub> <sup>12</sup>	NaO—CO—CF <sub>3</sub>	80	88°/725	90.2°/760	1.3390	1.3380	1.0742	1.077
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Si—O—NO <sub>2</sub>	KNO <sub>3</sub>	50	106–107°/20	— <sup>a</sup>	1.4400	—	0.9700	—
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Si—NCS <sup>9</sup>	NH <sub>4</sub> NCS	48	74°/4	210.5°/760	1.4942	1.4948	0.9377	0.9385
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Si—O—CO—CH <sub>3</sub> <sup>14</sup>	NaO—CO—CH <sub>3</sub>	45	58°/3	173.4°/760	1.4202	1.4190	0.8912	0.8926

<sup>a</sup> C<sub>6</sub>H<sub>15</sub>NO<sub>3</sub>Si calc. C 26.67 H 6.67 N 20.74  
(177.3) found 26.88 6.69 20.90

<sup>b</sup> Refractive index measured at 16°C.

**Table 2.** Reaction of Bis[trimethylsilyl] Sulfate **1** with Organic Compounds (Scheme B, C, and D)

Product	Molar Ratio of <b>1</b> : Substrate	Reaction Conditions Temperature/Time	Yield [%]	m.p. [°C] or b.p. [°C]/torr	
				found	reported
<b>5</b> , R=4-H <sub>3</sub> CO—C <sub>6</sub> H <sub>4</sub> <sup>a</sup>	1 : 1	125–170°C/2 h	78		
<b>5</b> , R=4-H <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub>	1 : 1	160°C/4 h	65	279°	280°
<b>5</b> , R=4-(H <sub>3</sub> C) <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub>	1 : 1	170°C/4 h	79	270°	270–271°
<b>5</b> , R=4-H <sub>3</sub> C—C <sub>6</sub> H <sub>4</sub> <sup>a</sup>	1 : 1	200–220°C/10 h	23		
<b>5</b> , R=2-thienyl <sup>a</sup>	3 : 1	100°C/7 h	77		
<b>7</b>	1 : 1	115–120°C/2 h	72	162°	155° <sup>25</sup> , 175° <sup>26</sup>
<b>9</b>	1 : 1.1	135–170°C/2 h	42	135°/3	155°/18° <sup>27</sup>

<sup>a</sup> Isolated as barium salt.

dure, hexamethyldisiloxane is distilled off; yield: 4.4 g (82%); b.p. 100°C/740 torr; n<sub>D</sub><sup>20</sup>: 1.3770 (Lit.<sup>28</sup>, b.p. 100°C/760 mm; n<sub>D</sub><sup>20</sup>: 1.3774). The residue in the flask is washed with ether and dried; yield of **11**: 5.7 g (77%).

Lithium, sodium, rubidium, caesium, and ammonium pyrosulfates were prepared analogously; yields: 13%, 24%, 78%, 85%, and 67% respectively.

#### Isocyanatotrimethylsilane (**13**):

As described above, dried urea (**12**; 3.6 g, 0.06 mol) is added to **1** (7.3 g, 0.03 mol) and the mixture heated at 150°C, isocyanatotrimethylsilane (**13**) being distilled; yield: 5.5 g (80%); b.p. 90–91°C; n<sub>D</sub><sup>20</sup>: 1.3960 (Lit.<sup>23</sup>, b.p. 91°C, n<sub>D</sub><sup>20</sup>: 1.3960).

#### Trimethylsilyl Chlorosulfate (**15**):

As described above, thionyl chloride (**14**; 13.0 g, 0.11 mol) is added to **1** (17.1 g, 0.07 mol) and gradually heated at 70–120°C until volatile products stop being liberated. The sulfur dioxide liberated is captured by a potassium permanganate solution (yield: 4.1 g, 90%) and chlorotrimethylsilane is distilled; yield: 7.0 g (90%); b.p. 56–58°C; (Lit.<sup>9</sup>, b.p. 58°C). Vacuum distillation of the residue gives trimethylsilyl chlorosulfate (**15**); yield: 12.9 g (97%); b.p. 48°C/2 torr; n<sub>D</sub><sup>20</sup>: 1.4230 (Lit.<sup>24</sup>, b.p. 74°C/20 torr; n<sub>D</sub><sup>20</sup>: 1.4220).

I.R. (neat): ν = 760, 860, 1260 [Si(CH<sub>3</sub>)<sub>3</sub>]; 1060 (Si—O—S); 1180, 1370 cm<sup>-1</sup> (SO<sub>2</sub>—Cl).

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