

Journal of Organometallic Chemistry, 118 (1976) 135–138
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NEW SILYLATING AGENTS.

I. TRIMETHYLSILYL TRIMETHYLSILYLAMIDOSULPHONATE

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Received April 20th, 1976

Summary

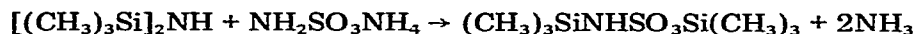
N,O-Bis(trimethylsilyl) sulphamate, $\text{Me}_3\text{SiNHSO}_3\text{SiMe}_3$, has been prepared via a new, more convenient route. It is a very efficient silyl donor; more efficient under our conditions than *N,O*-bis(trimethylsilyl) acetamide.

Introduction

There is a continuing need for new efficient silylating agents, particularly in pharmaceutical applications. Most efficient silyl donors include the linkages: $(\text{CH}_3)_3\text{SiNC}=\text{O}$ and $(\text{CH}_3)_3\text{SiNC}=\text{N}$; for example, the silyl ureas and *N*-trimethylsilylimidazole. We were interested in determining the silyl donor efficiency of the structure $(\text{CH}_3)_3\text{SiN}^{\text{H}}\text{S}^{\text{O}}=\text{O}$.

Results and discussion

Trimethylsilyl trimethylsilylamidosulphonate (I) (*N,O*-bis(trimethylsilyl) sulphamate) has previously been prepared by reaction of hexamethyldisilazane with ethylchlorosulphonate [1] and of trimethylchlorosilane with silver sulphamate [2]. We find that it may be very simply prepared by heating hexamethyldisilazane with ammonium sulphamate i.e.:



The product, a low melting point solid (m.p. 50°C), is soluble in most organic solvents.

We have used compound I to silylate a range of hydroxylic species, viz.: alcohols, phenols and carboxylic acids. In all cases high yields (>90%) of the

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TABLE 1
REACTION OF SILYL DONORS WITH 2,6-DI-S-BUTYLPHENOL

Silyl donor	Silylation ^a (%)	
(CH ₃) ₃ SiNHSi(CH ₃) ₃	3.2	
(CH ₃) ₃ SiNHSi(CH ₃) ₃ /(CH ₃) ₃ SiCl ^b	18.8	
(CH ₃) ₃ SiNHSi(CH ₃) ₃ /H ⁺ ^c	35.3	
(CH ₃) ₃ SiN(CH ₂ CH ₃) ₂	50.8	
(CH ₃) ₃ SiNCH=CHN=CH	100.0	
(CH ₃) ₃ SiNHC(O)OSi(CH ₃) ₃ ^d	7.5	
(CH ₃) ₃ SiN=C(CH ₃)OSi(CH ₃) ₃ (II)	74.5.	79.4 ^e
(CH ₃) ₃ SiNHS(O) ₂ OSi(CH ₃) ₃ (I)	100.0.	97.0 ^e

^a Determined by GLC analysis. ^b Equimolar mixture. ^c 1.6 mol% H₂SO₄. ^d Prepared as in ref. 3. ^e 20 mmol (CH₃)₃Si, 10 mmol phenolic OH in 20 ml dichloromethane, 5 min. at 21 °C.

silylated product were obtained after 30 min at 30°C (eq. 1). The sulphamic acid by-product is insoluble in most organic solvents and can be removed by filtration.

The efficiencies of well known silylating agents have been compared with I in the silylation of a sterically hindered phenol, 2,6-di-s-butylphenol. The results, in terms of percent yield of silylated phenol, are given in Table 1. Only I and *N*-trimethylsilylimidazole give 100% yield of silylated product under these conditions. I is a more efficient silyl donor than *N,O*-bis(trimethylsilyl) acetamide (II). The two (CH₃)₃Si groups in *N,O*-bis(trimethylsilyl) acetamide are of different reactivity; we compared I with II where the (CH₃)₃Si groups are in a 2 : 1 stoichiometric excess to the phenol. We are therefore comparing the silyl donor efficiency of I with the most reactive (CH₃)₃Si group in *N,O*-bis(trimethylsilyl) acetamide.

The nearest (CH₃)₃SiNĈ=O analogue to I is *N,O*-bis(trimethylsilyl) carbamate, (CH₃)₃SiNHCO₂Si(CH₃)₃, recently reported by Birkofer and Sommer [3]. Under our conditions I was the much more efficient silyl donor.

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Experimental

¹H NMR spectra were recorded using a Varian Associates T-60 NMR spectrometer. IR spectra were obtained using a Perkin-Elmer 457 IR spectrometer. GLC analyses were performed on a Hewlett-Packard 5750 chromatograph using a 1800 × 6.25 mm column packed with SE-52 silicone gum rubber on Diatoport 'S'.

Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, W. Germany and the Analytical Department, Dow Corning Ltd. Silylating agents used in this work were purchased, or synthesised by known methods; all were characterised by satisfactory elemental and spectroscopic analysis.

Trimethylsilyl trimethylsilylamidosulphonate (I) from ammonium sulphamate

To a 1 litre flask containing 250 ml of dry toluene was added ammonium sulphamate (114.12 g, 1.0 mol) and hexamethyldisilazane (170 g, 1.06 mol). The mixture was refluxed under dry nitrogen until a homogenous solution was obtained, and evolution of ammonia had ceased (27 h). Toluene and unreacted hexamethyldisilazane were removed by distillation at atmospheric pressure to leave a clear liquid residue which solidified on cooling. The crude product was recrystallised from light petroleum (60°–80°C fraction) under dry nitrogen to give 189 g (78%) of white crystals. m.p. (uncorr): 49.5–50°C, lit. [1]: 46°C. Found: C, 29.63; H, 7.74; N, 5.90; S, 13.37; Si, 22.85. $C_6H_{19}NSO_3Si_2$ calcd.: C, 29.85; H, 7.93; N, 5.80; S, 13.28; Si, 23.26%. IR (CH_2Cl_2): $\nu(N-H)$ 3365 cm^{-1} ; $\nu(S=O)$ 1350, 1175 cm^{-1} . $\nu(Si-O)$ 1050 cm^{-1} ; $\nu(Si-CH_3)$ 850 cm^{-1} . 1H NMR ($CDCl_3$, benzene int. std. τ 2.63 ppm): τ (ppm) 9.72, s, 9H, $((CH_3)_3Si)$; 9.61, s, 9H, $((CH_3)_3Si)$; 5.05, s, (br), 1H, (NH).

Silylations with I

To a 50 ml flask containing 25 ml dry dichloromethane was added 7.25 g (30 mmol) of I, and the compound to be silylated (30 mmol). Reaction usually occurred upon mixing. The flask was stoppered and maintained at 30°C for 0.5 h. Precipitated sulphamic acid was removed by filtration under dry nitrogen and the filtrate distilled to give the following yields of silylated products:

From ethanol, ethoxytrimethylsilane, 3.32 g (94%); b.p. 75–76°C, lit. [4]: 75°C; n_D^{22} 1.3745, lit. [4]: n_D^{20} 1.3745; Found: Si, 23.26; $C_5H_{14}OSi$ calcd.: Si, 23.75%.

From n-butanol, n-butoxytrimethylsilane, 4.06 g (93%); b.p. 123°C, lit. [4]: 123–124°C; n_D^{22} 1.3940, lit. [4]: n_D^{20} 1.3930; Found: Si, 18.39; $C_7H_{18}OSi$ calcd.: Si, 19.20%.

From n-pentanol, n-pentoxytrimethylsilane, 4.42 g (92%); b.p. 149°C, lit. [5]: 149°C; n_D^{20} 1.402, lit. [5]: n_D^{20} 1.400; Found: Si, 17.63; $C_8H_{20}OSi$ calcd.: 17.52%.

From 2,6-di-s-butylphenol, 2,6-di-s-butylphenoxytrimethylsilane, 7.92 g (95%); b.p. 77°C/0.6 mmHg; Found: Si, 10.63; $C_{17}H_{30}OSi$ calcd.: Si, 10.08%. Purity by GLC analysis >98%.

From benzoic acid, trimethylsilylbenzoate, 5.51 g (95%); b.p. 67–68°C/1.0 mmHg., lit. [6]: 56°C/0.7 mmHg; n_D^{25} 1.4760, lit. [6]: n_D^{20} 1.4860; Found: Si, 14.23; $C_{10}H_{24}OSi$ calcd.: Si, 14.45%.

From acetic acid, trimethylsilylacetate, 3.68 g (93%); b.p. 102–103°C, lit. [7]: 102°C; n_D^{20} 1.391, lit. [7]: n_D^{20} 1.389; Found: Si, 20.93; $C_5H_{12}OSi$ calcd.: Si, 21.24%.

Silylation of 2,6-di-s-butylphenol

Into a 10 ml vial were placed 2.06 g (10 mmol) 2,6-di-s-butylphenol, silyl donor (10 mmol monofunctional donors; 5 mmol difunctional donors) and 5 ml of dry dichloromethane. The vial was sealed and maintained at $30 \pm 0.1^\circ C$ for 0.5 h. Excess pressure generated by solvent vapour and volatile by-products was continuously vented via a syringe needle. The mixture was analysed by GLC and the relative concentrations of silylated and unsilylated 2,6-di-s-butyl phenol were determined.

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