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SYNTHESES AND REACTIONS OF SILYLATED DIAMINOSULFANES

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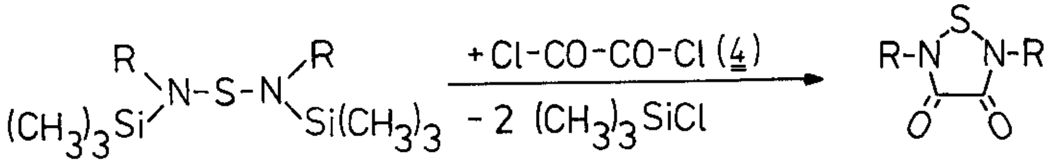
Abstract: The synthesis of unsymmetrically substituted silylated diaminosulfanes **3a** - **3e** with different alkylgroups at both nitrogen atoms are described; the reactions of **3a**, **3b** with oxalyl chloride yields the unsymmetrically substituted 2,5-dialkyl-1,2,5-thiadiazolidine-3,4-diones **5a**, **5b** in moderate yields; **5a**, **5b** were oxidized to the S-oxides **6a**, **6b** by H_2O_2. The reactions of **3c**, **3d** with oxalyl chloride lead to a mixture of reaction - products - S_8, oxalic acid-amides **7**, **8** and a corresponding ester **9b**.

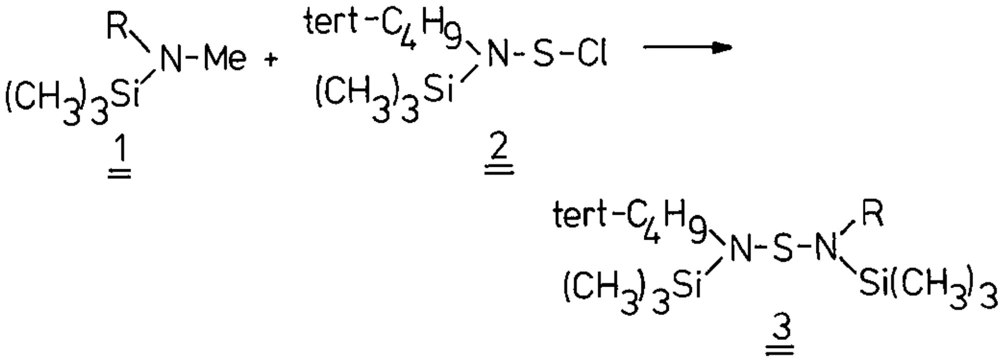
In connection with our investigations on sulfur-nitrogen-containing heterocycles 1-10) we recently reported the syntheses of some symmetrically substituted silylated diaminosulfanes and their reactions with oxalyl chloride which yielded the corresponding symmetrically substituted 2,5-dialkyl-1,2,5-thiadiazolidine-3,4-diones10).

The intentions were afterwards in finding methods in synthesizing unsymmetrically substituted 2,5-dialkyl-1,2,5-thiadiazolidine-3,4-diones as till now unknown heterocyclic systems.

The reactions of metallated N-(trimethylsilyl-)-alkylamines **1** with [tert.-butyl-(trimethylsilyl)amino]-sulfenyl chloride **2** provided a new route to unsymmetrically substituted silylated diaminosulfanes **3a** - **3e** with different alkyl groups at both nitrogen atoms. The experiments were done at - 78 °C in ether as solvent; the reaction products **3a** - **3e** were purified by distillation or recrystallization.

The reactions of the compounds **3a** - **3e** with oxalyl chloride **4** did not yield in all cases the expected 2,5-dialkyl-1,2,5-thiadiazolidine-3,4-diones **5**. We observed





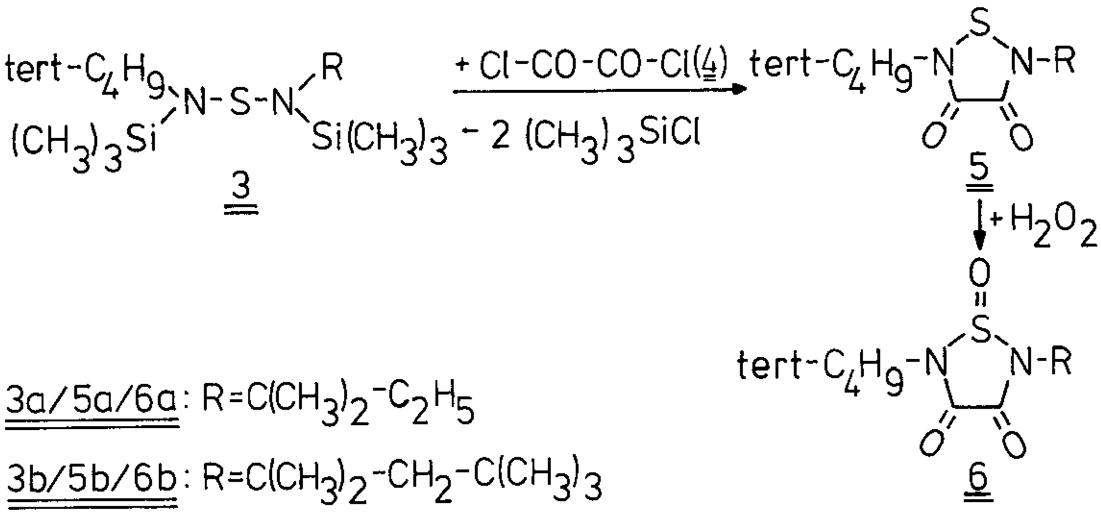
1a/3a: R=$C(CH_3)_2$-C_2H_5; Me = Li

1b/3b: R=$C(CH_3)_2$-CH_2-$C(CH_3)_3$; Me=Li

1c/3c: R=i-C_3H_7; Me = Li

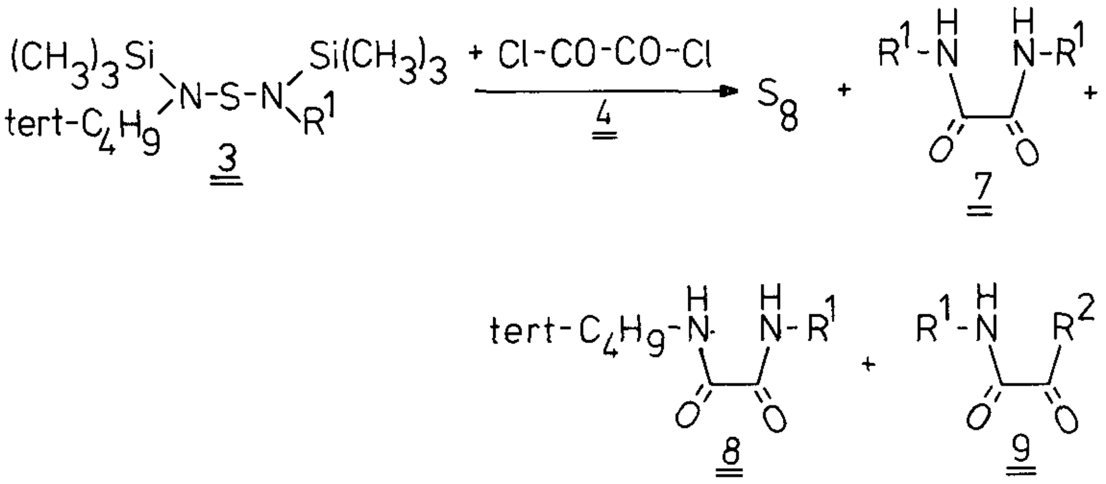
1d/3d: R=c-C_6H_{11}; Me = Li

1e/3e: R=$Si(CH_3)_3$; Me = Na



3a/5a/6a: R=$C(CH_3)_2$-C_2H_5

3b/5b/6b: R=$C(CH_3)_2$-CH_2-$C(CH_3)_3$

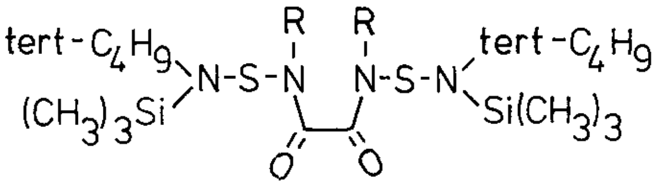


3c/7a/8: $R^1 = i\text{-}C_3H_7$

3d/7b : $R^1 = c\text{-}C_6H_{11}$

9a: $R^1 = i\text{-}C_3H_7$; $R^2 = Cl$

9b: $R^1 = i\text{-}C_3H_7$; $R^2 = OCH_3$



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that treatment of the products 3c, 3d with oxalyl chloride 4 at room temperature afforded a mixture of elemental sulfur, symmetrically and unsymmetrically substituted oxalic acid diamides 7, 8 and the oxalic acid chloride 9a, which could be isolated as the corresponding methyl ester 9b.

The reactions of the diaminosulfanes 3a, 3b with oxalyl chloride 4 yielded the 2,5-dialkyl-1,2,5-thiadiazolidine-3,4-diones 5a, 5b in moderate yields. All reactions occurred by formation of elemental sulfur and sulfur-nitrogen-polymers, which were easily removed by column chromatography. Concerning the formation of those by-products we suggest that the attack of oxalyl chloride 4 took place at the less hindered nitrogen-atom of the diaminosulfanes 3 forming an intermediate stage like compound 10 which is probably hydrolized during the purification yielding products like sulfur and the oxalic acid derivatives 7 - 9.

The oxidations of compounds 5a, 5b with H_2O_2 at + 50 °C yielded the corresponding S-oxides 6a, 6b. The reaction products 6a, 6b were separated from the starting materials 5a, 5b and the structure was confirmed by physical and spectral data particularly by ir spectra.

Table 1: yields, physical and spectral Data of compounds 3, 5, 6[a,b)]

compounds	yield (%)	mp (°C) or bp (°C/torr)	ir (cm^{-1}), KBr or liquid films
3a	44.5	$100\text{-}105/5\times10^{-4}$	2970, 2902, 2885 (CH)
3b	37	68 - 71	2960, 2940, 2907, 2842, 2828 (CH)
3c	40	$65/10^{-3}$	2972, 2930, 2900, 2878 (CH)
3d	45	$90/10^{-3}$	2973, 2930, 2905, 2855 (CH)
3e	41	61 - 62	3008, 2996, 2972, 2900 (CH)
5a	14	158-160	1690, 1659 (C=O)
5b	29	85,5	1686, 1660 (C=O)
6a	56	83	1743, 1697 (C=O), 1150 (S=O)
6b	71.5	oil	1742 (C=O), 1160 (S=O)

	^{1}H-nmr (60 or 90 MHz, $CDCl_3$)	ms, m/e (% rel. int.)
3a	0.30, 0.31 (2s, 2x$SiMe_3$), 0.85 (t, $CH_2\underline{CH_3}$), 1.29 (s, $C(CH_3)_2$), 1.36 (s, $C(CH_3)_3$), 1.78 (q, $\underline{CH_2}CH_3$).	334 (M^+, 9), 263 (8), 207 (100), 191 (10), 135 (6), 130 (15), 119 (20), 73 (74), 57 (42).
3b	0.32 (s, 2x$SiMe_3$), 1.03 (s, $-CH_2\text{-}C\underline{(CH_3)_3}$), 1.36 (s, $C(CH_3)_3$), 1.46 (s, $C(CH_3)_2$-), 1.85 (s, $-CH_2$-).	376 (M^+, 3), 264 (12), 207 (100), 119 (10), 73 (40), 57 (76).

Table 1 continued

$\underline{\underline{3c}}$	0.21, 0.28 (2s, 2x$\mathrm{SiMe_3}$), 1.22 (d, $\mathrm{CH(\underline{CH_3})_2}$), 1.33 (s, $\mathrm{C(CH_3)_3}$), 3.42 (sept., $\mathrm{C\underline{H}(CH_3)_2}$).	306 (M^+, 22), 249 (100), 207 (60), 119 (8), 73 (84), 57 (28).
$\underline{\underline{3d}}$	0.20, 0.28 (2s, 2x$\mathrm{SiMe_3}$), 1.58 (s, $\mathrm{C(CH_3)_3}$), 1.13-2.38, 2.64-3.06 (2m, c-$\mathrm{C_6H_{11}}$).	346 (M^+, 23), 289 (99), 217 (12), 207 (85), 170 (20), 135 (19), 119 (14), 98 (12), 73 (100), 59 (16).
$\underline{\underline{3e}}$	0.48 (s, 2x$\mathrm{SiMe_3}$), 0.58 (s, $\mathrm{SiMe_3}$), 2.64 (s, $\mathrm{C(CH_3)_3}$).	336 (M^+, 18), 279 (100), 265 (12), 191 (99), 146 (31), 119 (99), 73 (99), 57 (61).
$\underline{\underline{5a}}$	0.90 (t, $\mathrm{CH_2\underline{CH_3}}$), 1.57 (s, $\mathrm{C(CH_3)_3}$), 2.10 (q, $\mathrm{\underline{CH_2}CH_3}$).	244 (M^+, 4), 188 (2), 119 (10), 71 (43), 57 (100).
$\underline{\underline{5b}}$	0.96, 1.66 (2s, 2 $\mathrm{C(CH_3)_3}$), 1.63 (s, $\mathrm{C(CH_3)_2}$-), 2.15 (s, -$\mathrm{CH_2}$-).	286 (M^+, 10), 174 (78), 119 (83), 118 (82), 112 (12), 97 (51), 57 (100).
$\underline{\underline{6a}}$	0.87 (t, $\mathrm{CH_2\underline{CH_3}}$), 1.61 (s, $\mathrm{C(CH_3)_2}$), 1.65 (s, $\mathrm{C(CH_3)_3}$), 2.20 (q, $\mathrm{\underline{CH_2}CH_3}$).	260 (M^+, 2), 231 (21), 191 (3), 175 (20), 135 (42), 84 (16), 71 (100), 57 (94).
$\underline{\underline{6b}}$	0.98, 1.65 (2s, 2 $\mathrm{C(CH_3)_3}$), 1.73 (s, $\mathrm{C(CH_3)_2}$), 2.26 (s, -$\mathrm{CH_2}$-).	302 (M^+, 1), 231 (6), 191 (2), 175 (21), 112 (42), 97 (38), 84 (32), 57 (100).

a) Satisfactory microanalyses were obtained for all compounds.

b) For exact mass spectroscopic measurement of compounds $\underline{\underline{3}}$: see ref. 9)

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Experimental part:

mp: "Reichert"-micromelting apparatus, uncorrected.- ^{1}H-nmr: HX 90E of Bruker-Physik, Karlsruhe-Forchheim; T 60 A - Varian.- ms: MAT 311 A.- ir: Perkin-Elmer 325.- Microanalyses: C, H, N - analysator of Heraeus, Hanau.- All experiments were carried out under nitrogen.-

For each of the new classes of compounds 3, 5, 6 the typical details of the synthesis are given:

Bis-[Alkyl-(trimethylsilyl)amino]-sulfane 3: A solution of 0.05 M of an alkyl-(trimethylsilyl)amine[12-14] in 100 ml of ether as solvent was treated at room temperature with an equimolar amount of n-butyllithium in n-hexane. After cooling to - 78 °C a solution of (tert.-butyl-(trimethylsilyl)amino)-sulfenyl chloride 2 (0.055 M)[11] in 250 ml of ether was added; the mixture was slowly warmed up overnight, filtered and the solvent removed under reduced pressure. The residue was finally worked up by repeated distillation or recrystallization.

2,5-Dialkyl-1,2,5-thiadiazolidine-3,4-dione 5: A solution of 0.32 g (2,5 mM) oxalyl chloride 4 in 20 ml of dichloromethane was added to a solution of 2,5 mM of the corresponding diaminosulfane 3 in 20 ml of dichloromethane. After stirring overnight the solvent was removed and the residue purified by column chromatography (silica gel "Macharay and Nagel"; column: 4 x 60 cm; eluent: ethyl acetate/chloroform = 1/1); colourless crystals were obtained from n-hexane or cyclohexane.

2,5-Dialkyl-1,2,5-thiadiazolidine-3,4-dione-1-oxide 6: A solution of 0.35 mM 5 in 5 ml of ethanol was treated at 50 °C with 0.25 ml of an aqueous solution of H_2O_2 (30 %) and the addition of H_2O_2 was repeated after 7 h and 24 h. After complete oxidation (tlc control: silica gel, chloroform) the solution was boiled, water added and extracted five times with 10 ml of dichloromethane/chloroform (1/1). The combined extracts were dried with Na_2SO_4 and the solvent removed. The residue was recrystallized from n-pentane at - 20 °C.

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† Dedicated to Professor Tetsuji Kametani on the occassion of his retirement.

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