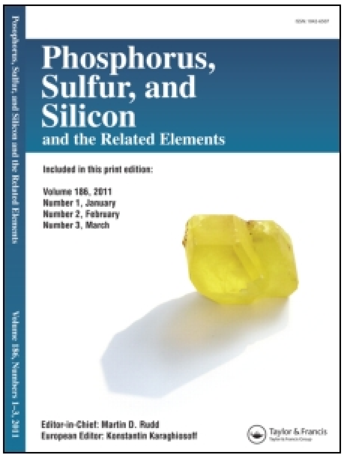

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Communication

DISILOXANO DITHIOCARBANILIDES AS NEW SILYL DONORS

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Thiocarbanilide and its derivatives were reacted with 1,3-dichloro-1,1,3,3-tetramethyl-disiloxane to afford the respective *N,N*-bis(thiocarbanilide) disiloxanes which are used as potent silyl donors when reacted with different phenols. The exchange of the tetramethyldisiloxyl group between tetramethyldisiloxanodithiocarbanilide and phenol, is achieved when the thiocarbanilide is precipitated in the reaction medium in few minutes. The newly prepared disiloxanodiaryl thiocarbanilides were examined by analytical and spectroscopic measurements.

Key words: Diarylthiocarbanilides; *N,N*-bis-(diarylthiocarbanilidetetramethyldisiloxanes); phenols.

INTRODUCTION

The silylation of ureas and thioureas has been the subject of a series of publications.[1–4] There is no difficulty in introducing a trimethylsilyl group into each amino group of amides and thioamides.[5] Aminosilanes react with phenylisocyanate or phenylisothiocyanate to form the corresponding silylurea or silylthiourea respectively.[6] The use of *N*-silyl substituted aromatic ureas and amides as powerful silyl donors has been reported by Klebe,[4] their effect depends on the insolubility of aromatic ureas in most organic solvents. The silylamine-amine exchange reaction was introduced by Larsson and Smith[1,7,8] to prepare *N*-silylsubstituted amines, amides and ureas. Other compounds having acidic protons are considered as acceptors for the silyl group.[9]

My intention is to prepare some tetramethyldisiloxyl donors. Thus derivatives of disiloxanothiocarbanilides have been prepared and reacted with different phenols as silyl acceptors. The synthesized compounds were identified by elemental analysis, IR and ^{1}H-NMR spectroscopy (Tables I and II).

RESULTS AND DISCUSSION

The diaryl thiocarbanilidedisiloxanes were synthesized from the reaction between the thioamidic hydrogen of the diarylthiocarbanilide and the highly reactive chlorine of the 1,3-dichloro-1,1,3,3-tetramethyl-disiloxane. These products were used for introducing the 1,1,3,3-tetramethyldisiloxane-1,3-diyl group into different phenols. Thus the IR spectra show very strong bands at 1010–1050 cm^{-1} (Si—O—Si) and 3140–3200 cm^{-1} (N—H), which means that no cyclic structures which may be

TABLE I

Analytical data of compounds Ia–e

Compound	M.p.°C	Yield %	Mol. formula (M.Wt.)	Analysis Found/calcd %					I.R. -cm^{-1})			
				C	H	N	S	Si	Si-O-Si	Si-N	C=S	N-H
Ia	173-174	70	$C_{30}H_{34}N_4OS_2Si_2$ (586)	60.95 61.43	6.00 5.80	9.70 9.55	10.88 10.92	9.43 9.55	1020(v.s)	930(s)	1220(s)	3190(v.s)
Ib	188-189	65	$C_{34}H_{42}N_4OS_2Si_2$ (642)	63.25 63.55	6.37 6.54	8.51 8.72	9.94 9.96	8.63 8.72	1030(v.s)	950(s)	1220(s)	3140(v.s)
Ic	198-199	72	$C_{34}H_{42}N_4O_5S_2Si_2$ (706)	57.63 57.79	5.72 5.95	7.70 7.93	9.01 9.06	7.85 7.93	1030(v.s)	920(s)	1230(v.s)	3200(v.s)
Id	188-189	67	$C_{30}H_{30}N_4OS_2Si_2Cl_4$ (722)	49.75 49.86	3.97 4.15	7.71 7.75	8.90 8.86	7.70 7.75	1010(s)	920(s)	1230(s)	3200(v.s)
Ie	275-276	70	$C_{30}H_{30}N_4OS_2Si_2Br_4$ (902)	40.22 39.99	3.22 3.32	6.17 6.20	6.93 7.09	5.98 6.20	1050(v.s)	950	1230(s)	3200(v.s)

All products are white crystals from benzene / light petroleum.

(v.s) = Very strong, (s) = strong, (w) = weak.

TABLE II

^{1}H-NMR spectral data of compounds* Ia–e

Compound	Chemical shift, δ_{TMS} = O [ppm]
Ia	-00.88 (s, 6H, Si-CH_3 A), -0.95 (s, 6H, Si-CH_3B), 7.0 - 7.45(m, 20 H, aromatic), 9.55 (s, 2H, NH).
Ib	-0.9 (s, 6H, Si-CH_3A), -0.95 (s, 6H, Si-CH_3 B), 2.15 (s, 12 H, CH_3), 6.9 - 7.25 (m, 16H, aromatic), 9.4 (s, 2H, NH).
Ic	-0.88 (s, 6H, Si-CH_3 A), -0.95 (s, 6H, Si-CH_3 B), 3.55 (s, 12 H, OCH_3), 6.5 - 7.2 (m, 16 H, aromatic).
Id	-0.85 (s, 6H, Si-CH_3 A), -0.9 (s, 6H, Si-CH_3 B), 6.9 - 7.3 (m, 16 H, aromatic), 9.55 (s, 2H, NH).
Ie	-0.85 (s, 6 H, Si-CH_3 A), -0.9 (s, 6H, Si-CH_3 B), 7.1 - 7.3 (m, 16H, aromatic), 9.55 (s, 2H, NH).

*Measured in DMSO

produced upon using equal moles of dichlorotetramethyldisiloxane and diarylthiocarbanilide and the elimination of two moles of HCl. This result is also supported by the ^{1}H-NMR data which show a signal at ≃9.0 ppm referring to the NH proton in the open chain disiloxane structure.

The ^{1}H-NMR spectra of all products revealed two different chemical shift values for the two methyl groups indicated by A and B in Equation 1. The configurational assignment is in accordance with the configuration which would be reached upon comparing the observed chemical shift values with the incremented values. Figure

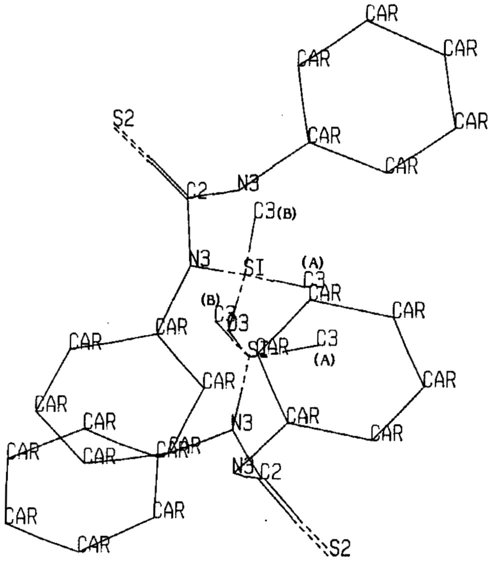
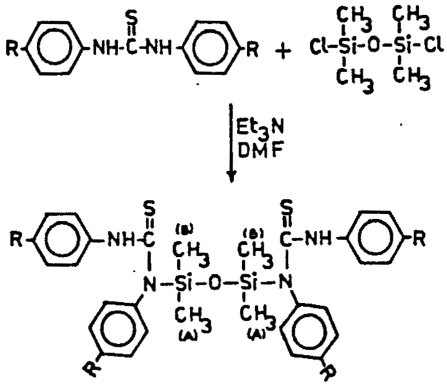


FIGURE 1 Optimum geometry of 1*a* by molecular forcefield.

1 shows the optimum molecular geometry of 1*a* which was analyzed by molecular force field "method MM2".[11] The Figure shows that the two methyl groups (A) and (B) in the disiloxane product are not identical in geometry, so groups (A) are partially embedded towards the aromatic ring. That causes the two different chemical shift values of the two types.

EXPERIMENTAL

The reaction equation of the preparation is as follows:



(1)

a, R = H; b, R = —CH$_3$; c, R = —OCH$_3$; d, R = —Cl; e, R = —Br

All melting points are uncorrected. Infrared spectra were recorded on specord 75 spectrophotometer using KBr discs. The ^{1}H-NMR spectra were recorded on a Perkin-Elmer R 12-60 MHz instrument using TMS as an internal reference. Analysis and spectral data were carried out in Analytical Chemistry Department, Technical University of Budapest, Hungary.

TABLE III

New silyl donors and products prepared via silylamine-hydroxy exchange: Ia–e = *N*,*N*-bis[diphenyl, di-*p*-tolyl, di-*p*-anisyl, di-*p*-chlorophenyl and di-*p*-bromophenyl]-tetramethyldisiloxane, respectively

Phenol	Silyl donor	product
Phenol	I - b	1,3-diphenoxy-1,1,3,3-tetramethyldisiloxane
o-Cresol	I - b	1,3-di-o-cresoxy-1,1,3,3-tetramethyldisiloxane
p-Cresol	I - b	1,3-di-p-cresoxy-1,1,3,3-tetramethyldisiloxane
p-Bromophenol	I - b	1,3-bis(p-bromophenoxy)-1,1,3,3-tetramethyldisiloxane

i) N,N-Tetramethyldisiloxano-bis(thiocarbanilide) (Ia–e)

To a solution of the corresponding thiocarbanilide (10 m mole) and triethylamine (30 m mole) in dry DMF (20 ml) 1,3-dichloro-1,1,3,3-tetramethyl-disiloxane (5 m mole), was added and the temperature was kept below 8°C. The whole reaction mixture was stirred at room temperature for five hours, allowed to stand overnight, the produced triethylaminehydrochloride was filtered off. The reaction solution was diluted with cold water and the resulting crystalline precipitate was filtered off, washed with cold water, dried and recrystallized from the proper solvent to give the title compounds Ia–e (Table III).

ii) Silylation Donor Properties

To a solution of previously prepared disiloxane (Ia–e) (1 m mole) in CS_2 *was added phenol, o*-cresol, *p*-cresol or *p*-bromophenol (2 m mole). The clear solution was shaken well for a few minutes, the precipitated thiocarbanilide derivative was filtered off and identified by m.p. and mixed m.p. of an authentic specimen. Evaporation of the filtrate afforded the corresponding 1,3-bis-phenoxy-1,1,3,3-tetramethyldisiloxane[10] (Table III). Compound Ib was used for example as silyl donor.

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