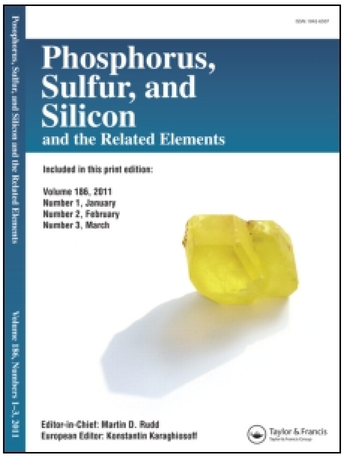

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SYNTHESIS AND REACTIONS OF SOME NEW ORGANOMETALLIC COMPOUNDS: SYNTHESIS OF TRIPHENYLSILYLSULFINYLAMINE

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Triphenylsilylsulfinylamine (**1**) was prepared via the reaction of triphenylsilylamine and thionylchloride. The reaction of (**1**) with copper and sodium metals gave the corresponding azo, and thioazo-derivatives (**2**, **3**). Also cycloaddition products (**4a–c**) were prepared through the reaction of (**1**) with some alkenes under Diels-Alder reaction conditions. The nitrilimine (**5**) was reacted with (**1**) to give 1,2,3,5-thia-triazole-1-oxide (**6**).

Key words: triphenylsilylsulfinylamine, triphenylsilylamine, thionylchloride, N-sulfinyl, sulfodimide, sufinyl amine.

Recently,[1] the N-sulfinyl (R—N═SO), sulfodimide (R—N═S═N—R) and sulfinylamine compounds has been discussed from their physical properties, their molecular structure and their reactivity towards cycloaddition reactions. This led us to prepare the triphenylsilylsulfinylamine (**1**) by heating of triphenylsilylamine with thionyl chloride in dry benezene.

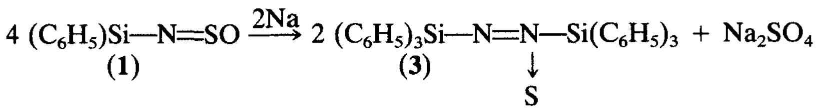
$$(C_6H_5)_3SiNH_2 + SOCl_2 \rightarrow \underset{(\mathbf{1})}{(C_6H_5)_3SiNSO}$$

The structure of (**1**) was supported from its correct analytical data, IR spectra showed absorption bands at 1300 cm^{-1} attributable to ν_{NSO}, and mass spectra which gave the correct molecular weight (321). The structure of (**1**) was, also confirmed from its reaction with finely divided copper in refluxing dry xylene[2] to give the azo-bisilyltriphenyl (**2**).

$$\underset{(\mathbf{1})}{2\,Ph_3SiN{=}SO} \xrightarrow{Cu} \underset{(\mathbf{2})}{Ph_3{-}Si{-}N{=}N{-}Si{-}Ph_3}$$

The structure of the azo-compound (**2**) was confirmed from the correct analytical and IR spectra which showed absorption band at 1630 cm^{-1} attributable to $\nu_{N=N}$, and the disappearance of ν_{NSO} group, mass spectra gave m/e at 456.

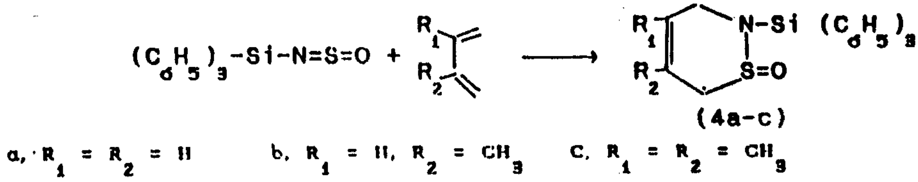
Also the triphenylsilysulfinylamine was heated with sodium powder in dry toluene[3] to give azo-thio-bisilyltriphenyl (**3**). The structure of (**3**) was established from its correct analytical and spectral data.



$$\underset{(\mathbf{1})}{4\,(C_6H_5)Si{-}N{=}SO} \xrightarrow{2Na} \underset{(\mathbf{3})}{2\,(C_6H_5)_3Si{-}N{=}\underset{\substack{\downarrow\\ S}}{N}{-}Si(C_6H_5)_3} + Na_2SO_4$$

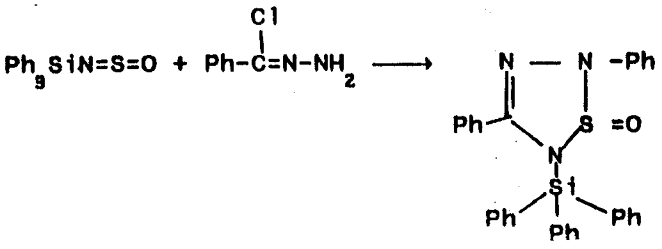
Reviews[4,5] dealing with the reactivity of N-sulfinylamines as dienophile in cycloaddition reactions showing that the addition takes place with all aromatic N-sulfinylamines, but sometimes the reaction is very slow, so an excess of the diene is generally beneficial. On the other hand, the steric hindrance due to substituents in position 1 and 4 of the diene component generally affects the rate of the cycloaddition reaction.[6] Thus butadiene, 2-substituted and 2,3-substituted butadiene were reacted under Diels-Alder reaction conditions.

So when the triphenylsilylfinylamine (**1**) was heated with butadiene, 2-methylbutadiene and 2,3-dimethylbutadiene gave the corresponding cycloaddition products (**4a–c**).



The structure of compounds (**4a–c**) was confirmed from analytical and spectral data, thus Ir spectra showed absorption band at 1060 cm^{-1} attributable to $\nu_{S=O}$, also NMR spectrum of (**4c**) showed signals at δ 2.8 (*s*, 4H, $2CH_2$), 3.4 (*s*, 6H, $2CH_3$) and at δ 6.5–7.6 (*m*, 15H, aromatic protons). The mass spectra of compounds (**4a**) showed m/e = 375.

The nitrilimine (**5**)[7] (prepared in situ from benzoylchloridephenyldrazone and triethylamine) was reacted with (**1**) to give 2-triphenylsilyl-3,5-diphenyl-2,5-dihydro-1,2,3,5-thiatriazole-1-oxide (**6**) in 75% yield. The structure of (**6**) was confirmed from its correct analytical data, Ir spectra which showed bands at 1290 and 1640 cm^{-1} attributed to $\nu_{C=N}$ and $\nu_{S=O}$ respectively. Also, NMR spectra showed signals at δ 7.4–8.3 (*m*, 25H, aromatic protons).



Characterization and physical data are listed in Table I.

TABLE I

Comp.	M.P. (°C)	Solvent yield, %	Formula	Analysis % Found/Req.			
				C	H	N	S
1	85–6	Benzene	$C_{18}H_{15}NSSiO$	67.06	4.53	4.79	9.78
		87		67.28	4.67	4.36	9.96
2	220–2	Benzene	$C_{36}H_{30}N_2Si_2$	78.69	5.38	5.01	
		54		79.12	5.49	5.12	
3	268–9	Toluene	$C_{36}H_{30}N_2SSi$	77.49	4.87	4.68	5.41
		32		77.74	5.19	4.84	5.53
4a	785–6	Benzene	$C_{22}H_{21}NSSiO$	70.21	5.35	3.52	8.39
		47		70.40	5.60	3.73	8.53
4b	771–3	Benzene	$C_{23}H_{23}NSSiO$	69.28	5.69	3.26	7.94
		59		70.95	5.91	3.59	8.22
4c	798–9	Benzene	$C_{24}H_{25}NSSiO$	70.49	5.63	3.19	7.75
		66		71.46	6.20	3.47	7.94
6	135–6	Ethanol	$C_{31}H_{25}N_3SSiO$	72.23	4.85	8.15	6.21
		75		72.03	4.73	8.07	5.98

EXPERIMENTAL

Melting points are not corrected. Infrared spectra (KBr) were measured on a Perkin Elmer Infrared 137 spectrophotometer-^{1}H-NMR spectra were recorded at 60 MHz on a Varian EM-360-L spectrometer. Mass spectra were recorded with a VG 7070-E spectrometer at an ionizing voltage 70 CV.

Formation of Triphenylsilysulfinylamine (**1**): A mixture of triphenylsilylamine (0.01 mol) and thionyl chloride (0.01 mol) in dry benzene (10 ml) was heated under reflux for 10 hrs. Benzene was evaporated and the solid produced was crystallized from benzene, m.p. 85–6°C in yield 87%.

Formation of Azo-bisilyltriphenyl (**2**): A mixture of (**1**) (0.01 mole) and finely divided copper (0.01 mol) in dry toluene (5 ml) was refluxed for 15 hrs, then filtered off. The filtrate was left to cool. The solid produced was filtered and recrystallized from benzene, m.p. 220°C in yield 54%.

Formation of Azo-thio-bisilyltriphenyl (**3**): In dry toluene (10 ml) a mixture of (**1**) (0.01 mole) and finely divided sodium metal (0.01 mole) (prepared by heating Na metal in xylene) was heated under reflux for 10 hrs, the reaction mixture was filtered, then the filtrate was left to cool. The solid produced was collected and recrystallized from toluene into pale yellow precipitate, m.p. 268°C in yield 32%.

Reaction of (**1**) *with Dienes; Formation of* (**4a–c**): Heat under reflux a mixture of (**1**) (0.01 mol) and the dienes (10 ml) namely, butadiene, 2-methylbutadiene and 2,3-dimethylbutadiene for 6 hrs. The reaction mixture was evaporated by using rotatory evaporator. The solids obtained were filtered off, dried and recrystallized from benzene.

Formation of 2-triphenylsilyl-3,5-diphenyl-2,5-dihydro-1,2,3,5-thiatriazole-1-oxide (**6**): Triethylamine (1.5 ml) was added to a solution of 0.92 g of benzoylchloride phenylhydrazone and 1.85 g of triphenylsilylsulfinylamine (**1**) in 10 ml of benzene. The reaction mixture was heated for one hour, then kept at room temperature 5 hrs. The reaction mixture was filtered and the filtrate evaporated to dryness under vacuum. The crystalline residue was recrystallized from ethanol, yield 75%.

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