[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Silylamines: The Reactions of Silyllithium Compounds with Aliphatic Amines

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Silyllithium compounds react with primary and secondary aliphatic amines to form silylamines in good yields. *n*-Butyl-1,1,1-triphenylsilylamine, obtained from the reaction of triphenylsilyllithium with *n*-butylamine, was cleaved by methanol or ethanol to give the corresponding alkoxysilanes. A case of apparent dimorphism for methoxytriphenylsilane is discussed. Silylamines derived from di-*n*-butylamine, morpholine, piperidine and piperazine were resistant to cleavage by alcohols.

The reactions of chlorosilanes with amines, the classical method for the formation of silylamines,[1] were unsuccessful for the preparation of triarylsilylamines.[2] As an alternative, a series of triarylsilylamines were prepared[2] from the reactions of triphenylsilane with lithium dialkylamides.

$$R_3SiH + R_2'NLi \longrightarrow R_3SiNR_2' + LiH \qquad (1)$$

We have found that a variety of silylamines can be synthesized from the reactions of silyllithium compounds with primary and secondary aliphatic amines. Thus triphenylsilyllithium, methyldiphenylsilyllithium and dimethylphenylsilyllithium[3] react with di-*n*-butylamine to give N,N-di-*n*-butyl-1,1,1-triphenylsilylamine, N,N-di-*n*-butyl-1-methyl-1,1-diphenylsilylamine and N,N-di-*n*-butyl-1,1-dimethyl-1-phenylsilylamine, respectively.[4] In like manner, triphenylsilyllithium reacts with morpholine, piperidine and piperazine to give 1-(triphenylsilyl)-morpholine, 1-(triphenylsilyl)-piperidine, and 1,4-bis-(triphenylsilyl)-piperazine, respectively, in high yields.

$$R_3SiLi + R_2'NH \longrightarrow R_3SiNR_2' + LiH \qquad (2)$$

From the reaction of triphenylsilyllithium with *n*-butylamine, N-*n*-butyl-1,1,1-triphenylsilylamine was isolated by distillation. This waxy solid was cleaved rapidly by methanol or ethanol to give the corresponding alkoxysilanes.[5] Methoxytriphenylsilane obtained in this manner melted at 42–43° (reported 55°).[6,7] Methoxytriphenylsilane obtained from the reaction of chlorotriphenylsilane with sodium methoxide also melted at 42–43°. The lower melting form (42–43°) was readily converted to the higher melting form[8] (55°) by a simple seeding technique. Attempts to reverse this procedure failed. Apparently the higher melting isomer is the stable form. When admixed, the two forms gave no melting point depression. The infrared spectra were practically superimposable.

$$Ph_3SiNH(n\text{-}C_4H_9) + CH_3OH \longrightarrow Ph_3SiOCH_3 + n\text{-}C_4H_9NH_2$$

The silylamines derived from secondary amines were highly resistant to alcoholysis.

It is probable that the over-all reaction (equation 2) for the formation of silylamines takes place in two fast steps, an initial metalation of the amine (equation 3) followed by coupling (equation 1).

$$R_3SiLi + R_2'NH \longrightarrow R_3SiH + R_2'NLi \qquad (3)$$

In support of this view, it was found that triphenylsilyllithium metalated diphenylamine, but no silylamine was isolated. Similarly, N-diphenylmethylaniline was metalated by triphenylsilyllithium[9] to give, after hydrolysis, triphenylsilane (70%), N-diphenylmethylaniline (66%) and none of the silylamine. Apparently, the presence of a phenyl group on the nitrogen atom reduces the nucleophilicity of the lithium amide to a degree where it is not capable of displacing a hydride ion from triphenylsilane. It has been reported[2] that lithium diphenylamide does not react with triphenylsilane.

While silicon–oxygen[1] and silicon–sulfur[10,11] bonds are cleaved by organolithium compounds, the silicon–nitrogen bond was found to be remarkably stable. Treatment of N,N-di-*n*-butyl-1,1,1-triphenylsilylamine with phenyllithium resulted in 60% recovery of the rather soluble amine. No tetraphenylsilane, easily detected by its insolubility, was formed.

Physical constants and related data for the silylamines prepared are presented in Table I.

Experimental[12]

Materials.—Triphenylsilyllithium, methyldiphenylsilyllithium and dimethylphenylsilyllithium were prepared according to published directions.[3] Di-*n*-butylamine, *n*-butylamine, morpholine and piperidine were commercial products. Piperazine, generously supplied by Dr. Myrl Lichtenwalter of Jefferson Chemical Co., was recrystallized from anhydrous benzene and dried at 0.01 mm. before use.

1-(Triphenylsilyl)-morpholine.—To a solution of 3.4 g. (0.0386 mole) of morpholine in 50 ml. of tetrahydrofuran (THF) was added 100 ml. of a THF solution of triphenylsilyllithium prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and excess lithium. Color Test I[13] was negative after the addition was complete. The THF was distilled, and ethanol was added cautiously. When the evolution of hydrogen subsided, 100 ml. of ethanol was added. 1-(Triphenylsilyl)-morpholine weighing 11.1 g. (83%) was removed by filtration. The melting point, 179–181°, was

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[1] See E. G. Rochow, "Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951.

[2] H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

[3] For the preparations of these compounds see H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 608 (1958).

[4] The nomenclature used through this paper is in accordance with the conventions of "Chemical Abstracts."

[5] Similar cleavages of hexamethyldisilazane by alcohols were reported recently by S. H. Langer, S. Connell and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

[6] A. G. Brook and H. Gilman, THIS JOURNAL, **77**, 2322 (1955).

[7] R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952).

[8] The higher melting form was kindly furnished by Dr. A. G. Brook, who was successful in converting the lower melting to the higher melting form, but was unable to reverse the procedure.

[9] D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles and H. Gilman, THIS JOURNAL, **80**, 4532 (1958).

[10] H. Gilman and D. Wittenberg, *ibid.*, **79**, 6339 (1957).

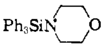
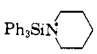
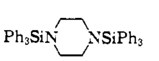
[11] G. D. Lichtenwalter, unpublished studies.

[12] Organometallic reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using dry glassware. Temperatures are uncorrected.

[13] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

TABLE I

PHYSICAL CONSTANTS AND RELATED DATA FOR SILYLAMINES

Compound	Yield, %	M.p., °C.	B.p. °C.	Mm.	$n^{20}D$	d^{20}_{20}	Silicon, % Calcd.	Silicon, % Found	Recrystn. solvent
$Ph_3SiN(n\text{-}C_4H_9)_2$	62	64–65[a]							Ethanol
$Ph_2CH_3SiN(n\text{-}C_4H_9)_2$[b]	41		117–118	0.02	1.5337	0.963	8.65	8.90 8.83	
$Ph(CH_3)_2SiN(n\text{-}C_4H_9)_2$[c]	29		72–74	0.04	1.4933	0.902	[c]		
$Ph_3SiNH(n\text{-}C_4H_9)$	56	[d]	138–139	0.02			8.48	8.37 8.44	
	83	179–181					8.13	8.14 8.13	Petr. eth.[e]
	86	131–132					8.18	8.27 8.17	Petr. eth.[e]
	93	287–288					9.32	9.45 9.38	Xylene

[a] Reported[2] 62°. [b] Calcd. for $C_{21}H_{31}NSi$: *MR*, 105.7. Found: *MR*, 105.4. [c] Calcd. for $C_{16}H_{29}NSi$: C, 72.93; H, 11.09; *MR*, 85.6. Found: C, 72.67, 72.55; H, 10.62, 10.33; *MR*, 84.8. [d] Waxy solid. [e] B.p. 60–70°.

not changed by recrystallization from a benzene–petroleum ether (b.p. 60–70°) mixture.

Experimental Variations for Other Silylamines Derived from Secondary Amines.—The silylamines derived from piperidine, piperazine and di-*n*-butylamine were prepared in the manner described above. In the latter case it was necessary to cool the ethanol solution in an ice-bath to crystallize the N,N-di-*n*-butyl-1,1,1-triphenylsilylamine.[14] N,N-Di-*n*-butyl-1-methyl-1,1-diphenylsilylamine and N,N-dibutyl-1,1-dimethyl-1-phenylsilylamine were isolated by a slightly different technique. After the addition of the silylmetallic compound was complete, a small volume of ethanol was added. When the evolution of hydrogen had ceased, the solvents were distilled. Dry petroleum ether (b.p. 60–70°) was added, and the gelatinous lithium ethoxide was removed by filtration. The petroleum ether was distilled off, and the silylamine was purified by distillation under reduced pressure. Consult Table I for the physical properties of these silylamines.

N-*n*-Butyl-1,1,1-triphenylsilylamine.—A solution of triphenylsilyllithium, prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and excess lithium in 100 ml. of tetrahydrofuran (THF), was added to an excess[15] of *n*-butylamine in 50 ml. of THF. Color Test I[13] was negative after the addition was complete. The THF was distilled and replaced by dry petroleum ether (b.p. 60–70°). Filtration of the suspension gave a clear solution from which the petroleum ether was removed. The resulting oil was distilled to give 7.16 g. (56%) of N-*n*-butyl-1,1,1-triphenylsilylamine, b.p. 138–139° (0.02 mm.), which solidified on standing to give a waxy solid.[16] The infrared spectrum showed a strong N-H band at 2.9 μ.

Reactions of N-*n*-Butyl-1,1,1-triphenylsilylamine with Methanol and Ethanol.—A small amount of N-*n*-butyl-1,1,1-triphenylsilylamine was dissolved in warm methanol. The odor of *n*-butylamine became intense. The solution was cooled to give crystals of methoxytriphenylsilane, m.p. 42–43°. The infrared spectrum was almost superimposable with that of a sample of methoxytriphenylsilane, m.p. 55°.[8] A mixture of the two apparent dimorphs melted at 42–55°. A methanol solution of the 42–43° form was seeded with the 55° form and cooled to give crystals, m.p. 55°. Attempts to reverse this technique by seeding with the 42–43° form failed. The 55° form was recovered in each case.

Anal. Calcd. for $C_{19}H_{18}OSi$ (m.p. 42–43°): Si, 9.67. Found: Si, 9.58, 9.60.

Ethoxytriphenylsilane, m.p. 65° (reported[17] 63–64°), was obtained by a similar technique using ethanol. No dimorphism was observed.

Methoxytriphenylsilane from Chlorotriphenylsilane and Sodium Methoxide.—To a solution of sodium methoxide, prepared by addition of 0.415 g. (0.018 g. atom) of sodium to 50 ml. of methanol, was added 5.0 g. (0.0175 mole) of chlorotriphenylsilane. The reaction mixture was allowed to cool to room temperature, and the suspended sodium chloride was removed by filtration. The clear, colorless filtrate was cooled without seeding to give 2.15 g. (41%) of methoxytriphenylsilane, m.p. 42–43°. This product was shown, by the method of mixed melting points and a comparison of infrared spectra, to be identical with the methoxytriphenylsilane prepared in the previous experiment.

Attempted Cleavage of N,N-Di-*n*-butyl-1,1,1-triphenylsilylamine by Phenyllithium.—To a solution of 2.0 g. (0.00514 mole) of N,N-di-*n*-butyl-1,1,1-triphenylsilylamine in 25 ml. of ether was added 25 ml. of an ethereal solution containing 0.0095 mole of phenyllithium. The solution remained clear after 48 hr., indicating no tetraphenylsilane had formed. The ether was distilled and replaced by ethanol. Cooling gave 1.2 g. (60%) of recovered silylamine, m.p. 64–65° (mixed m.p.).

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(14) This compound was identical with the compound obtained from the reaction of lithium dibutylamide and triphenylsilane.[2]

(15) In a previous run, two moles of triphenylsilyllithium was added to one mole of *n*-butylamine. The only product obtained was N-*n*-butyl-1,1,1-triphenylsilylamine. None of the desired N-*n*-butyl-bis-(triphenylsilyl)-amine was isolated.

(16) R. A. Benkeser, R. E. Robinson and H. Landesman, THIS JOURNAL, **74**, 5699 (1952), report m.p. 47–48° for N-ethyl-1,1,1-triphenylsilylamine.

(17) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **19**, 441 (1954).