

From the ΔpH given in Table I and using $pK_{\text{HOCl}} = 7.45^3$ at 19, we obtain for $pK_{\text{HOBr}} = 8.70$ in excellent agreement with Shilow and Gladchikova.²

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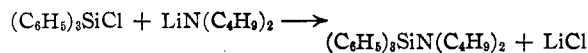
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The Preparation of Some Triarylamino-silanes

BY HENRY GILMAN, BURT HOFFERTH, H. W. MELVIN AND G. E. DUNN

In connection with some proposed cleavage studies, it was desired to prepare a series of triarylamino-silanes. In accordance with general procedures reported in the literature,¹ the reaction of triphenylchlorosilane with diethylamine in refluxing ether was attempted. Only a trace of unidentified material melting at 78–80° was obtained, the principal product being triphenylsilanol. When triphenylchlorosilane was refluxed with hydrazine, alone or in benzene, no nitrogen-containing product was obtained, and triphenylchlorosilane was recovered in 58% yield after recrystallization.

Results were not significantly better when alkali metal amides were substituted for the amines. With lithium or sodium di-*n*-butylamide and triphenylchlorosilane at 200° only 10% yields of the desired triphenyl-(di-*n*-butylamino)-silane were obtained. Lithium hydrazide in ether apparently

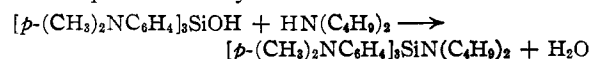


gave a small yield of a nitrogen-containing silicon compound which hydrolyzed upon brief exposure to air. When triphenylchlorosilane and *N*-lithiocarbazole were refluxed in ether for twenty hours, or heated at 270–280° for four hours, starting materials were recovered to the extent of 91 and 86%, respectively.

Next was attempted the reaction of triphenylsilanol with amines. Di-*n*-butylamine at 165° converted triphenylsilanol to hexaphenyldisiloxane in 54–94% yields. Aniline and diethyl-

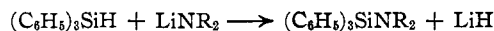


amine failed to give any reaction at their respective boiling points; however, diethylamine in a sealed tube at 180–195° gave a 91% conversion to the disiloxane. A catalytic amount of di-*n*-butylamine in boiling xylene did not cause any condensation. It is of interest to point out here the anomalous behavior of tris-(*p*-dimethylamino-phenyl)-silanol, which reacts in the desired manner with di-*n*-butylamine to give tris-(*p*-dimethylaminophenyl)-di-*n*-butylamino-silane almost quantitatively.



(1) Kraus and Rosen, *THIS JOURNAL*, **47**, 2739 (1925); Reynolds, Bigelow and Kraus, *ibid.*, **51**, 3067 (1929); Sauer and Hasek, *ibid.*, **68**, 241 (1946).

Since it is well known that hydrogen can be displaced from silicon by strongly basic reagents, reactions were attempted between triphenylsilane and some lithium amides. Good yields of dimethyl-, diethyl- and di-*n*-butyl-aminotriphenylsilanes were obtained from the corresponding lithium amides, but lithium hydrazide gave a nitrogen-containing material which hydrolyzed to triphenylsilanol and hexaphenyldisiloxane on attempted purification. When the lithium salts



of carbazole, *N*-methylaniline, diphenylamine, and 2,5-dimethylpyrrole were employed, triphenylsilane was recovered to the extent of 60–90%. It may be noted that, with the exception of *N*-methylaniline, these unreactive lithium salts did not give Color Test IV.²

Experimental

Table I reports the yields, physical constants and analyses of the four triarylamino-silanes prepared in this study. All melting points are uncorrected. Representative preparations and the standard procedure used in this Laboratory for the analysis of non-volatile organometallic compounds for silicon are described below.

Silicon Analysis.—From 0.1 to 0.2 g. of sample is weighed accurately into a previously ignited 15-ml. platinum crucible with cover. About 1 ml. of pure concentrated sulfuric acid is added cautiously to the sample in the partially covered crucible. It is essential that the sample be thoroughly wetted by the sulfuric acid before heating is begun. This may be facilitated in stubborn cases by previously wetting the sample with glacial acetic acid, or by adding two or three drops of concentrated nitric acid to the sulfuric acid and sample in the crucible. The partially covered crucible is then placed in the platinum wire support of a Rogers ring burner. The supporting structure of the burner is lowered so that the flame impinges on the crucible above the level of the acid. The flame is adjusted, and the crucible support is raised at such a rate that sulfuric acid fumes are continuously evolved. When all the acid has been vaporized, the crucible is ignited to constant weight at dull red heat.³ The percentage silicon is calculated using the factor 0.4672 for conversion of SiO₂ to Si.

Triphenyl-(di-*n*-butylamino)-silane from Triphenylchlorosilane and Lithium Di-*n*-butylamide.—A solution of phenyllithium in ether was added under dry nitrogen to an ether solution of 0.0463 mole of silicon tetrachloride in the usual way.⁴ The mixture was refluxed for one-half hour and the salts were allowed to settle. The ether solution was added to 0.171 mole of lithium di-*n*-butylamide in about 30 ml. of di-*n*-butylamine. The ether was removed over a steam-bath and the residue was heated at 200° for an hour. After cooling the flask, dry benzene was added and refluxed for an hour. Salts were filtered off under nitrogen and the solvent was evaporated. Distillation of the residue under reduced pressure gave a red-brown product which, after being washed with petroleum ether (b. p. 60–70°), melted at 62° and weighed 1.8 g. (10%).

Triphenyl-(di-*n*-butylamino)-silane from Triphenylsilane and Lithium Di-*n*-butylamide.—To 0.034 mole of *n*-butyllithium⁵ was added 5 g. (0.039 mole) of di-*n*-butyl-

(2) Gilman and Woods, *ibid.*, **65**, 33 (1943).

(3) Ignition at too high a temperature may produce silicon carbide instead of silica: see McHard, Servais, and Clark, *Anal. Chem.*, **20**, 325 (1948).

(4) Gilman and Clark, *THIS JOURNAL*, **68**, 1675 (1946).

(5) Gilman, Beel, Brannen, Bullock, Dunn and Miller, *ibid.*, **71**, 1499 (1949).

TABLE I
 TRIARYLAMINOSILANES

Silicon compound	Nitrogen compound	Product	M. p., °C.	Yield, %	Silicon, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found
(C ₆ H ₅) ₃ SiH	(CH ₃) ₂ NLi	(C ₆ H ₅) ₃ SiN(CH ₃) ₂	80-81	74.5	9.24	9.2	4.67	4.6
(C ₆ H ₅) ₃ SiH	(C ₂ H ₅) ₂ NLi	(C ₆ H ₅) ₃ SiN(C ₂ H ₅) ₂	84-85	74.2	8.46	8.6	4.23	4.3
(C ₆ H ₅) ₃ SiH	(<i>n</i> -C ₄ H ₉) ₂ NLi	(C ₆ H ₅) ₃ SiN(C ₄ H ₉ - <i>n</i>) ₂	60-62	63	7.23	7.6	3.61	3.6
(C ₆ H ₅) ₃ SiCl	(<i>n</i> -C ₄ H ₉) ₂ NLi	(C ₆ H ₅) ₃ SiN(C ₄ H ₉ - <i>n</i>) ₂	62	10	7.23	7.2	3.61	3.9
[<i>p</i> -(CH ₃) ₂ NC ₆ H ₄] ₃ SiOH	(<i>n</i> -C ₄ H ₉) ₂ NH	[<i>p</i> -(CH ₃) ₂ NC ₆ H ₄] ₃ SiN(C ₄ H ₉ - <i>n</i>) ₂	62-64	92	5.42	5.3		

amine in 25 ml. of anhydrous ether. The suspension was refluxed for one-half hour, after which time Color Test 11-A⁶ was negative and Color Test IV² was positive. Then 8.8 g. (0.034 mole) of triphenylsilane in 50 ml. of dry ether was added to the suspension of lithium di-*n*-butylamide, and the mixture was refluxed for one-half hour. The suspension was filtered and the solvent was removed by distillation. The residue from the distillation was refluxed with benzene for one hour, filtered, and the solvent was distilled. A similar treatment of this residue with petroleum ether (b. p. 60-70°) yielded a gummy solid which, after crystallization from absolute ethanol, weighed 7.6 g. (63%) and melted at 60-62°. A mixed melting point with the triphenyl-(di-*n*-butylamino)-silane obtained from triphenylchlorosilane was not depressed. Triphenyldimethyl- and triphenyldiethylaminosilane were prepared from triphenylsilane by suitable modification of this procedure.

Tris-(*p*-dimethylaminophenyl)-di-*n*-butylaminosilane.

—One gram (0.0025 mole) of tris-(*p*-dimethylaminophenyl)-silanol⁷ (m. p. 183°) was refluxed with 50 ml. of di-*n*-butylamine for thirty minutes. About two-thirds of the di-*n*-butylamine was then distilled off very slowly so as to remove water continuously as it formed during the reaction. The remaining solution, on cooling, deposited a sticky solid which, when recrystallized from di-*n*-butylamine and washed with petroleum ether (b. p. 30-60°), melted at 62-64° and weighed 1.2 g. (92%). This material was shown to be tris-(*p*-dimethylaminophenyl)-di-*n*-butylaminosilane by the following procedure. The material was agitated in 50 ml. of water at 70° for thirty minutes, filtered, and the precipitate (0.88 g.) was shown to be tris-(*p*-dimethylaminophenyl)-silanol by a mixed melting point determination. The filtrate was extracted with ether, and the extract was dried and distilled. The liquid remaining was identified as di-*n*-butylamine by a mixed melting point between its picrate and that of an authentic specimen.

Conversion of Triphenylsilanol to Hexaphenyldisiloxane. (a) **By Di-*n*-butylamine.**—Fifteen grams of triphenylsilanol (m. p. 151-153°) was refluxed with 25 ml. of di-*n*-butylamine for one and one-half hours. After removal of the insoluble solid and repeated concentration of the mother liquor, 13.7 g. (94.5%) of crude hexaphenyldisiloxane was obtained. The yield after recrystallization was 12.8 g. (88%), m. p. 222-224°. In a subsequent run, 10 g. of triphenylsilanol was converted to 5.2 g. (54%) of hexaphenyldisiloxane after being refluxed for three hours in 25 ml. of di-*n*-butylamine. The excess amine was washed out with acid, and the product was obtained by fractional crystallization.

(b) **By Diethylamine.**—Triphenylsilanol (0.0181 mole) was heated in a Carius tube with 0.0487 mole of diethylamine for three and three-quarter hours at 180-195°. The crystalline product, after being washed free of amine with petroleum ether (b. p. 60-70°), weighed 4.35 g. (91%). A mixed melting point with an authentic specimen showed no depression.

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(6) Gilman and Swiss, *THIS JOURNAL*, **62**, 1847 (1940).

(7) The preparation of this compound will be reported in a forthcoming publication.

A Quantitative Evaluation of Small-Angle X-Ray Scattering by Various Cellulose Fibers for the Determination of Crystallite Size with Special Reference to the Problem of Inter-particle Interference

BY A. N. J. HEYN

Previous articles by the author¹ discussed the scattering of X-rays at small angles by various cellulose fibers and the relation of this scattering to the orientation of the particles on a qualitative basis.

The quantitative evaluation of scattering to determine the size and distance of the particles was complicated because inter-particle interference was found to play an important role in this scattering. Therefore, application of simple approximation formulas for the calculation of the particle size as given by Guinier did not appear permissible under such conditions of "densely packed systems," as has been stressed already by Kratky and collaborators.² This is so because these formulas are based on the assumption that the particles scatter independently.

Interpretation of the increased intensity of scattering and the different distribution of intensity caused by the swelling of fibers (compare diagrams a and b of Fig. 1 of dry and wet flax) in previous experiments¹ offered a means of solving this problem; whereas with fibers in the dry state particle interference plays an important part, it was presumed that this no longer proved to be the case with fibers that have been swollen in various ways so as to increase the distance between the particles. The experiments discussed in this article show that when applying this new swelling technique it is indeed possible to use the above approximation formulas for the calculation of particle size. The results so obtained with different natural cellulose fibers and rayons are reported here.

Experimental

The formula by which Guinier, as based on Debye's general scattering formula, approximated the theoretical formula is given as formula (a). This approximation holds only for small angles, but if this condition is fulfilled—as in the present case—it affords one of the simplest methods for calculating of the particle size from the distribution of intensity.

$$I = NI_0 n^2 e^{-4\pi^2/3\lambda^2} R^2 e^2 \quad (a)$$

(1) A. N. J. Heyn, *THIS JOURNAL*, **70**, 3138 (1948); **71**, 1873 (1949); **72**, 2284 (1950); *Text. Res. J.*, **19**, 163-172 (1949).

(2) O. Kratky, *Naturwissenschaften*, **26**, 94 (1938); **30**, 542 (1942); O. Kratky, A. Sekora and R. Treer, *Z. Elektrochem.*, **48**, 587 (1942); O. Kratky and Wurster, *ibid.*, **50**, 249 (1944).