tively. Analyses consisted of titration of the available acidity and of molecular weights by depressing the freezing point of camphor; fuming nitric acid and sulfuric acid converted the organogermanium oxide finally into GeO_2. Refractive indices are in white light.

Interchangeable equipment was used, bearing ground joints and thermometers with ground joints; all transfers were by pipet.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Methylanilinosilanes and Ethylanilinosilanes; Reactions of Anilinosilanes

BY HERBERT H. ANDERSON

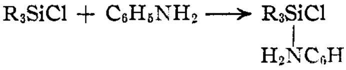
Methylchlorosilanes, ethylchlorosilanes and diphenyldichlorosilane react with aniline to furnish anilinium chloride and five (new) methylanilinosilanes, ethylanilinosilanes and diphenyldianilinosilane, the properties of which are in Table I. Alkylanilinosilanes react with various acids, especially inorganic acids. Trimethylchlorosilane and triethylchlorosilane react reversibly with aniline $R_3SiCl + 2C_6H_5NH_2 \leftrightarrows R_3Si(HNC_6H_5) + C_6H_5NH_3Cl$. A study of numerous exchange reactions, such as $4(CH_3)_3Si(HNC_6H_5) + SiBr_4 \rightarrow 4(CH_3)_3SiBr + Si(HNC_6H_5)_4$, indicates that substituted alkylsilanes react easily under reflux conditions, accompanied by the distillation of the most volatile component possible; alkyl groups do not migrate.

Ruff[1] converted trichlorosilane into triiodosilane, in benzene solution, and recently we similarly prepared numerous new alkyliodosilanes by the same method[2,3]; the following equations illustrate the principles involved (for Ruff R was hydrogen)

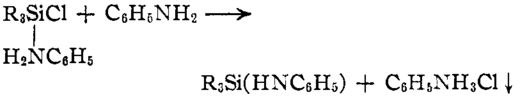
$$RSiCl_3 + 6C_6H_5NH_2 \longrightarrow RSi(HNC_6H_5)_3 + 3C_6H_5NH_3Cl\downarrow$$

$$RSi(HNC_6H_5)_3 + 6HI \longrightarrow RSiI_3 + 3C_6H_5NH_3I\downarrow$$

As done in the manner recommended by Ruff,[1] dialkyldiiodosilanes could be prepared, but trialkyliodosilanes could not be made.[2] The following equations represent the first step of the Ruff process for R_3SiX



$$R_3SiCl + C_6H_5NH_2 \longrightarrow \underset{H_2NC_6H_5}{\underset{|}{R_3SiCl}} \qquad (1)$$



$$\underset{H_2NC_6H_5}{\underset{|}{R_3SiCl}} + C_6H_5NH_2 \longrightarrow R_3Si(HNC_6H_5) + C_6H_5NH_3Cl\downarrow \qquad (2)$$

This process is rapid when conditions are forcing, namely: omission of solvent benzene; reaction at 25° or lower. On the other hand, high temperature results in a reversal, with formation of a completely liquid system, and solvent also prevents reaction, at least the step in the second equation. In the first equation the silane with five substituents decomposes with elimination of HCl, which combines with a molecule of aniline in the second equation to produce insoluble anilinium chloride.

By using the forcing conditions to convert $(CH_3)_3SiCl$ into the anilino derivative, and then dissolving the anilino compound in benzene, followed by use of pure HI gas, it should be possible to prepare $(CH_3)_3SiI$.

Table II presents a number of exchange reactions; these constitute a new approach to preparative problems. At present there is a "volatility series" $(C_6H_5NH) \rightarrow (C_2H_5)_2N \rightarrow I \rightarrow Br \rightarrow Cl \rightarrow F$, with slight uncertainty regarding the diethylamino group and iodine; the element or group as far to the right in this series as possible appears in the most volatile compound, which distils out of the system. Alkylamino derivatives of silanes enter exchange reactions easily with halides of silicon, phosphorus and germanium, as well as aniline or anilinium halides. This "volatility series" appears to be associated with volumes of groups or atoms, rather than with masses (weights).

Larsson and Mjörne have already prepared trimethylanilinosilane,[4a] listed as b.p. 96–98° under 24 mm., from $(Me_3Si)_2NH$ and aniline, also triethylanilinosilane,[4b] listed as b.p. 130–132° under 12 mm., from triethylchlorosilane and aniline. There are some advantages in making the trimethylanilinosilane from the chloro compound, the process being shorter and perhaps more exact.

Experimental

Preparation of Alkylanilinosilanes and Diphenyldianilinosilane (a) Alkyltrianilinosilanes and Dialkyldianilinosilanes.—Because the preparations of the monomethyl, monoethyl and diethyl derivatives are similar, only directions for making the dimethyl analog are necessary. Twenty grams of dimethyldichlorosilane and 70 g. of aniline (2.4 mols. of aniline per chlorine atom) upon combination in 150 ml. of pure benzene reacted with much heat; after a half-hour of reflux, with shaking, the mixture cooled overnight; then the precipitate of anilinium chloride was filtered, washed with benzene and discarded. The filtrate contained benzene, excess aniline and dimethyldianilinosilane; after distilling the benzene and nearly all the aniline—up to 250° at 760 mm.—the remaining liquid was transferred to smaller distillation equipment and finally a center fraction taken at low pressure as in Table I. A single unit of Pyrex glass, except for a thermometer with a ground joint, was the best equipment for monoalkyl derivatives, while dialkyl derivatives could tolerate a receiver with a ground joint. According to volumes involved, yields were about 80%.

(b) **Trialkylanilinosilanes.**—Thirty grams of pure Et_3SiCl and 45 g. of aniline (7 g. excess) formed much precipitate in the cold, but the precipitate redissolved when heated to 140° and then the solution boiled at 158°; after standing at 0° overnight, the pasty mass was filtered using suction and pressing as dry as possible, but without washing; the solid discarded. Careful distillation of the 37 g. of filtrate furnished 7 g. of excess aniline and then, as in Table I, 30 g. of triethylanilinosilane, or a yield of 72%.

Forty-eight grams of $(CH_3)_3SiCl$ and 26 g. of aniline, a deficiency, reacted with a temperature rise of 38°; after cooling to 0°, the pasty mass was filtered without washing, on a buchner funnel. Then distillation yielded first unchanged trimethylchlorosilane and later 13 g., or 56% based on aniline, of trimethylanilinosilane. A center cut was collected as in Table I.

(c) **Diphenyldianilinosilane.**—Twenty grams of diphenyldichlorosilane and 50 g. of aniline in 40 ml. of benzene fur-

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(1) O. Ruff, *Ber.*, **41**, 3738 (1908).

(2) H. H. Anderson, D. L. Seaton and R. P. T. Rudnicki, THIS JOURNAL, **73**, 2144 (1951).

(3) H. H. Anderson, *ibid.*, **73**, 2351 (151).

(4) (a) E. Larsson and O. Mjörne, *Kem. Tid.* (*Sweden*), **61**, 59 (1949). (b) O. Mjörne, *ibid.*, **62**, 120 (1950); see *Chem. Abstr.*, **43**, 5739*d* (1949); **44**, 1402*f*, 9342*f* (1950).

TABLE I

PROPERTIES OF NEW COMPOUNDS (EXCEPT 1ST AND 4TH)

All distillations at reduced pressure; diphenyl compound crystallized.

Compound	B.p., °C.	B.p., Mm.	M.p., °C.	d^t_4	t	Mol. wt. Calcd.	Mol. wt. Found	C_6H_5NH, % Calcd.	C_6H_5NH, % Found
$(CH_3)_3Si(HNC_6H_6)^{4a}$	206	760	None	0.940	20	165.3	158	55.7	56.2
	98–99	19							
$(CH_3)_2Si(HNC_6H_5)_2$	328	760	45 ± 2	1.07	30	242.4	231	76.1	75.4
	185–186	9							
$(CH_3)Si(HCN_6H_5)_3$	345	760	None	1.14	30	319.4	300	86.5	86.1
	212	1							
$(C_2H_5)_3Si(HNC_6H_5)^{4b}$	270	760	None	0.934	20	207.4	194	44.5	44.3
	134–135	12							
$(C_2H_5)_2Si(HNC_6H_5)_2$	350	760	58	...		270.4	256	68.0	67.5
	172–173	1							
$(C_2H_5)Si(HNC_6H_5)_3$	381	760	None	...		333.5	300	82.9	82.0
	232–234	1							
$(C_6H_5)_2Si(HNC_6H_5)_2$	413 dec.	760	153	...		366.5	320	50.2	49.7

TABLE II

REACTIONS OF SUBSTITUTED ALKYLSILANES

Starting materials				Reaction products			
				Most volatile member			
Compound	Wt., g.	Compound	Wt., g.	T, °C.	Wt., g.	Compound	Residue
$Me_3SiHNPh$	3	$PhNH_3Cl$	2	58	1.2	Me_3SiCl	$PhNH_2$
$Me_3SiHNPh$	0.5	$SiBr_4$	2.8	80–81	0.3	Me_3SiBr	$Si(HNPh)_4$
$Me_3SiHNPh$	.4	$GeBr_4$	1.6	80–90	.2	Me_3SiBr	$Ge(HNPh)_4$
$Me_2Si(HNPh)_2$	.57	PBr_3	1.5	112–118	.4	Me_2SiBr_2	$P(HNPh)_3$
$MeSi(HNPh)_3$	1.8	Ph_2SiCl_2	2.2	64–70	.6	$MeSiCl_3$	$Ph_2Si(HNPh)_2$
Me_3SiNEt_2	3.6	$PhNH_2$	1.0	64	1.0	Et_2NH	$Me_3SiHNPh$
$Et_3SiHNPh$	0.6	$PhNH_3F$	0.9	109	0.4	Et_3SiF	$PhNH_2$
$Et_3SiHNPh$	5.5	$PhNH_3Cl$	5.5	142–195	3.0	Et_3SiCl	$PhNH_2$[a]
$Et_3SiHNPh$	1.8	Ph_2SiCl_2	1.8	141–152	0.8	Et_3SiCl	$Ph_2Si(HNPh)_2$
$Et_3SiHNPh$	0.6	*n*-$AmSiI_3$	0.4	190–193	.4	Et_3SiI	*n*-$AmSi(HNPh)_3$
$Et_2Si(HNPh)_2$	1.8	Ph_2SiCl_2	1.8	126–131	.7	Et_2SiCl_2	$Ph_2Si(HNPh)_2$
$EtSi(HNPh)_3$	1.2	$PhNH_3F$	1.2	0–3	.4	$EtSiF_3$	$PhNH_2$

[a] Reacts with Et_3SiCl to reform the starting materials. Ph is phenyl.

nished a temperature rise of 20°; after a few minutes of reflux the mixture stood overnight. Filtration and washing with benzene left 45 g. of solid on the buchner funnel, only 20 g. of which could be anilinium chloride. Therefore, the filtrate was discarded and extraction of the 45 g. of solid in 125 ml. of boiling benzene carried out; the rest of the process consisted of evaporating down to 90 ml., adding an equal volume of (30–60°) petroleum ether, and then allowing to stand two hours at 0°; the 10 g. of white crystals that formed were filtered and washed, later dried.

Physical Properties and Analysis; see Table I.—Only the monoanilino derivatives were truly mobile liquids; only the dianilino compounds had melting points; the trianilino compounds were highly viscous at 25° and had no melting points. Two densities are approximate. Despite the physical characteristics of the alkylanilinosilanes, in many cases they may be preferable to alkylaminosilanes, some of which are known,[5] both in yield and purity. Reynolds prepared the related $Si(HNC_6H_5)_4$,[6] which melts at 137–138° and decomposes above that.

All molecular weights were by freezing point of solutions in camphor. All anilino compounds were dissolved in benzene, anhydrous HCl passed in and then anilinium chloride precipitated, which was transferred and washed—first with benzene, later with light petroleum ether—then dried and weighed.

Reactions of Alkylanilinosilanes. (a) **With Acids.**—Ruff and we demonstrated the reaction with HI gas amply[1,2,3]; 7 g. of $(CH_3)Si(HNC_6H_5)_3$ in benzene and an excess of dry HBr similarly furnished 3.5 g. of $(CH_3)SiBr_3$, b.p. 134°; in the analyses herein the use of dry HCl was made; since anhydrous HF was not momentarily available, concentrated aqueous acid and a deficiency of $(C_2H_5)_3Si(HNC_6H_5)$ were shaken vigorously together. The resultant top layer was a liquid of penetrating odor, boiling at 110° and with n^{22} 1.395, in general agreement with 109° and 1.3900 (25°).[7] Sulfuric acid and triethylanilinosilane reacted with much warming, while a white solid precipitated—anilinium sulfate; the solution contained crude $(C_2H_5)_3SiOSO_2$–$OSi(C_2H_5)_3$.[8] Dimethyldianilinosilane reacted to form a paste when either 85% phosphoric acid or dichloroacetic acid was added; with 90% formic acid there was much heat but no precipitate; acetic anhydride yielded much heat but no precipitate.

Water does not react with alkylanilinosilanes with much vigor.

(b) **With Halides**; see Table II.—A dozen reactions demonstrated the reactivity of the alkylanilinosilanes, as in Table II; however, dimethyldianilinosilane did not react with carbon tetrabromide, benzyl chloride, stannic bromide or mercuric chloride. In connection with this section new small distillation equipment has been designed and may be reported separately elsewhere; five plates and 1 ml. are the chief factors. Some decomposition of anilino derivatives occurs, and thus the least volatile product in Table II should not be considered pure. Periods of distillation averaged 15 minutes approximately.

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[5] R. O. Sauer and R. H. Hasek, THIS JOURNAL, **68**, 241 (1946).

[6] J. E. Reynolds, *J. Chem. Soc.*, 474 (1889).

[7] J. A. Gierut, F. J. Sowa and J. A. Nieuwland, THIS JOURNAL, **58**, 897 (1936).

[8] L. H. Sommer, *et al.*, *ibid.*, **68**, 156 (1946).