

sulfuric acid react rapidly at 25°, yielding (new) bis-(triethylgermanium) sulfate, $[(C_2H_5)_3Ge]_2SO_4$. Bis-(triethylgermanium) sulfate melts at -4° into a colorless liquid which boils at 165° under 3-mm. pressure, or, with slight decomposition, at 342° under 760-mm. pressure. This sulfate is readily miscible with carbon tetrachloride, methyl acetate, carbon disulfide, cyclohexane, benzene and concentrated sulfuric acid. In the system $[(C_2H_5)_3Ge]_2O + H_2SO_4 \rightleftharpoons [(C_2H_5)_3Ge]_2SO_4 + H_2O$ a concentration of 11 *M* in sulfuric acid produces one liquid phase, with a shift of the equilibrium to the right.

2. Tetrameric (or trimeric) diethylgermanium

oxide, $[(C_2H_5)_2GeO]_3$ or 4, and 100% sulfuric acid react rapidly at room temperature, yielding (new) dimeric diethylgermanium sulfate, $[(C_2H_5)_2Ge(SO_4)]_2$, a fluffy, crystalline white solid melting at 116°, and only moderately soluble in benzene, 21 g./l. at 17.5° and 38 g./l. at 23.5°.

3. Diethylgermanium oxide, previously found by Flood to polymerize easily, has polymerized very slowly in these studies, so slowly as to render separation of $[(C_2H_5)_2Ge]_2O$ and $[(C_2H_5)_2GeO]_4$ difficult in two instances. The polymeric form of diethylgermanium oxide appears to be variable, although Flood found it to be trimeric.

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Ethylsilicon Isocyanates. Monopropylsilicon Isocyanates and Isothiocyanates

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In continuation of previous studies on alkylsilicon isocyanates and isothiocyanates, the present paper includes: the synthesis of all three ethylsilicon isocyanates, which are the second complete series of alkylsilicon isocyanates; the synthesis of *n*-propylsilicon triisocyanate, isopropylsilicon triisocyanate, *n*-propylsilicon triisothiocyanate and isopropylsilicon triisothiocyanate; an investigation of analytical possibilities including the titration of isocyanic acid, and also the unsuccessful use of semicarbazide hydrochloride to yield hydrazodicarbamide—in the actual procedure the hydrazodicarbamide weight was far short of the expected amount.

New Alkylsilicon Pseudo Halides

Preparation.—The following halides served as starting materials: Et_3SiCl_3 , boiling at 98.5–98.6° under 771 mm. pressure, prepared from silicon tetrachloride and ethylmagnesium bromide, the presence of a little bromine being of no consequence in any of these reagents, since isocyanate and isothiocyanate both replace chlorine and bromine; Et_2SiCl_2 , obtained similarly; $EtSiCl$, obtained pure from Anderson Laboratories, Inc., of Adrian, Michigan; *i*- $PrSiCl_3$, boiling at 119.0–120.0° under 760 mm. pressure,¹ distilled from antimony trichloride to remove all bromine²; *n*- $PrSiCl_3$, boiling at 124–126°, prepared from silicon tetrachloride and *n*-propylmagnesium bromide.

For the most part, the preparations followed the previous general method used with silicon tetraisocyanate,³ with methylsilicon triisocyanate,⁴ and with methylsilicon isothiocyanates.⁵ Twenty grams of the individual alkylchlorosilane and a 30% excess of silver isocyanate (or isothiocyanate) constituted the typical amounts, while the solvent varied somewhat; 50 ml. of benzene was satisfactory for the monoethyl and diethyl derivatives, with a half-hour of reflux.⁵ However, the triethylsilicon re-

action was incomplete under similar circumstances. To remedy this, 20 g. of Et_3SiCl and 30 g. of silver isocyanate were mixed with 30 ml. of nitromethane and 20 ml. of benzene, whereupon the temperature of the system rose from 18 to 40° within ten minutes, with good agitation; an hour on the steam-bath ensured completion of the reaction. (Nitromethane, at present under investigation, does not dissolve all organosilicon halides completely; hence dilution with benzene was advantageous.) A mixed solvent consisting of 90 volume % benzene and 10 volume % nitromethane was satisfactory in making *n*-propylsilicon triisocyanate and isopropylsilicon triisocyanate; although both reactions started slowly, they reached completion in an hour of reflux, and the purified liquid isocyanates contained no chlorine. *n*-Propylsilicon triisothiocyanate and isopropylsilicon triisocyanate were prepared in the usual manner,⁶ with the addition of 0.05 ml. of water to serve as a catalyst. In all cases the yields were 80–90%.

Chemical Properties.—The hydrolysis of $EtSi(NCO)_3$ when shaken with an equal volume of water was slow at first, then speeded up in rate; this compound hydrolyzes at a slower rate than does $Si(NCO)_4$, and the amount of heat involved is less. When emulsified with water, $Et_2Si(NCO)_2$ hydrolyzes at a moderate rate, without detectable heat. Triethylsilicon isocyanate can be heated to 85° and shaken with water at the same temperature without a reaction of detectable speed or heat; however, if shaken with 50% ethanol the monoisocyanate reacts rapidly with warming. Both *n*-propylsilicon triisocyanate and isopropylsilicon triisocyanate when emulsified with an equal volume of water hydrolyze at an initially slow rate, but suddenly, after about five minutes, build up to a very fast rate of hydrolysis; because of this, such mixtures should never be prepared on a large scale. In comparison, it would be dangerous to shake either $Si(NCO)_4$ or $Si_2O(NCO)_6$ with an equal volume of water. All seven new compounds decompose completely within five minutes in 95% ethanol; they should all dissolve easily in a variety of organic solvents.

Physical Properties (See Table I).—All seven new compounds are colorless liquids of approximately the same viscosity as that of carbon tetrachloride. Triethylsilicon isocyanate had a camphoraceous odor, while the other isocyanates had an odor similar to that of isocyanic acid. Although the variation in indices of refraction of the new isocyanates is small, there is a more characteristic spread in densities and the observed molar refractions are in good

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(1) Booth and Spessard, *THIS JOURNAL*, **68**, 2660 (1946).

(2) See prototype in Schumb and Anderson, *ibid.*, **59**, 651 (1937).

(3) Forbes and Anderson, *ibid.*, **62**, 761 (1940).

(4) Forbes and Anderson, *ibid.*, **70**, 1222 (1948).

(5) Anderson, *ibid.*, **69**, 3049 (1947).

(6) Forbes and Anderson, *ibid.*, **69**, 3048 (1947).

TABLE I
 PROPERTIES OF COMPOUNDS

Compound	B. p., °C.	d_{20}^4	n_{20}^{20}	R, ml.	Mol. wt. (camphor)		Distillation range °C.	Mm.
					Calcd.	Found		
Et ₃ Si	153.7 ⁷	0.7662 ⁸	1.4268 ⁸	48.34 ⁸
Et ₃ Si(NCO)	165.1	0.8895	1.4295	45.6	157.3	164	99-100	101
Et ₂ Si(NCO) ₂	176.7	1.0223	1.4348	43.4	170.2	177	112-113	101
EtSi(NCO) ₃	183.5	1.2191	1.4468	40.1	184.2	181	124-125	103
Si(NCO) ₄	185.6	1.442	1.4610	37.3
<i>n</i> -PrSi(NCO) ₃	198.2	1.1726	1.4462	44.9	197.2	191	101.5-102.0	30
iso-PrSi(NCO) ₃	192.0	1.1626	1.4444	45.2	197.2	194	78.0-78.5	16
<i>n</i> -PrSi(NCS) ₃	289.5	1.2248	1.6014	68.7	245.4	234	152-153	13
iso-PrSi(NCS) ₃	279	1.2177	1.6066	69.5 ⁹	245.4	232	137-138	12

agreement with the calculated values. Minor corrections in boiling points to 760 mm. pressure were made; the compounds boiled at the following temperatures at the pressures following (°/mm.): Et₃Si(NCO), 165.6/776; Et₂Si(NCO)₂, 176.7/775; EtSi(NCO)₃, 183.4/757; *n*-PrSi(NCO)₃, 198.6/770; iso-PrSi(NCO)₃, 192.0/762; *n*-PrSi(NCS)₃, 289.9/770; iso-PrSi(NCS)₃, 279.0/758.

Analyses.—Using the previous method of delivering the individual *isothiocyanate* into a slightly less than equivalent quantity of ethanolic sodium hydroxide solution,¹⁰ the estimation was quite satisfactory. Calcd. for iso-PrSi(NCS)₃: NCS, 71.0. Found: NCS, 71.1, 71.0 (phenolphthalein as indicator). Calcd. for *n*-PrSi(NCS)₃: NCS, 71.0. Found: NCS, 71.1 (phenolphthalein), 70.8 (brom phenol blue as indicator—not as good as phenolphthalein).

Dumas nitrogen determinations on all three monoalkylsilicon triisocyanates were made, using a self-filling quartz capillary holding 0.0999 ml.¹¹ Calcd. for EtSi(NCO)₃: N, 22.8. Found: N, 22.9, 22.6. Calcd. for *n*-PrSi(NCO)₃: N, 21.3. Found: N, 21.8, 21.6. Calcd. for iso-PrSi(NCO)₃: N, 21.3. Found: N, 21.4, 21.7.

Titration for available isocyanic acid were suitable only with the triethylsilicon isocyanate and diethylsilicon diisocyanate (because of yet unexplained complications, not probably due to impurities, this method is erroneous for monoalkylsilicon triisocyanates¹²). Isocyanic acid has a dissociation constant of 2×10^{-7} , requiring the use of thymolphthalein as the indicator. The compound was delivered from a micropipet into double the theoretical equivalent of 0.0325 *N* alkali, sodium hydroxide in 95% ethanol, with a waiting period of five minutes; then the solution was brought to a pale blue of thymolphthalein, using standard hydrochloric acid. Calcd. for Et₃Si(NCO)₃: NCO, 26.8. Found: NCO, 27.3, 26.4. Calcd. for Et₂Si(NCO)₂: NCO, 49.4. Found: NCO, 49.7, 49.1.

After decomposition of EtSi(NCO)₃ in 80% ethanol, the determination of the resultant isocyanic acid in the form of hydrazodicarbamide was not satisfactory, since only 72%

of the calculated amount was recovered; potassium (iso)-cyanate has been analyzed to 0.36% through conversion into potassium chloride and insoluble hydrazodicarbamide.¹³

Discussion

1. Triethylsilicon isocyanate, Et₃Si(NCO), shows an unexpectedly strong "organic character," since the compound is best prepared in the presence of the polar solvent nitromethane (now under investigation), and since an emulsion of the monoisocyanate in water produces a very slow hydrolysis at 30°. Similarly, the other new compounds herein exhibit a slowing down in rate of hydrolysis.

2. It is much easier to determine isothiocyanate than it is to determine isocyanate in organosilicon compounds.

3. All three ethylsilicon isocyanates boil between the boiling points of tetraethylsilane and silicon tetraisocyanate.

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Summary

1. Upon reaction with silver isocyanate or isothiocyanate, the appropriate alkylchlorosilanes yielded seven new compounds: triethylsilicon isocyanate, diethylsilicon diisocyanate, ethylsilicon triisocyanate; *n*-propylsilicon triisocyanate and isopropylsilicon triisocyanate; *n*-propylsilicon triisothiocyanate and isopropylsilicon triisothiocyanate.

2. Table I of the text lists boiling points, indices of refraction, densities and molar refractions.

3. All in all, the Dumas nitrogen determination, despite difficulties at times, best meets the requirements for alkylsilicon isocyanates.

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(13) Leboucq, *J. pharm. chim.*, **5**, 531 (1927).

(7) Listed by Lewis and Newkirk, *THIS JOURNAL*, **69**, 701 (1947).

(8) Whitmore, *et al.*, *ibid.*, **68**, 475 (1946).

(9) Calcd. refractions (L. and L.): 45.6, 42.8, 40.1, 44.7, 44.7, 69.2, 69.2 ml., respectively.

(10) Anderson, *THIS JOURNAL*, **71**, 1801 (1949); part 2 of discussion.

(11) In justification of this method, Miss Doris L. Clegg, of this laboratory, kindly obtained satisfactory results on the known compound, pure nitrobenzene; two U-shaped quartz capillaries (designed by the author of this paper) were self-filling, and contained 0.00593 and 0.00779 ml. Calcd. for nitrobenzene: N, 11.38. Found: N, 11.3, 11.2 (without weighing).

(12) The extra acidity, 0.6-0.8 equivalent found per mole, may indicate the presence of the yet unknown EtSiOOH and *n*-PrSiOOH.