butyl alcohol; or with *n*-butylsodium in petroleum ether (b. p. 35–55°).

Summary

1. Triethylsilane reacts with alkyl and aryllithium compounds in diethyl ether to give tetrasubstituted silanes.

2. No reaction occurs between triethylsilane and propyllithium or butylsodium in low-boiling petroleum ether.

3. Triethylsilane and ethanol in the presence of lithium ethoxide give ethoxytriethylsilane.

4. Ethyldichlorosilane has been prepared by direct action of ethyl chloride on copper silicon.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

New Alpha and Beta Chloroalkyl Silanes. Further Studies on the Alpha Silicon Effect[1]

BY L. H. SOMMER, D. L. BAILEY, W. A. STRONG AND F. C. WHITMORE

In continuation of work on the synthesis and properties of chloroalkyl silanes, we have prepared the monochlorinated triethylchlorosilanes and triethylfluorosilanes. The alpha C–Cl compounds have been used to prepare some new neosilicon chlorides (chlorides containing silicon attached to four carbon atoms). These have been used in a further study of the alpha silicon effect.[2]

Triethylchlorosilane was prepared from a concentrated sulfuric acid solution of hexaethyldisiloxane and ammonium chloride.[1] Triethylfluorosilane was prepared by a similar method, using ammonium fluoride. Chlorination of these compounds with sulfuryl chloride activated by benzoyl peroxide gave excellent yields of the following monochlorinated products.[3]

	$(CH_3CHCl)(C_2H_5)_2SiX$	$(ClCH_2CH_2)(C_2H_5)_2SiX$
X = Cl	I	II
X = F	III	IV

Experimental

Chlorinations.—In a 1-liter round-bottomed flask there were placed 411 g. (2.7 moles) of triethylchlorosilane, 297 g. (2.2 moles) of sulfuryl chloride and 2 g. of benzoyl peroxide. The flask was fitted with an efficient reflux condenser and the system was protected from moisture by a phosphorus pentoxide tube. The reactants were then heated on the steam-bath, resulting in a vigorous evolution of sulfur dioxide and hydrogen chloride. After four hours of refluxing, the reaction product was distilled in a column of 20 theoretical plates. In addition to unreacted triethylchlorosilane, 183.5 g. (1.2 moles), there were obtained: 99.5 g. (0.5 mole) of I, b. p. 114° (100 mm.); and 72.5 g. (0.4 mole), of II, b. p. 132° (100 mm.). This represents a 60% yield of monochlorinated products based on the unrecovered starting material. Compounds (I) and (II) were analyzed for chlorine content by fusion with sodium peroxide and sucrose in a Parr bomb followed by Volhard titration for chloride ion.

Anal. Calcd. for $C_6H_{14}SiCl_2$: Cl, 38.3. Found: for I, 38.2; for II, 38.6.

A similar procedure was used for the synthesis of III and IV. Chlorination of 463 g. (3.5 moles) of triethylfluorosilane gave: 195 g. (1.5 moles) of unreacted triethylfluorosilane; 113 g. (0.7 mole) of III, b. p. 93° (113 mm.); and 91 g. (0.6 mole) of IV, b. p. 101° (77 mm.). This is a 60% yield of monochlorinated products based on the unrecovered triethylfluorosilane.

Anal. Calcd. for $C_6H_{14}SiFCl$: Cl, 21.0. Found: for III, 20.9; for IV, 21.2.

Alkali Titrations of Compounds I–IV.—Compounds I–IV were titrated with 0.2 *N* alkali in the following manner: Weighed samples were added to 20 cc. of methanol and excess alkali, followed by back-titration with standard acid. Titration of I and III gave neutral equivalents 183 and 168, respectively. The calculated neutral equivalents corresponding only to halogen attached to silicon are 185 and 168, respectively. Titration of II and IV gave neutral equivalents 95 and 85, respectively. The calculated neutral equivalents corresponding to halogen attached to carbon and to silicon (total halogen) are 93 and 84, respectively.

The alpha C–Cl bonds were left intact. The beta C–Cl bonds were broken to the extent of 98%. The formation of ethylene in this reaction,[4] and in the reactions of these compounds with other reagents, is being further studied.

α-Chloroethyldiethylsilanol, $(CH_3CHCl)Et_2SiOH$. (V).—Compounds I and III gave this compound with dilute alkali. In a 1-liter separatory funnel there were placed 60 g. (0.32 mole) of I, 200 g. of cracked ice, and 20 g. (0.5 mole) of sodium hydroxide pellets. Shaking resulted in a considerable evolution of heat which melted the ice and made external cooling necessary. After thirty minutes, the reaction product was extracted with 150 cc. of ether in three portions and the ether extracts were washed with water and dried over anhydrous magnesium sulfate. Upon removal of the ether by distillation, the residual liquid (53 g.) was distilled in a column of 20 theoretical plates. There was obtained 44 g. (0.27 mole) of α-chloroethyldiethylsilanol, b. p. 101° (29 mm.), a yield of 84%. This compound was analyzed for chlorine content in the usual manner.

Anal. Calcd. for $C_6H_{14}ClSiOH$: Cl, 21.3. Found: Cl, 21.0.

A similar treatment of III gave an 82% yield of the same silanol.

α-Chloroethyldiethylsilanol is the first example of a chloroalkyl silanol. Its synthetic possibilities are being developed. No disiloxane was formed in the above reactions, indicating that this silanol is exceptionally stable toward intermolecular dehydration.[5]

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[1] Paper VII on organo-silicon compounds. For VI see Di Giorgio, Strong, Sommer and Whitmore, THIS JOURNAL, **68**, 1380 (1946).

[2] Whitmore and Sommer, *ibid.*, **68**, 481 (1946).

[3] Kharasch and Brown, *ibid.*, **61**, 2142 (1939); see (a) Sommer and Whitmore, *ibid.*, **68**, 485 (1946); (b) Sommer, Dorfman, Goldberg and Whitmore, *ibid.*, **68**, 488 (1946).

[4] For similar β-eliminations involving silicon see Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, **68**, 1083 (1946). (Paper V).

[5] (a) In the preparation of triethylsilanol from triethylchlorosilane, a special method of hydrolysis must be used to avoid formation of large amounts of hexaethyldisiloxane (unpublished work of Sommer, Pietrusza and Whitmore); (b) Krieble and Elliott [THIS JOURNAL, **67**, 1810 (1945)] have reported that hydrolysis of chloromethyldimethylchlorosilane gives the disiloxane exclusively.

TABLE I

No.	Name	B. p., °C.[a] 200 mm.	B. p., °C.[a] 760 mm.	Calcd. heat vap. cal./mole	d^{20}	n^{20}_D	Molecular refraction M_D	Atomic refr. of silicon SiR$_D$
I[b]	α-Chloroethyldiethylchlorosilane	134	182	10,200	1.0401	1.4561	48.40	6.55
II[b]	β-Chloroethyldiethylchlorosilane	153	201	11,200	1.0552	1.4636	48.38	6.54
III[b]	α-Chloroethyldiethylfluorosilane	107	152	9,500	0.9955	1.4208	42.95	6.08
IV[b]	β-Chloroethyldiethylfluorosilane	126	171	10,500	1.0100	1.4277	42.95	6.08
V[c]	α-Chloroethyldiethylsilanol	150	195	11,600	1.0238	1.4607	44.66	6.16
VI[d]	α-Chloroethylmethyldiethylsilane	125	172	10,000	0.9036	1.4452	48.54	6.93
VII[d]	α-Chloroethyldiethylphenylsilane	219	274	13,000	1.0109	1.5229	68.51	7.43

[a] Boiling points are obtained from vapor pressure curves drawn from six or more points covering the range 20–735 mm. Heats of vaporization were calculated by use of the Clausius–Clapeyron equation for the range 200 to 730 mm. Refractive indices are accurate to 0.0002 unit. Densities are corrected to the vacuum values. Molecular refraction was calculated by use of the Lorentz–Lorenz equation. Atomic refraction of silicon was calculated by difference from the molecular refraction. The atomic refraction value used for fluorine was 1.00. [b] In compounds I–IV, boiling points, densities and refractive indices are higher for the beta C–Cl compounds. Boiling points are greater by 19°, densities by 0.015 unit, and refractive indices by 0.007 unit. It is noteworthy that the atomic refraction of silicon is independent of whether the chlorine atom is bound to alpha or beta carbon in these compounds. Moreover, SiR$_D$ in triethylchlorosilane is 6.52 indicating that substitution of alpha or beta hydrogen in this compound by chlorine has little effect on the atomic refraction of silicon. Also, SiR$_D$ in triethylfluorosilane is the same as in III and IV. [c] The change from I to V (substitution of OH for Cl) raises the boiling point by 13°, lowers the density by 0.016 unit, raises the refractive index by 0.0046 unit, and lowers the atomic refraction of silicon by 0.39 unit. A similar relationship exists between the physical properties of triethylchlorosilane and triethylsilanol. It is noteworthy that SiR$_D$ is the same for triethylsilanol and α-chloroethyldiethylsilanol. [d] The SiR$_D$ values in VI and VII show that the substitution of alkyl or phenyl for negative groups (halogen or hydroxyl) on silicon, raises the atomic refraction of silicon. This is in line with the relationship between SiR$_D$ in unchlorinated halosilanes and in the corresponding alkyl or phenyl silanes.

TABLE II

REACTIVITY OF SECONDARY NEOSILICON CHLORIDES AND α-CHLOROETHYLDIETHYLSILANOL

Reagent	Solvent	Reagent concn., *N*	Vol. reaction mixture, cc.	Moles of Si Cpd.	Per cent. reaction[a] (R = CH_3CHCl—)				
					$RSi(CH_3)_3$	$RSiCH_3(C_2H_5)_2$	$RSi(C_2H_5)_2(C_6H_5)$	$R(C_2H_5)_2SiOH$	RC_2H_5
(1) EtONa	EtOH	2.08	5	0.005	31.0	29.0	31.5	76.0	35.0
(2) AcOK	AcOH	2.04	5	.005	0.5	0.5	7.0	86.0	8.0
(3) KOH	EtOH	1.64	5	.005	14.0	13.0	18.0	57.0	34.0
(4) KOH	50% EtOH-H_2O	1.76	5	.005	3.0	2.0	6.0	65.0	16.2
(5) 50% EtOH-H_2O[b]			10	.005	0.5	<0.5	<0.5	2.0	8.0
(6) $AgNO_3$[c]	H_2O	20%	5	*ca.* .002	None	None	None	None	AgCl ppt.
(7) $AgNO_3$[c]	EtOH	Sat.	5	*ca.* .002	None	None	None	None	AgCl ppt.

[a] The data, unless otherwise indicated, are after four hours refluxing. [b] Refluxing for eight hours. [c] At the boiling point for five minutes.

Synthesis of New Neosilicon Chlorides

In line with our interest in the alpha silicon effect, we have prepared two new neosilicon chlorides.[2] These are: α-chloroethylmethyldiethylsilane (VI), and α-chloroethyldiethylphenylsilane (VII). They were prepared by the method used for the preparation of α-chloroethyltrimethylsilane.[3a]

In a 500-cc. flask equipped with a mercury-sealed stirrer, reflux condenser and dropping funnel, there was prepared 0.5 equivalent of methylmagnesium bromide in 250 cc. of ethyl ether. The Grignard reagent was added to an ether solution of 62 g. (0.33 mole) of I contained in a 500-cc. flask equipped as described above. Addition, which took two hours, was followed by refluxing of the reaction mixture for four hours on the steam-bath. The reaction product was then treated with ice and acid followed by separation of the ether layer and extraction of the water layer with 100 cc. of ether. The ether solution of the product was washed with carbonate solution and water, and was then dried over anhydrous magnesium sulfate. Upon removal of the ether by distillation, the 53 g. of residual liquid was distilled in a column of 20 theoretical plates. There was obtained 48 g. (0.29 mole) of α-chloroethylmethyldiethylsilane, b. p. 80° (40 mm.), a yield of 87% based on the chlorosilane. This compound was analyzed for chlorine content in the usual manner.

Anal. Calcd. for $C_7H_{17}ClSi$: Cl, 21.5. Found: Cl, 21.3.

α-Chloroethyldiethylchlorosilane, 70 g. (0.38 mole), was added to 0.67 equivalent of phenylmagnesium bromide during one hour. After refluxing for three hours, the ether was distilled from the reactants and the residual material was heated on the steam-bath for ten hours. Treatment of the reaction product with ice and acid was followed by separation of the ether layer and extraction with ether of the water layer. Upon removal of the ether from the product, the residual liquid (95 g.) was fractionally distilled under reduced pressure. α-Chloroethyldiethylphenylsilane, 44.5 g. (0.20 mole), b. p. 104° (4 mm.), was obtained in 52% yield. Other products were 14 g. of V (from the hydrolysis of unreacted starting material) and 7.5 g. of biphenyl.

These compounds, like chloromethyltrimethylsilane[2] and α-chloroethyltrimethylsilane,[3a] are colorless, stable liquids which can be distilled like ordinary organic chlorides.

Table I gives the physical properties of the seven new chloroalkyl silanes.

Reactivity Studies

Compounds (V), (VI), (VII) and α-chloroethyltrimethylsilane[3a] have been compared with *s*-butyl chloride as to reactivity. This study extends our data on the alpha silicon effect to secondary C–Cl compounds. Results with seven reaction mixtures are given in Table II. The significance of these data is discussed below.

The per cent. reaction given by reaction mixtures 1, 3, 4 and 5 was determined in the following manner: Aliquots (5 cc.) of the reaction mixtures were titrated with standard acid to determine the concentration of the reagent. After refluxing for the desired time, the reaction product was titrated with standard acid. Per cent. reaction given by reagent 2 was determined by a Volhard titration for chloride ion. Under these conditions silver nitrate does not attack *s*-butyl chloride.

Physical Properties.—Boiling points were determined in a modified Cottrell apparatus.[6] Temperatures were read on high precision thermometers graduated in 0.2° (Double Diamond, H. B. Instrument Co.) and pressures were corrected.

Densities were measured with pycnometers of about 5-cc. capacity. All determinations were checked by running each compound in two different pycnometers. The instruments were calibrated with triply-distilled water.

Discussion

The data of Table II on the neosilicon chlorides are in line with results previously reported for a comparison of the reactivity of silico-neopentyl chloride (chloromethyltrimethylsilane) with that of *n*-hexyl chloride.[2]

These data show that the inertness of the *primary* alpha C–Cl bond in silico-neopentyl chloride toward silver nitrate reagents[2] is paralleled by that of *secondary* C–Cl bonds alpha to silicon. This inactivity of secondary neosilicon chlorides is even more unusual than that of silico-neopentyl chloride. Although secondary alkyl chlorides are more reactive than primary alkyl chlorides with silver nitrate, secondary C–Cl bonds alpha to silicon are *less* reactive with these reagents than are primary C–Cl bonds in ordinary alkyl chlorides. This is further evidence for the strong electronegativity of neosilicon groups, since reagents such as silver ion act with organic chlorides by attacking the halogen together with its shared electron pair (electrophilic attack on halogen).[7] Reaction mixture (5) which acts with alkyl chlorides by the same mechanism (electrophilic attack on halogen by a solvent),[8] is also far less effective with the neosilicon chlorides than with *s*-butyl chloride. Results with this reaction mixture are thus in complete agreement with those obtained from reaction mixtures (6) and (7).

Results with reaction mixtures 1–4, which act with alkyl halides *via* a rearward attach mechanism (bimolecular nucleophilic reactions), show that the neosilicon halides are somewhat less reactive here than is *s*-butyl chloride. However, the differences in reactivity are generally much less than with reaction mixtures 5–7. This parallels the differences in reactivity with similar reagents of silico-neopentyl chloride and *n*-hexyl chlorides.[2] α-Chloroethyldiethylphenylsilane is the most reactive of the neosilicon chlorides. α-Chloroethyldiethylsilanol is more reactive than the neosilicon chlorides. Thus substitution of alkyl on silicon by phenyl or hydroxyl increases the activity of an alpha C–Cl bond.

Summary

1. Seven new chloroalkyl silanes have been prepared.

2. α-Chloroethyldiethylsilanol, the first example of a chloroalkyl silanol, is unusually stable toward intermolecular dehydration.

3. The beta C–Cl bonds in β-chloroethyldiethylchlorosilane and in β-chloroethyldiethylfluorosilane are broken by titration with 0.2 *N* alkali with the formation of ethylene by beta fission.

4. Further studies on the alpha silicon effect provide additional evidence for the action of silicon as an electron sink.

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[6] Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

[7] For a more complete discussion of the theoretical significance of these results, see ref. 2.

[8] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 153–155 and 166–167.

[9] Original manuscript received November 16, 1945.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Pressure–Volume Relations of the Gaseous Methylamines at 0° and Reduced Pressures

BY J. C. ARTHUR[1] WITH W. A. FELSING

Introduction.—The deviation from ideality of a gas may be calculated by obtaining an equation which relates the pressure–volume product to the pressure. Experimentally determined densities constitute the data for such an equation. This Laboratory has concerned itself with the thermodynamic properties of the methylamines[2] but has not determined the deviations at low pressures. Such data have not previously been reported in the literature; their determination has been the object of this investigation.

Method Used.—The method of this investigation of the determination of the minimum densities of the gaseous methylamines is based upon a procedure proposed by Maass and Russell[3] and

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[2] (a) Felsing and Thomas, *J. Ind. Eng. Chem.*, **21**, 1269 (1929); (b) Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); (c) Felsing and Breckley, *J. Phys. Chem.*, **37**, 779 (1933); (d) Felsing and Jessen, THIS JOURNAL, **55**, 4418 (1933); (e) Felsing and Ashby, *ibid.*, **56**, 2226 (1934); (f) Felsing and Phillips, *ibid.*, **58**, 1973 (1936); (g) Patterson with Felsing, *ibid.*, **60**, 2693 (1938); (h) Kenner with Felsing, *ibid.*, **61**, 2451 (1939); (i) Felsing and Ball, *ibid.*, **63**, 2525 (1941); (j) Jones, Spuhler with Felsing, THIS JOURNAL, **64**, 965 (1942); (k) Whitlow with Felsing, *ibid.*, **66**, 2028 (1944).

[3] Maass and Russell, *ibid.*, **40**, 1847 (1918).