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

Organo-silicon Compounds. III.[1] α- and β-Chloroalkyl Silanes and the Unusual Reactivity of the Latter[2]

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The successful chlorination of tetramethylsilane[1] led to a similar study of organo-silicon trichlorides ($RSiCl_3$), compounds which give polymers on hydrolysis.[3] The chlorination products of such compounds would provide additional data on the silicon effect.[1]

In 1939 Kharasch reported sulfuryl chloride activated by benzoyl peroxide as a good chlorinating agent for aliphatic hydrocarbons and many of their derivatives.[4] The application of this method to organo-silicon compounds gives excellent yields of monochlorinated products. It is much more convenient than photochemical chlorination.

Ethyltrichlorosilane, prepared from silicon tetrachloride and ethylmagnesium bromide,[5] was refluxed with sulfuryl chloride in the presence of a small amount of benzoyl peroxide to give a 90% yield of monochlorinated product. There were obtained: α-chloroethyltrichlorosilane (I), b. p. 138° and β-chloroethyltrichlorosilane (II), b. p. 152°. The molar ratio of I to II was 1 to 2.5.

$$CH_3CH_2SiCl_3 \xrightarrow[Bz_2O_2]{SO_2Cl_2} \underset{I}{CH_3—CHCl—SiCl_3} + \underset{II}{CH_2Cl—CH_2—SiCl_3}$$

Like other organic compounds, ethyltrichlorosilane is not chlorinated by sulfuryl chloride in the absence of an organic peroxide.

Methyltrichlorosilane[6] could not be chlorinated with sulfuryl chloride. In this respect it resembles its carbon analog, methylchloroform.[4b] Thus, the $—SiCl_3$ group, like $—CCl_3$, does not permit chlorination of an alpha methyl group with sulfuryl chloride. The more reactive methylene group in ethyltrichlorosilane, however, can be chlorinated. The inactivation of the alpha carbon is still reflected in the predominance of the beta chloro product. This effect is due to the $—SiCl_3$ group and not to silicon alone, as will be shown in a later paper on the chlorination of tetraethylsilane, in which alpha chlorination predominates.

Benzyltrichlorosilane, prepared from silicon tetrachloride and benzylmagnesium chloride,[7] was chlorinated with sulfuryl chloride to give α-chlorobezzyltrichlorosilane, $C_6H_5—CHCl—SiCl_3$, b. p. 243° (735 mm.) and 162° (75 mm.), in 90% yield. This structure is assigned because sulfuryl chloride, catalyzed by organic peroxides, does not chlorinate aromatic nuclei, but does chlorinate aromatic side chains.[4] This is confirmed by the non-chlorination of phenyltrichlorosilane under the same conditions.

Remarkable Activity of a C–Cl Bond Beta to Silicon.—Titration of an organo-silicon chloride with 0.5 *N* alkali gives a neutral equivalent corresponding to the quantitative hydrolysis of the Si–Cl bonds. Titration of α-chloroethyltrichlorosilane gave a value corresponding to the three chlorine atoms attached only to silicon. *The alpha C—Cl bond was left intact.* In this respect α-chloroethyltrichlorosilane resembles silico-neopentyl chloride.[1] Both contain alpha C—Cl bonds inactive to aqueous alkali.

In striking contrast to the above, are the results from alkali titration of β-chloroethyltrichlorosilane. *The beta C—Cl bond reacts as completely as do the Si—Cl bonds.*

$$ClCH_2CH_2SiCl_3 + 4NaOH \longrightarrow CH_2{=}CH_2 + 4NaCl + Si(OH)_4$$

A neutral equivalent corresponding to the *total chlorine* is obtained. It should be recalled that no alkyl chloride can be titrated with cold 0.5 *N* alkali in this manner. The significance of the formation of ethylene in this reaction will be considered in a later paper. Titration of α-chlorobenzyltrichlorosilane attacked only the Si—Cl bonds.

α-Chloroethyltrimethylsilane, Silico-pinacolyl Chloride (I).—The fact that Si–Cl bonds are more reactive than C—Cl bonds with Grignard reagents suggested that these would preferentially attack the former in a compound containing both types of bonds. In line with our interest in highly branched organic chlorides containing a neo silicon atom (silicon attached to four carbons),[1] we have synthesized silico-pinacolyl chloride by the reaction of α-chloroethyltrichlorosilane with methylmagnesium bromide.

$$CH_3—CHCl—SiCl_3 + 3CH_3MgBr \longrightarrow \underset{(I)}{CH_3—CHCl—Si(CH_3)_3}$$

Silico-pinacolyl chloride, like silico-neopentyl chloride, is a colorless stable liquid which can be distilled at atmospheric pressure without decomposition. It readily forms a Grignard reagent. Reaction of silico-pinacolylmagnesium

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[1] Paper II, Whitmore and Sommer, THIS JOURNAL, **68**, 481 (1946).

[2] Presented before the Division of Organic Chemistry at the Cleveland Meeting of the American Chemical Society, April 5, 1944.

[3] *Cf.* Rochow and Gilliam, THIS JOURNAL, **63**, 798 (1941); Hyde and Delong, *ibid.*, **63**, 1194 (1941).

[4] (a) Kharasch and Brown, *ibid.*, **61**, 2142 (1939); (b) *ibid.*, **62**, 926 (1940).

[5] Kipping, *J. Chem. Soc.*, **91**, 214 (1907).

[6] Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 801 (1941).

[7] Martin, Kipping and Meads, *J. Chem. Soc.*, **107**, 463 (1915).

chloride with mercuric chloride gave silico-pinacolylmercuric chloride.

In contrast to the activity with alcoholic silver nitrate of secondary alkyl chlorides, including even pinacolyl chloride, is the inactivity of silico-pinacolyl chloride with this reagent.

Table I gives important physical properties of the silicon compound and its carbon analog.

TABLE I

	B. p.			
	°C.	Mm.	d^{20}	$n^{20}D$
Silico-pinacolyl chloride	117.8	734	0.8768	1.4242
Pinacolyl chloride[8]	109.9	734	0.877	1.4181

Boiling point and refractive index are higher in the silicon compound due to its higher molecular weight. Similarity in density is in accord with the small density change on going from *n*-hexyl chloride to *n*-heptyl chloride. The calculated atomic refraction of silicon (SiRD) in silico-pinacolyl chloride is 7.36, about the same as that in alkyltrimethylsilanes.[9]

Discussion

The assignment of the alpha and beta structures to the two chloroethyltrichlorosilanes was based on the following: (a) Since methylchloroform and methyltrichlorosilane cannot be chlorinated by sulfuryl chloride it is evident that the $—CCl_3$ and $—SiCl_3$ groups reduce the activity of alpha hydrogen in this reaction. Thus the alpha structure is assigned to the chloro compound formed in lesser amount (the lower boiling isomer). (b) The C—Cl bond in the lower boiling isomer is inactive to alkali and thus resembles α-chlorobenzyltrichlorosilane and chloromethyltrimethylsilane. This offers further confirmation of its alpha structure. (c) Treatment of the lower boiling chloro compound with methyl Grignard reagent gives a chloroethyltrimethylsilane which resembles chloromethyltrimethylsilane in its inertness to alcoholic silver nitrate. Again, the alpha structure is confirmed. (d) Aside from the above evidence, it is logical to assume that the alpha isomer would have the lower boiling point because it is the more highly branched. (e) In contrast to the behavior of the alpha compound, the higher boiling chloro compound reacts readily with dilute alkali, with silver nitrate, and with the Grignard reagent with the breaking of both the C—Cl and C—Si bonds and the formation of ethylene. These reactions will be discussed in subsequent papers.

Experimental

Ethyltrichlorosilane.[5]—The Grignard reagent from 570 g. of ethyl bromide was treated as usual with 850 g. of silicon tetrachloride. The product was fractionated through a glass-helix packed column of 30 theoretical plates. There was obtained 475 g. of ethyltrichlorosilane, b. p. 99–100°, yield 60%.

Chlorination of Ethyltrichlorosilane.—A solution of 1300 g. (8 moles) of ethyltrichlorosilane in 1070 g. (8 moles) of sulfuryl chloride was placed in a 5-liter round-bottomed flask fitted with a reflux condenser attached to a phosphorus pentoxide tube. Refluxing of the reaction mixture for twelve hours gave no reaction. Addition of 1 g. of benzoyl peroxide initiated a vigorous reaction resulting in vigorous evolution of hydrogen chloride and sulfur dioxide. The reactants were refluxed on the steam-bath for ten hours. The resulting products were then fractionally distilled in a column of 30 theoretical plates. There were obtained: 440 g. (2.7 moles) of unreacted ethyltrichlorosilane; 216 g. (1.1 moles) of α-chloroethyltrichlorosilane, b. p. 138° (734 mm.) and 550 g. (2.8 moles) of β-chloroethyltrichlorosilane, b. p. 152° (734 mm.). The chloroethyltrichlorosilanes were analyzed for chlorine content by the following method. Samples of these compounds, about 0.1 g., were weighed into gelatin capsules and were fused with 15 g. of sodium peroxide and 1 g. of sucrose in a Parr bomb. The resulting fused melt was dissolved in distilled water and the solution was acidified with nitric acid. Volhard titrations for chloride ion were then performed.

Anal. Calcd. for $C_2H_4SiCl_4$: Cl, 71.7. Found: for α-chloroethyltrichlorosilane, Cl, 71.5, 71.4; for β-chloroethyltrichlorosilane, Cl, 71.7, 71.8.

Alkali Titration of the Chloroethyltrichlorosilanes.—Weighed samples, about 0.5 g., were dissolved in 20 cc. of methanol. Addition of 50 cc. of distilled water was followed by titration with 0.5 *N* alkali using phenolphthalein.

Titration of α-chloroethyltrichlorosilane gave: Cl, 53.8, 53.8; calcd. Cl attached only to silicon, 53.8.

Titration of β-chloroethyltrichlorosilane gave: Cl, 71.7, 71.6; calcd. total Cl attached to silicon and carbon, 71.7.

Benzyltrichlorosilane.[7]—This was prepared from the Grignard reagent from 264 g. of benzyl chloride. Distillation through a 20-plate column gave 125 g. of benzyltrichlorosilane, b. p. 145–148° (100 mm.), yield 26%.

Chlorination of Benzyltrichlorosilane.—In a round-bottomed flask there was placed 125 g. (0.5 mole) of benzyltrichlorosilane. To this was added 54 g. (0.4 mole) of sulfuryl chloride activated by 1 g. of benzoyl peroxide. The flask was fitted with a reflux condenser connected to a phosphorus pentoxide tube and the reaction mixture was refluxed for ten hours. The product was then fractionated in a column of 20 theoretical plates. There were obtained 75 g., 0.3 mole, of unreacted benzyltrichlorosilane and 43 g., 0.17 mole, of α-chlorobenzyltrichlorosilane, b. p. 162° (75 mm.). The latter was analyzed for chlorine content by a peroxide fusion in a Parr bomb.

Anal. Calcd. for $C_7H_6SiCl_4$: Cl, 54.6. Found: Cl, 54.4, 54.3.

Alkali Titration of α-Chlorobenzyltrichlorosilane.—Weighed samples, about 0.8 g., of this compound were titrated in the usual manner. Calcd.: Cl attached only to silicon, 40.8. Found: Cl, 40.8, 40.8.

Methyltrichlorosilane.[6]—The material from 9.9 moles (titrated) of methylmagnesium bromide was fractionated in a column of 30 theoretical plates to give 564 g. of methyltrichlorosilane, b. 64.9–65.1°, yield 38%.

Attempted Chlorination of Methyltrichlorosilane with Sulfuryl Chloride.—In a 500-cc. round-bottomed flask there was placed 75 g. (0.5 mole) of methyltrichlorosilane and 54 g. (0.4 mole) of sulfuryl chloride activated by 1 g. of benzoyl peroxide. The flask was fitted with a reflux condenser connected to a phosphorus pentoxide tube and the reaction mixture was refluxed for forty hours. During this time there was no evolution of hydrogen chloride and sulfur dioxide. Fractionation of the reaction product yielded only starting material.

Two other attempts were made using a procedure similar to the above. In one run carbon tetrachloride, 100 cc., was used as solvent, and in another 100 cc. of nitrobenzene was used. Both of these gave negative results.

Attempted Chlorination of Phenyltrichlorosilane with Sulfuryl Chloride.—By the reaction of 170 g. (1 mole) of

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(8) Whitmore, Bernstein and Mixon, THIS JOURNAL, **60**, 2539 (1938).

(9) Whitmore *et al.*, Paper I, THIS JOURNAL, **68**, 475 (1946).

silicon tetrachloride with one equivalent of phenylmagnesium bromide there was prepared 81 g. (0.4 mole) of phenyltrichlorosilane, b. p. 198° (744 mm.). The compound was analyzed for chlorine content by titration with standard alkali.

Anal. Calcd. for $C_6H_5SiCl_3$: Cl, 50.3. Found: Cl, 50.1.

In a 1-liter round-bottomed flask there was placed the above 81 g. of phenyltrichlorosilane and 54 g. (0.4 mole) of sulfuryl chloride plus 1 g. of benzoyl peroxide. The flask was then equipped with a reflux condenser attached to a phosphorus pentoxide tube and the reaction mixture was refluxed on the steam-bath for twelve hours. During this time there was no evolution of sulfur dioxide and hydrogen chloride. Fractionation of the reaction product yielded only starting material.

Synthesis of Silico-pinacolyl Chloride. α-Chloroethyltrimethylsilane.—By the usual method, there was prepared 3.5 equivalents of methylmagnesium bromide in 1500 cc. of dry ether. Next, α-chloroethyltrichlorosilane, 200 g. (1 mole), was dissolved in 400 cc. of anhydrous ether and the solution was placed in a 5-liter three-necked flask. The flask was equipped with a mercury-sealed stirrer, a reflux condenser and a dropping funnel. The system was protected from moisture by a sulfuric acid scrubber. The reaction flask was cooled in an ice-bath and the methylmagnesium bromide was added at a slow rate. Time of addition was three hours. The reaction mixture was then stirred at room temperature for eleven hours. Then, the reaction flask was cooled in an ice-bath and 2 liters of water was added, followed by 50 cc. of concentrated hydrochloric acid. The ether layer was separated and the water layer extracted with 500 cc. of ether. The ether solution of the product was fractionated in a 12-plate, glass-helix packed column. There was obtained 72.3 g. (0.53 mole) of silico-pinacolyl chloride, b. p. 117.8° (735 mm.), $n^{20}D$ 1.4242. This is a yield of 53% based on the amount of α-chloroethyltrichlorosilane used. The compound was analyzed for chlorine content by peroxide fusion in a Parr bomb.

Anal. Calcd. for $C_5H_{11}SiCl$: Cl, 26.0. Found: Cl, 25.7, 25.6.

Silico-pinacolylmercuric Chloride, α-Chloromercuriethyltrimethylsilane.—The method used was essentially that of Marvel, Gauerke and Hill.[10] The Grignard reagent was prepared from 4 g. (0.03 mole) of silico-pinacolyl chloride and 0.8 g. (0.03 mole) of magnesium turnings in 20 cc. of anhydrous ether. Reaction of silico-pinacolylmagnesium chloride with 17 g. (0.06 mole) of dry mercuric chloride in 25 cc. of ether gave as product 4.1 g. of silico-pinacolylmercuric chloride, m. p. 97°, a yield of 40%. Silico-pinacolylmercuric chloride was analyzed for mercury by the titration method of Whitmore and Sobatzki.[11]

Anal. Calcd. for $C_5H_{11}SiHgCl$: Hg, 59.5. Found: Hg, 58.4.

Silico-pinacolyl Chloride with Silver Nitrate.—To 10 cc. of ethanolic silver nitrate was added 0.5 cc. of silico-pinacolyl chloride. After one hour at room temperature no reaction had taken place. A similar experiment using 10 cc. of 20% aqueous silver nitrate also gave a negative result.

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Summary

1. Sulfuryl chloride, catalyzed by benzoyl peroxide, is an excellent chlorinating agent for alkyltrichlorosilanes other than methyl.

2. The $—SiCl_3$ group, like the $—CCl_3$ group, decreases the ease of alpha chlorination. Thus methyltrichlorosilane and methylchloroform are inert to sulfuryl chloride and peroxide. Moreover, in spite of the usual greater reactivity of secondary hydrogen, the primary hydrogen atoms in ethyltrichlorosilane are more readily replaced than the secondary H atoms.

3. α-Chloroethyltrichlorosilane, β-chloroethyltrichlorosilane and α-chlorobenzyltrichlorosilane have been prepared.

4. Methylmagnesium bromide reacts with the silicon–chlorine bonds in α-chloroethyltrichlorosilane to give α-chloroethyltrimethylsilane (silico-pinacolyl chloride).

5. In addition to the normal reaction of dilute alkali with silicon–chlorine bonds, it reacts quantitatively with the beta chlorine atom in β-chloroethyltrichlorosilane. This high reactivity of the $—CH_2Cl$ group is unique. Similar titration of the alpha isomer attacks only the silicon–chlorine bonds.

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[10] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[11] Whitmore and Sobatzki, *ibid.*, **55**, 1171 (1933).