4. The silicon compounds have lower viscosities than alkanes of corresponding molecular weight.

5. Comparison of trimethyl and triethyl silicon compounds with trimethyl and triethyl alkanes of corresponding molecular weight, *i. e.*, Me_3SiEt with Me_3CPr, reveals that the silicon compounds have lower boiling points, higher densities and higher refractive indices than the carbon compounds. This is attributed to the greater compactness of the tetraalkylsilanes.

6. The change of viscosity and density with temperature is about the same in tetraalkylsilanes and in alkanes.

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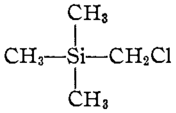
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Organo-silicon Compounds. II.[1] Silicon Analogs of Neopentyl Chloride and Neopentyl Iodide. The Alpha Silicon Effect[1]

BY FRANK C. WHITMORE AND LEO H. SOMMER

The rapidly growing importance of organosilicon chemistry suggested a thorough study of haloalkyl silicon compounds as of practical as well as theoretical interest. Only a few of these compounds have been reported.[2] Among these are the monochlorinated derivatives of tetraethylsilane.[2a] The lower boiling of these two isomers was assigned the α-chloroethyltriethylsilane structure. Since we wished first to investigate the properties of a simple α-haloalkyltrialkylsilane, we synthesized Compound I, chloromethyltrimethylsilane (silico-neopentyl chloride).[3]



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CH_2Cl \qquad (I)$$

We are interested in this compound because of the importance of the analogous neopentyl grouping.[4]

We have compared the properties of chloromethyltrimethylsilane with those of its carbon analog; neopentyl chloride. Such studies give information on the "silicon effect," the effect of a silicon atom on the reactivity of a functional group in an attached carbon chain.

Tetramethylsilane was prepared from silicon tetrachloride and methylmagnesium bromide.[5]

The liquid phase, photochemical chlorination of tetramethylsilane goes about as readily as that of neopentane.[4] It gives Compound I in fair yield.

$$(CH_3)_4Si + Cl_2 \longrightarrow \underset{(I)}{(CH_3)_3SiCH_2Cl} + HCl$$

Silico-neopentyl chloride (I) is a colorless stable liquid which can be distilled at atmospheric pressure without decomposition. It readily forms a Grignard reagent, the first aliphatic example of such a compound containing silicon. The synthetic possibilities of this reagent are being developed.

Reaction with mercuric chloride gave siliconeopentylmercuric chloride (chloromercurimethyltrimethylsilane, trimethylsilylmethylmercuric chloride).

Silico-neopentyl chloride (I) is less reactive than *n*-hexyl chloride, but far more reactive than the very inert neopentyl chloride.[4a] Results with nine reaction mixtures justify these important conclusions. Unless otherwise indicated each reaction was carried out at the boiling point of the solvent for four hours. Whereas *n*-hexyl chloride reacted completely with sodium ethylate in absolute ethanol, (I) reacted only about 40% under the same conditions. The activity of the two compounds with the following four reagents was approximately the same. The figures in parentheses indicate the percentage reaction, the first figure in each case corresponding to chloromethyltrimethylsilane (I) and the second to *n*-hexyl chloride: potassium acetate in absolute ethanol (23–29); potassium acetate in glacial acetic acid (26–32); potassium hydroxide in absolute ethanol (52–69); potassium hydroxide in 70:30 aqueous ethanol (16–22). It will be noted that (I) appears slightly less active in each case. Aqueous potassium hydroxide gave no reaction with (I) but gave about 1% conversion with the alkyl halide. Refluxing for eight hours with aqueous ethanol (1:1) gave no reaction with (I) and less than 1% change with the other chloride. Boiling (I) for five minutes with ethanolic silver nitrate gave no action, whereas similar treatment of

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(1) Presented before the Division of Organic Chemistry at the Pittsburgh Meeting of the American Chemical Society, September 6, 1943. Paper I, Whitmore, *et al.*, THIS JOURNAL, **68**, 475 (1946).

(2) (a) Ushakov and Itenberg, *J. Gen. Chem. U. S. S. R.*, **7**, 2495 (1937); (b) Krieble and Elliot, THIS JOURNAL, **67**, 1810 (1945).

(3) We use the silico-neopentyl naming as well as that suggested by Sauer, *J. Chem. Ed.*, **21**, 303 (1944), and the unpublished Dow Committee Report of July 1, 1944.

(4) (a) Whitmore and co-workers, *ibid.*, **55**, 4161 (1933); **61**, 1585, 1586 (1939); **63**, 124 (1941); **64**, 1783 (1942); (b) Skell and Hauser, *ibid.*, **64**, 2633 (1942); (c) Aston and co-workers, *J. Chem. Phys.*, **12**, 336 (1944); (d) Kharasch and Fineman, THIS JOURNAL, **63**, 2776 (1941); (e) van Wijk and others, *Physica*, **7**, 45 (1940); (f) Halford, *J. Chem. Phys.*, **8**, 496 (1940); (g) Kincaid and Henriques, Jr., THIS JOURNAL, **62**, 1474 (1940); (h) Silver, *J. Chem. Phys.*, **7**, 1113 (1939); (i) Frey, *C. A.*, **37**, 5079 (1943).

(5) (a) Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Berlin, 1937, p. 260; (b) Bygden, *Ber.*, **44**, 2640 (1911).

n-hexyl chloride gave a copious precipitate of silver chloride. Similar treatment with aqueous silver nitrate gave no precipitate with either chloride. In contrast to the inactivity of neopentyl chloride with sodium iodide in dry acetone,[4a] its silicon analog (I) gave the corresponding iodide in good yield.

$$(CH_3)_3SiCH_2Cl + NaI \longrightarrow \underset{(II)}{(CH_3)_3SiCH_2I} + NaCl$$

Iodomethyltrimethylsilane, silico-neopentyl iodide (II) is the first iodoalkyl silicon compound reported. It is a colorless, stable liquid which can be distilled at atmospheric pressure without decomposition. It underwent no decomposition or discoloration on standing in an ordinary corked vial in the dark for over a year.

All alkyl iodides, including even neopentyl iodide,[4a] react with aqueous and alcoholic silver nitrate. Silico-neopentyl iodide (II) *does not react* with these reagents. In this respect the iodide and chloride are alike. Inertness of both compounds with silver nitrate reagents is in sharp contrast to the reactivity of silico-neopentyl chloride (I) with other reagents, including sodium iodide. Silico-neopentyl iodide readily forms the Grignard reagent in excellent yield.

Table I gives physical properties for silico-neopentyl chloride and iodide and for their carbon analogs.

TABLE I

	B. p.					
	°C.	Mm.	$n^{20}D$	d^{20}	*M*RD	SiRD
Chloromethyltrimethylsilane (I)	97.1	734	1.4180	0.8791	35.17	7.42
Neopentyl chloride	83.3	740	1.4043	0.865		
Iodomethyltrimethylsilane (II)	139.5	747	1.4917	1.4431	43.02	7.34
Neopentyl iodide	132.6	734	1.4890	1.494		

The silicon compounds have higher boiling points and refractive indices, possibly due to their higher molecular weights. Although substitution of the central carbon by silicon decreases the density of the iodide by 0.05 unit, as would be expected from the increase in molecular weight surprisingly the same substitution *increases* the density of the chloride slightly (0.014 unit). Thus, the greater compactness of the silicon compound[1] in this case overbalances the increase in molecular weight. Atomic refraction of silicon in the two compounds is about the same as in the *n*-alkyltrimethylsilanes.[1]

Relative Electronegativity of the Silico-neopentyl Group (Trimethylsilylmethyl Group)

In 1926 Kharasch defined the electronegativity of an organic group as the affinity of that group for electrons in a stable molecule and proposed a method for measuring the relative electronegativities of organic groups.[6] The method involves preparation of an unsymmetrical organo-mercury compound. This is then treated with ethanolic hydrogen chloride

$$R{-}Hg{-}R' + HCl \longrightarrow RHgCl + R'H$$

The group which takes the proton, in this case R′, and forms the hydrocarbon is more electronegative than the other group, in this case R. Thus R′ is above R in the Kharasch table of decreasing electronegativities.

Earlier work in this Laboratory placed the highly branched aliphatic groups, including neopentyl, in the Kharasch table.[7] The relative electronegativity of the silico-neopentyl group was determined to throw more light on the alpha silicon effect.

Silico-neopentylmercuric chloride was treated with the appropriate Grignard reagents for the synthesis of silico-neopentyl methyl mercury, silico-neopentyl *n*-hexyl mercury and silico-neopentyl phenyl mercury. These compounds were treated with ethanolic hydrogen chloride with the following results ($R = Me_3SiCH_2{-}$)

$$RHgCH_3 + HCl \longrightarrow RH + CH_3HgCl$$
$$RHg{-}n\text{-}C_6H_{13} + HCl \longrightarrow RH + n\text{-}C_6H_{13}HgCl$$
$$RHgC_6H_5 + HCl \longrightarrow RHgCl + C_6H_6$$

The silico-neopentyl group (R) is therefore more electronegative than the methyl and *n*-hexyl groups, and less electronegative than phenyl. The phenyl group is known to be more electronegative than alkyl groups, of which methyl is the most electronegative; the neopentyl group has been shown to be less electronegative than other primary alkyl groups.[7] The relative capacity of the silico-neopentyl group for electron-attraction is given in Table II. The silico-neopentyl group is therefore more electron-attracting than any alkyl group and less electron-attracting than phenyl.

TABLE II

ORDER OF DECREASING ELECTRONEGATIVITY

$$\text{Phenyl} \longrightarrow (CH_3)_3SiCH_2{-} \longrightarrow CH_3{-} \longrightarrow n\text{-}C_6H_{13}{-} \longrightarrow (CH_3)_3CCH_2{-}$$

Discussion of the Alpha Silicon Effect

A. The Steric Factor.—Neopentyl halides are inert in reactions involving attack of a reagent at the back of the carbon holding the halogen (bimolecular nucleophilic substitutions).[8] Typical reagents for this type of reaction are: sodium ethylate in ethanol, alcoholic potassium hydroxide, alcoholic potassium acetate and sodium iodide in dry acetone. With these reagents silico-neopentyl chloride is reactive, but less so than is *n*-hexyl chloride.

The extreme lack of reactivity of the neopentyl halides is attributed to the shielding effect of the *t*-butyl group which prevents rearward attack of a reagent on the back face of the methylene car-

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(6) Kharasch and Marker, THIS JOURNAL, **48**, 3140 (1926).

(7) Whitmore and Bernstein, *ibid.*, **60**, 2626 (1938).

(8) (a) Hughes, *Trans. Faraday Soc.*, **37**, pp. 620–625 (1941); (b) Bartlett and Rosen, THIS JOURNAL, **64**, 543 (1942).

bon opposite to the vertex occupied by the halogen.[8] Such rearward attack is apparently made easier by substitution of the Me_3Si– group for *t*-butyl. Additional evidence for this is provided by certain physical studies, and by the striking difference between molecular models of silico-neopentyl chloride and neopentyl chloride.

Physical evidence for the crowding of methyl groups in neopentane has been found by Aston[9] in his studies on hindered rotation. Similar studies on tetramethylsilane have shown that the larger size of the silicon atom, covalent radius 1.17 Å., compared to 0.77 Å. for carbon, results in greatly increased clearance and decreased interaction between the methyl groups in the silicon compound.[10] This greater clearance between methyl groups on silicon is clearly shown by a comparison of scale molecular models of silico-neopentyl chloride and neopentyl chloride. These models indicate that the shielding effect of the Me_3Si– group is far less than that of the Me_3C– group, and that silico-neopentyl chloride should therefore undergo rearward attack more readily than its carbon analog.

B. **Electronegativity.**—The activity of silico-neopentyl chloride in rearward attack reactions is in sharp contrast to the inertness of both the chloride and iodide with aqueous and alcoholic silver nitrate. These reagents act with organic halides by attacking the halogen together with its shared electron pair (electrophilic attack on halogen). The driving force of the reaction is the "affinity" of silver ion for halide ion.[11] Halides of highly electronegative groups are least reactive with silver ion because of the tenacity with which such groups hold the shared electron-pair of the halogen. For example, the order of *increasing* reactivity for alkyl halides is primary $<$ secondary $<$ tertiary.[12] This corresponds to the order of *decreasing* electronegativity of the three types of alkyl groups. The inertness of silico-neopentyl chloride and iodide with silver nitrate reagents may, therefore, be attributed to the high electronegativity of the silico-neopentyl group.

It will be shown in a later paper that the inertness of I and II with silver nitrate is merely one of many differences between organo-silicon and organic compounds which result from the following difference between silicon and carbon: A tetravalent silicon atom, in contrast to tetravalent carbon, is electronically unsaturated and thus behaves as an electron sink relative to carbon.[13] An observed shortening of the carbon–silicon bond lengths in chloromethyltrimethylsilane as well as a shortening of the carbon–chlorine bond length in this compound appear to result from this same fundamental difference between silicon and carbon.[14]

Experimental

Tetramethylsilane.—The chief difficulty encountered in the preparation of this material is due to its volatility (b. p. 26°). In order to prevent extensive losses, suitably placed traps, cooled to −70° by a mixture of Dry Ice and acetone, were used. Methylmagnesium bromide, 19.1 equivalents in 6 liters of dry ether, was prepared in a 12-liter flask equipped with a mercury-sealed stirrer, an efficient reflux condenser and a dropping funnel. The flask was cooled in an ice-bath and a solution of 748 g. (4.4 moles) of silicon tetrachloride in 1 liter of dry ether was added to the Grignard reagent over a period of eight hours. The reactants were then stirred at room temperature for fourteen hours. The tetramethylsilane which resulted was separated from ethyl ether by the use of concentrated sulfuric acid.[5b] In a 5-liter three-necked flask equipped with a mercury-sealed stirrer and a reflux condenser, there was placed 1800 cc. of concentrated sulfuric acid, and the flask was surrounded with an ice-bath. The mixture of tetramethylsilane and ether was then slowly distilled into the acid. The tetramethylsilane, which appeared as a clear layer above the sulfuric acid solution of ether, was then distilled into a receiver maintained at −70°. Fractional distillation gave 240 g. of tetramethylsilane, b. p. 26°, a yield of 63% based on the silicon tetrachloride used.

Silico-neopentyl Chloride (I).—To prevent loss of tetramethylsilane, suitably placed traps maintained at −70° were used. A solution of 174 g. (2 moles) of tetramethylsilane in 150 cc. of dry carbon tetrachloride was placed in a 1-liter three-necked flask equipped with a mechanical stirrer, an efficient reflux condenser and a chlorine inlet tube extending almost to the bottom of the flask. There was then added 3 g. of phosphorus pentachloride, and the contents of the flask were illuminated by a 450 watt G. E. sunlight lamp. Dry chlorine was then passed in for four hours at the rate of half a mole per hour. Fractionation of the product by means of a 15-plate glass-helix packed column gave 53 g. (0.44 mole) of silico-neopentyl chloride, b. p. 97.1° (734 mm.), n^{20}_{D} 1.4180, 93 g. of polychlorinated tetramethylsilane and 62 g., 0.7 mole, of unreacted tetramethylsilane. The yield of silico-neopentyl chloride based on the unrecovered tetramethylsilane was 33%. Silico-neopentyl chloride was analyzed for chlorine as follows: A weighed sample of the compound, about 0.2 g., was placed in a gelatin capsule and fused in a Parr bomb with 15 g. of sodium peroxide and 1 g. of sucrose. The resulting fused melt was then treated with hot distilled water followed by acidification with nitric acid. The resulting solution was then titrated for chloride ion by the Volhard method.

Anal. Calcd. for $C_4H_{11}SiCl$: Cl, 28.92. Found: Cl, 28.84, 28.89.

Silico-neopentylmagnesium Chloride, $(CH_3)_3SiCH_2MgCl$.—In a 200-cc. flask there was placed 2.5 g., 0.1 mole, of magnesium turnings and 50 cc. of dry ether. The flask was equipped with a mercury-sealed stirrer, a reflux condenser and a dropping funnel. The system was connected to the atmosphere through a concentrated sulfuric acid trap. Next, 12.2 g., 0.1 mole, of silico-neopentyl chloride was dissolved in 25 cc. of dry ether and placed in the dropping funnel. About 5 cc. of this solution was added to the magnesium but reaction failed to start. On addition of one drop of ethyl bromide reaction started vigorously. Addition of silico-neopentyl chloride was then resumed and reaction continued to take place. Addition was complete in two hours. The reaction mixture

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(9) Aston, *Chem. Rev.*, **27**, 67 (1940).

(10) Aston, Kennedy and Messerly, This Journal, **63**, 2343 (1941).

(11) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 138–140.

(12) Reference 11, p. 154.

(13) Sidgwick has shown that silicon, in common with the other elements of the second short period, has a maximum covalency of 6 compared to 4 for carbon. See Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1927, pp. 155–157.

(14) Unpublished electron diffraction data by Bauer and Hastings of Cornell University indicate that the C–Si bond lengths and the C–Cl bond length are shortened to the extent of 0.06 and 0.03 Å., respectively.

was then stirred at room temperature for ten hours, and was then titrated in the usual manner to determine the yield of Grignard reagent. The yield of silico-neopentylmagnesium chloride was 90% of the theoretical.

Silico-neopentylmercuric Chloride (Chloromercurimethyltrimethylsilane), $(CH_3)_3SiCH_2HgCl$.—According to the method of Marvel,[15] the Grignard reagent from 4 g. of the chloride was converted to the mercury compound, m. p. 74–76°, wt. 9.2 g., yield 80%. Recrystallization from 60% aqueous ethanol gave material melting sharply at 76°. It was analyzed for mercury by the titration method of Whitmore and Sobatzki.[16]

Anal. Calcd. for $C_4H_{11}SiHgCl$: Hg, 63.5. Found: Hg, 62.3.

Silico-neopentyl Iodide, Iodomethyltrimethylsilane, $(CH_3)_3SiCH_2I$.—Acetone, U. S. P., was refluxed with calcium oxide and potassium permanganate for six hours and fractionated. In a 2-liter flask there was placed 500 cc. of dry acetone and 75 g. (0.5 mole) of dry sodium iodide. To this solution there was added 36 g. (0.3 mole) of silico-neopentyl chloride. After refluxing for twenty-four hours, the precipitated sodium chloride was removed by filtration. The acetone solution was then charged to a fractionating column and most of the acetone was distilled. The residue was treated with 150 cc. of water and the lower layer was dried and fractionated. There was obtained 43.5 g. (0.2 mole) of silico-neopentyl iodide, b. p. 139.5° (744 mm.), n^{20}_{D} 1.4917. The yield was 70%. Silico-neopentyl iodide was analyzed for iodine by peroxide fusion in a Parr bomb.

Anal. Calcd. for $C_4H_{11}SiI$: I, 59.31. Found: I, 59.19, 59.23.

Silico-neopentylmagnesium Iodide.—In a 50-cc. flask there was placed 2.14 g., 0.01 mole, of silico-neopentyl iodide and 0.24 g., 0.01 mole, of magnesium plus 5 cc. of anhydrous ether. A crystal of iodine was added to the reaction mixture. Reaction started immediately and continued until almost all of the magnesium was used up. The reaction mixture was then refluxed for twenty minutes. The usual titration indicated 0.0095 equivalent of Grignard reagent, yield 95%.

Silico-neopentyl Iodide with Silver Nitrate.—To 10 cc. of 20% aqueous silver nitrate there was added 0.5 cc. of silico-neopentyl iodide. No precipitate of silver iodide formed even after one hour at room temperature. Methyl iodide in a similar experiment reacted instantaneously. Silico-neopentyl iodide did not react with aqueous silver nitrate even after five minutes of boiling.

Silico-neopentyl iodide, 0.5 g., gave no reaction with ethanolic silver nitrate after five minutes at room temperature. Even on boiling with this reagent for five minutes the halide gave only slight opalescence. In similar experiments methyl iodide reacted instantaneously.

Relative Electronegativity of the Silico-neopentyl Group.—The Grignard reagent was prepared from 2.4 g., 0.02 mole, of *n*-hexyl chloride and 0.48 g., 0.02 mole, of magnesium in dry ether. Silico-neopentylmercuric chloride, 2.4 g., 0.007 mole, was added to the Grignard reagent in small portions with stirring. The reaction mixture warmed up slightly but at no time was the heat of reaction sufficient to cause refluxing of the ether. The silico-neopentylmercuric chloride dissolved readily in the Grignard solution and a gelatinous precipitate of magnesium chloride etherate was formed. Next, the reaction mixture was allowed to stand at room temperature for three hours. The excess Grignard reagent was then decomposed by addition of 20 cc. of 4% sulfuric acid solution. During the hydrolysis, which was done very slowly, the reaction flask was cooled in an ice-bath. The ether layer was separated and dried with 7 g. of anhydrous sodium sulfate. Next, the ether was removed under vacuum at room temperature and the residue divided into two portions.

To one portion of the silico-neopentyl *n*-hexyl mercury was added 4 cc. of saturated alcoholic hydrogen chloride. Reaction took place instantaneously and the alkyl mercuric chloride precipitated in the form of plates. The reaction mixture was heated on the steam-bath for ten minutes and then 2 cc. of water was added. The reaction mixture was cooled and the crystals of the product were filtered and dried at 110°. Melting point of the product was 121–123°; melting point of pure *n*-hexylmercuric chloride is 125°. Mixed melting point of the product with pure *n*-hexylmercuric chloride was 124°.

To the second portion of the silico-neopentyl *n*-hexyl mercury was added a saturated solution of mercuric chloride in absolute ethanol. Rapid reaction took place and a white solid precipitated. By fractional crystallization from 80% ethanol–water solution there was obtained *n*-hexylmercuric chloride, m. p. 120–122°, and silico-neopentylmercuric chloride m. p. 75–76°. The *n*-hexylmercuric chloride precipitated first.

Using a procedure like that above it was found that silico-neopentyl methyl mercury, on treatment with ethanolic hydrogen chloride, gave methylmercuric chloride m. p. 169–170°. Silico-neopentyl phenyl mercury gave silico-neopentylmercuric chloride, m. p. 76°, on treatment with ethanolic hydrogen chloride.

Acknowledgments.—We thank the Miner Laboratories of Chicago and the Minnesota Mining and Manufacturing Company of St. Paul for help in this work.

Summary

1. Silicon analogs of neopentyl chloride and neopentyl iodide have been synthesized and their reactions have been studied.

2. These halides are far more active than their carbon analogs with reagents such as non-aqueous sodium iodide solutions which attack alkyl halides by a Walden inversion mechanism (bimolecular nucleophilic substitutions, S_N2), but are inactive with silver nitrate, aqueous or alcoholic, which attacks alkyl halides by a different mechanism (electrophilic attack on halogen).

3. By the Kharasch method, the electronegativity of the silico-neopentyl group (Me_3SiCH_2—) has been determined. It falls just below phenyl in the decreasing series: phenyl, Si-neopentyl, methyl, *n*-hexyl, neopentyl.

4. The strong electronegativity of the carbon–silicon grouping is attributed to the electronic unsaturation of the tetracovalent silicon atom.

5. The higher activity in S_N2 reactions and the inactivity toward silver nitrate are explained on the basis of steric relations and of high electronegativity respectively.

STATE COLLEGE, PA. RECEIVED NOVEMBER 5, 1945

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

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