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# TETRAKIS(TRIMETHYLSILYL)SILANE*

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## INTRODUCTION

In 1959 the preparation of tetrakis(triphenylsilyl)silane was attempted by a reaction between triphenylsilyllithium and silicon tetrachloride[2]. The only products isolated were hexaphenyldisilane, triphenylsilane and polymeric material. Recently, Merker and Scott, in a study concerned with a related tetrakis type, described a technique they termed the *in situ* Grignard reaction which involved the addition of a polyhalide of carbon to a solution of a monochlorosilane in tetrahydrofuran in which magnesium metal was suspended[3,4,5]. The broad utility of this one-step reaction is illustrated by the variety of structurally novel compounds that have been synthesized from readily available starting materials. Of considerable interest is the preparation of tetrakis(trimethylsilyl)methane by a reaction between some polyhalides ($CBr_nCl_{4-n}$), chlorotrimethylsilane and magnesium[5].

$$CBr_nCl_{4-n} + 4\,(CH_3)_3SiCl + 4\,Mg \xrightarrow{\text{THF}} [(CH_3)_3Si]_4C$$

The yield of the tetrakis compound, using various perhalomethyl compounds was low (*ca.* 30%) and little or no reaction was observed when carbon tetrachloride was used. Tetrakis(trimethylsilyl)methane was prepared in *ca.* 65% yield from a reaction between carbon tetrachloride, chlorotrimethylsilane and lithium in tetrahydrofuran[6,7], employing the procedure we have reported for the synthesis of tetrakis(trimethylsilyl)silane[1].

We now wish to report in more detail the preparation and some of the properties of tetrakis(trimethylsilyl)silane. This compound has provided access to highly interesting organosilicon compounds heretofore unavailable[8-11].

## RESULTS AND DISCUSSION

Tetrakis(trimethylsilyl)silane (I), the first known tetrasilylsubstituted silane, was synthesized in yields of 60–70% (see Table 1) by reactions between silicon tetrachloride, chlorotrimethylsilane and lithium in THF:

$$SiCl_4 + 4\,(CH_3)_3SiCl + 8\,Li \xrightarrow{\text{THF}} \underset{\text{(I)}}{[(CH_3)_3Si]_4Si} + 8\,LiCl$$

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* A preliminary communication of the preparation of tetrakis(trimethylsilyl)silane has been published[1].

The highest yields were obtained when silicon tetrachloride was added to an excess of chlorotrimethylsilane and an excess of lithium; and the reaction mixture was very vigorously stirred for more than 24 hours at room temperature, and the product was purified by sublimation.

### *Mechanism of formation of (I)*

Compound (I) may result via a sequence of consecutive formations of silyllithium compounds, followed by a coupling reaction with chlorotrimethylsilane (Scheme 1). Thus, the mode of formation of (I) may be explained on the basis of the "heterogeneity"[12] of the system. This mechanism is in agreement with the experimental observations: the highest yields of (I) were obtained when silicon tetrachloride dissolved in THF was added to chlorotrimethylsilane and lithium in THF.

SCHEME 1

$SiCl_4 + Li \rightarrow LiSiCl_3 + LiCl$
$LiSiCl_3 + (CH_3)_3SiCl \rightarrow (CH_3)_3SiSiCl_3 + LiCl$
$(CH_3)_3SiSiCl_3 + Li \rightarrow (CH_3)_3SiSiCl_2Li + LiCl$
$(CH_3)_3SiSiCl_2Li + (CH_3)_3SiCl \rightarrow [(CH_3)_3Si]_2SiCl_2 + LiCl$
$[(CH_3)_3Si]_2SiCl_2 + Li \rightarrow [(CH_3)_3Si]_2SiClLi + LiCl$
$[(CH_3)_3Si]_2SiClLi + (CH_3)_3SiCl \rightarrow [(CH_3)_3Si]_3SiCl + LiCl$
$[(CH_3)_3Si]_3SiCl + Li \rightarrow [(CH_3)_3Si]_3SiLi + LiCl$
$[(CH_3)_3Si]_3SiLi + (CH_3)_3SiCl \rightarrow (I) + LiCl$

Another possible route leading to the formation of (I) might involve the intermediate formation of some higher branched-chain polysilane compounds such as hexakis(trimethylsilyl)disilane[13].

An additional possibility is the intermediate formation of silirenes and dilithiosilanes of the types $Cl_n[(CH_3)_3Si]_{2-n}Si$: and $Cl_n[(CH_3)_3Si]_{2-n}SiLi_2$, respectively. These intermediates probably have very little significance in the formation of (I), since there is no definitive evidence for the existence of dilithiosilanes of this nature[2] and the existence of silirenes in reactions of this type is not well documented[14]. The intermediate formation of silyl radicals is possible.

### *Physical properties of (I)*

Compound (I) is a white, crystalline, waxy, odorless solid, which sublimes in the form of fern-shaped crystals. It is very soluble in most organic solvents, sparingly soluble in ethanol and insoluble in methanol.

Unexpected for a permethylated polysilane, compound (I) is an extraordinarily high melting solid and it exhibits a high degree of volatility. In a sealed tube, it melts at 319–321°* without decomposition, and does not melt in an open tube but sublimes readily and completely below 265°. Even upon standing at room temperature and atmospheric pressure, it sublimes very slowly. The uncommonly high melting point of (I) is associated with its branched-chain and its very high degree of symmetry. Timmerman[15] has suggested that branched-chain molecules of high symmetry can absorb a considerable amount of energy, before their vibration cause a disruption in the

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* The previously reported melting point of 261–263° (ref. 1) is presumably a transition point. The authors are grateful to R. L. HARRELL and S.-Y. SIM for their assistance in checking this melting point.

crystal lattice. That is, the more symmetrical a molecule, the more rotational freedom it can attain in the solid state before melting. This causes a relatively large gain in entropy in the solid state as the temperature increases and the entropy of fusion correspondingly decreases*. For example, hexamethylethane melts at 104.1° and has a liquid interval of only 2.8°. Compound (I) and adamantane represent extreme examples of the effect of symmetry on the melting point. Like compound (I), adamantane does not melt under ordinary conditions but sublimes readily. In a sealed tube, adamantane melts at 268°. The known isomers of (I) and adamantane have considerably lower melting points: isocyclene, 4,7,7-trimethyltricyclo [2.2.0] heptane, an isomer of adamantane, has the next highest melting point of 119° and a boiling point of 150–151°; and dodecamethylpentasilane[18], the only known isomer of (I), has a boiling point of 268°. The great disparity between the melting point of adamantane and its isomer, and (I) and its isomer, is undoubtedly associated with their high symmetry which is best depicted by molecular models as a sphere. It is noteworthy that compound (I) melts appreciably higher than some of its related highly symmetrical derivatives: namely, tetrakis(dimethylsilyl)silane (II) (m.p. 40–42°)[8] and tetrakis(dimethylphenylsilyl)silane (III) (m.p. 133–135°)[9].

$[H(CH_3)_2Si]_4Si$ (II)

$[Ph(CH_3)_2Si]_4Si$ (III)

Another interesting thermal property exhibited by (I) is that it appears to undergo a phase transition to another solid form at 170–180°**. Similar behavior is displayed by other highly symmetrical molecules; for example, adamantane[19] undergoes a phase transition at −64.38° and tetrakis(trimethylsilyl)methane[5] at 195–210°. The transition is probably of the pseudo-rotational-reorientation type[19]. That is, the transition presumably involves an increase in molecular freedom in which the molecules rotate more freely, or assume different, random orientation on the lattice sites of the high temperature form.

Compound (I) also possesses a high degree of thermal stability; it is stable above 400°***.

### *Chemical properties*

The silicon–silicon bond of (I) is cleaved by a wide variety of reagents. When (I) was treated with either one mole of bromine in benzene or carbon tetrachloride, or phosphorous pentachloride in benzene, sym-tetrachloroethane or carbon tetrachloride, 60–65% recovery of (I) was realized; but no other products have so far been isolated. In reactions between (I) and nucleophilic reagents, such as aqueous piperidine or sodium methoxide in methanol, none of (I) was recovered. The products of these reactions were mixtures of compounds which were not separated; but their infrared spectra indicated the presence of Si–O and Si–OH groups. Presumably, the primary cleavage products of these reactions are more reactive than the tetrakis compound. The less symmetrical compounds, tris(trimethylsilyl)methylsilane and

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* For a review of the effect of symmetry on the melting point see ref. 16 and 17.

** No attempt was made to determine all of the transition points.

*** The thermal stability was determined in a sealed tube which was completely submerged in a Mel Temp melting point block. No change in the melting point was observed when the compound was remelted after heating above 400°.

tris(trimethylsilyl)silane, undergo cleavage of the silicon–silicon bond by phosphorus pentachloride or chlorine in carbon tetrachloride, affording good yields of chlorinated derivatives[10,20]:

$$[(CH_3)_3Si]_3SiCH_3 + PCl_5 \text{ or } Cl_2 \xrightarrow{CCl_4} [(CH_3)_3Si]_2Si(CH_3)Cl$$

$$[(CH_3)_3Si]_3SiH + PCl_5 \text{ or } Cl_2 \xrightarrow{CCl_4} [(CH_3)_3Si]_2SiCl_2$$

The cleavage of only one silicon–silicon bond of (I) was achieved by its reaction with organo- and silyllithium compounds[9], sodium–potassium alloy[9], lithium aluminum hydride[9], and lithium or sodium and biphenyl[20].

## EXPERIMENTAL

All glassware was oven-dried before use and purged while hot with oxygen-free nitrogen. The tetrahydrofuran was freed from moisture before use by storing over sodium wire for 24 h unless otherwise specified.

Compound (I) was identified by vapor phase chromatography and infrared because of difficulties in obtaining reproducible melting points on an analytical sample. VPC was carried out with an F and M Model 500 gas chromatograph using an 18 in. × 1/4 in. column packed with silicone gum rubber SE 30 on Chromosorb W (1 : 20). The injection port temperature was 225° and the column was at 175°.

### *Preparation of tetrakis(trimethylsilyl)silane (I)*

*From silicon tetrachloride, chlorotrimethylsilane and lithium in THF (general procedure).* The general procedure involves the addition of *ca.* 15% of a solution of silicon tetrachloride dissolved in THF (*ca.* 1.1 volume ratio) to a vigorously stirred* solution of a 20% excess of chlorotrimethylsilane and THF (*ca.* 1.1 volume ratio) in which a small excess of lithium is suspended. After stirring at room temperature for a few minutes, the reaction mixture usually warms up and turns brown. Once the reaction has started, the addition of silicon tetrachloride dissolved in THF may be rapid without decreasing the yield of (I) appreciably. However, to maintain control of the exothermic reaction moderate to slow addition is preferable. Upon completed addition (*ca.* 2–4 h), the reaction mixture should be stirred at room temperature for more than 24 h. At this time, appreciable amounts of insoluble salts and a small amount of unreacted lithium wire are present. Also, the reaction mixture should be at room temperature. If these criteria are not satisfied, continued stirring of the reaction mixture at room temperature is necessary.

In the work-up of the mixture, unreacted lithium wire and insoluble salts are removed by filtration**. Hydrolysis of the homogeneous dark brown solution by the addition to a mixture of crushed ice and hydrochloric acid is followed by the separation of the organic layer. The organic layer is dried over anhydrous sodium sulfate, filtered, and the organic solvents are removed under reduced pressure. Pure (I) is obtained by crystallization of the semi-solid from 95% ethanol or acetone sub-

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* A Hershberg stirrer and a high speed stirring motor was used.

** The salts were treated with 95% ethanol or stored under mineral oil immediately because, in some instances, they inflamed when dry.

sequent to sublimation. When a slight excess of silicon tetrachloride is used and/or when the reaction does not proceed to completion, a white colloidal precipitate is observed upon the hydrolysis of the reaction mixture subsequent to the removal of undissolved salts and lithium metal by filtration. Due to its colloidal nature, sometimes a sharp distinction between the organic and aqueous layer is not observed, even after varying the pH of the mixture or adding more ether. At this stage, a filtering aid* is added and the mixture is filtered under reduced pressure. Further work-up in the usual manner is continued.

*Run* 1**. To 3.36 g (0.48 g-atom) of lithium was added 10 ml of a solution of 11.7 g (0.069 mole) of silicon tetrachloride and 50 ml of THF. After stirring the reaction mixture for 30 min at room temperature, the mixture turned brown and the addition of the silicon tetrachloride solution was continued over a period of 30 min. After this time, a solution of 25.9 g (0.24 mole) of chlorotrimethylsilane in 100 ml of THF was added dropwise. The reaction mixture became warm and upon complete addition (*ca.* 1 h), the mixture was refluxed overnight. Work-up in the usual manner gave a brown oil which was chromatographed on neutral alumina. Elution with petroleum ether (b.p. 60–70°) gave a solid from which 6 g (31.6%) of (I) was obtained after two recrystallizations from 95% ethanol followed by sublimation. (Found: C, 45.76; H, 11.22%; mol.wt., 319; hydrogen value, 277. $C_{12}H_{36}Si_5$ calcd.: C, 44.91; H, 11.31%; mol.wt., 321; hydrogen value, 279.)***

The infrared spectrum (carbon disulfide) showed prominent absorptions in $\mu$ at: 3.40 (m), 3.46 (m), 7.20 (w), 7.70 (m), 8.05 (s), 12.0 (s), 13.5 (w) and 14.6 (w).

The NMR spectrum (carbon tetrachloride) showed a sharp singlet at $\tau$ 9.79 ppm. Symmetrically disposed about this peak were $^{13}C$–H satellite side bands, $J(^{13}C\text{–}H) = 119$ cps, and $HC^{29}Si$ side bands, $J(HC^{29}Si) = 6.24$ cps.

There were no absorptions in the ultraviolet spectrum above 210 m$\mu$ in cyclohexane as solvent.

*Run* 2. To 94.2 g (0.86 mole) of chlorotrimethylsilane dissolved in 200 ml of THF, and 15.1 (2.15 g-atoms) of lithium was added 20 ml of a solution of 30 g (0.18 mole) silicon tetrachloride dissolved in 150 ml of THF. After 4 h of stirring at room temperature, the reaction mixture warmed up and turned brown. Dropwise addition of the silicon tetrachloride solution was continued and upon complete addition (*ca.* 4 h), the reaction mixture was stirred overnight at room temperature. Work-up in the usual manner gave 40.5 g (70%) of (I).

*Run* 3. To 238 g (2.2 moles) of chlorotrimethylsilane dissolved in 300 ml of THF, 30.8 g (4.4 g-atoms) of lithium was added 50 ml of a solution of 85 g (0.5 mole) of silicon tetrachloride dissolved in 200 ml of THF. After *ca.* 5 min of stirring at room temperature, the reaction mixture warmed up and turned brown. At this stage, the dropwise addition of the silicon tetrachloride solution was continued over a

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* The filtering aid used was Celite (Johns–Mansville registered trade-mark for diatomaceous silica products).

** The tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride immediately before use.

*** The molecular weight was determined with a vapor pressure osmometer, Model 301A, manufactured by Mechrolab Inc. The authors are grateful to Dr. J. M. HOLMES for the hydrogen value determination.

TABLE 1

PREPARATIONS OF TETRAKIS(TRIMETHYLSILYL)SILANE (I)

The THF was freed from moisture and peroxides before use by storage over sodium wire for 24 h, unless otherwise specified

| *Run* | *Li* [*g*(*g-atom*)] | *SiCl₄* [*g*(*mole*)] | *(CH₃)₃SiCl* [*g*(*mole*)] | *Pot contents at start of reaction* | *Addn. time* (*min*) | *React. time* (*h*) | *Yield* (*%*) |
|---|---|---|---|---|---|---|---|
| 1[a,b] | 3.36<br>(0.48) | 11.7<br>(0.069) | 25.9<br>(0.24) | 3.36 g of Li, 10 ml of a solution of 11.7 g of $SiCl_4$ in 50 ml of THF | 30 | overnight | 31.6 |
| 2[a] | 15.1<br>(2.15) | 30<br>(0.18) | 94.2<br>(0.86) | 94.2 g of $(CH_3)_3SiCl$, 15.1 g of Li, 200 ml of THF, and 20 ml of a solution of 30 g of $SiCl_4$ in 150 ml of THF | 240 | overnight | 70.0 |
| 3[c] | 30.8<br>(4.4) | 85<br>(0.5) | 238<br>(2.2) | 238 g of $(CH_3)_3SiCl$, 30.8 g of Li, 300 ml of THF, and 50 ml of a solution of 85 g of $SiCl_4$ in 200 ml of THF | 120 | 36 | 61.0 |
| 4[d] | 37<br>(5.3) | 102<br>(0.6) | 284<br>(2.6) | 284 g of $(CH_3)_3SiCl$, 37 g of Li, 300 ml of THF, 25 ml of a solution of 102 g of $SiCl_4$ in 100 ml of THF | *ca.* 120 | 48 | 65.0 |
| 5[e] | 28<br>(4.0) | 102<br>(0.6) | 218<br>(2.0) | 218 g of $(CH_3)_3SiCl$, 28 g of Li, 200 ml of THF, and 25 ml of a solution of 102 g of $SiCl_4$ in 100 ml of THF | 120 | 26 | 48.0 |

[a] THF was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride immediately before use. [b] The reaction mixture was refluxed. [c] Seven repeat runs of this reaction gave an average yield of 62%. [d] Five repeat runs gave an average yield of 62%. [e] A repeat run gave 52.0% of (I).

period of 2 h, after which the reaction mixture was stirred for 36 h at room temperature. Work-up in the usual manner gave 98 g (61%) of (I).

*Run* 4. To 284 g (2.6 moles) of chlorotrimethylsilane and 37 g (5.3 g-atoms) of lithium suspended in 300 ml of THF was added 25 ml of a solution of 102 g (0.6 mole) of silicon tetrachloride dissolved in 100 ml of THF. After *ca.* 10 min of stirring at room temperature, the reaction mixture warmed up and turned brown. At this stage the dropwise addition of the silicon tetrachloride solution was continued and, upon complete addition (*ca.* 2 h), the reaction mixture was stirred at room temperature for 48 h. Work-up in the usual manner gave 124 g (65%) of (I).

*From silicon tetrachloride, chlorotrimethylsilane and magnesium in THF (attempted).* A mixture of 13.6 g (0.56 g-atom) of magnesium and 25 ml of a solution of 11.7 g (0.069 mole) of silicon tetrachloride in 100 ml of THF was stirred at room temperature for 3 h and refluxed for 1 h. Color Test I[21] was negative and addition of the remainder of the silicon tetrachloride solution was followed by the addition of a solution of 25.9 g (0.24 mole) of chlorotrimethylsilane in 100 ml of THF. Color Test I was negative and the unreacted magnesium metal was separated from the reaction mixture. Upon acid hydrolysis of the decanted solution, a white gummy mass precipitated. An infrared spectrum of this material showed absorptions for Si–OH and Si–O–Si. No (I) was isolated.

*From silicon tetrachloride, chlorotrimethylsilane and lithium in* 1,2,3,4-*tetramethyltetrahydrofuran (attempted).* In this experiment 1,2,3,4-tetramethyltetrahydrofuran* was used in place of tetrahydrofuran. An infrared spectrum of the white gummy material obtained after work-up showed absorptions for Si–OH and Si–O–Si. No (I) was isolated.

### *Tetrakis(trimethylsilyl)silane (I) with aqueous piperidine*

A solution of 20 g (0.06 mole) of (I) and 4.5 ml of water in 104 ml of piperidine was refluxed for 4 days prior to acidifaction and work-up in the usual manner. Distillation of the residue afforded 11 g of a liquid which consisted of two compounds (by VPC), b.p. 109–110°/22 mm, $n_D^{20}$ 1.4190. An infrared spectrum showed a strong absorption at 9.55 $\mu$ and a weak band at 2.9 $\mu$, indicative of Si–O and Si–OH, respectively. No starting material, (I), was recovered.

### *Tetrakis(trimethylsilyl)silane (I) with sodium methoxide in methanol*

Sodium metal (0.4 g) was dissolved in 150 ml of methanol. To this solution was added 15 g (0.05 mole) of (I) and the reaction mixture was stirred for two days at room temperature prior to acidification and work-up in the usual manner. VPC of the liquid indicated no starting material and the presence of three compounds; and an infrared spectrum showed a strong absorption band at 9.4 $\mu$, indicative of Si–O.

### *Tetrakis(trimethylsilyl)silane (I) with bromine*

To 20 g (0.06 mole) of (I) dissolved in 150 ml of benzene was added dropwise at 4° a solution of 11.2 g (0.06 mole) of bromine in 80 ml of benzene. The bromine color was discharged instantaneously and, upon complete addition (*ca.* 20 min), the

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* The authors are grateful to Dr. J. B. DICKEY for this material.

reaction mixture was stirred for 1 h at room temperature. The solvent and volatile products were removed by distillation, affording a brown semi-solid. An excess (100%) of phenylmagnesium bromide was added and the reaction mixture was heated at reflux temperature overnight. After this time Color Test I[21] was positive. A semi-solid was obtained on work-up, and from this was recovered 12.1 g (60.5%) of (I).

Another run using 8 g (0.03 mole) of (I), 4 g (0.03 mole) of bromine and 120 ml of carbon tetrachloride gave a 6 g (63%) recovery of (I).

*Tetrakis(trimethylsilyl)silane (I) with phosphorus pentachloride*

A solution of 20 g (0.06 mole) of (I) and 12.4 g (0.06 mole) of phosphorus pentachloride in 200 ml of benzene was refluxed overnight. The solvent and volatile products were then removed by distillation. Subsequent to the addition of an excess (*ca.* 100%) of phenylmagnesium bromide, the reaction mixture was refluxed overnight. Acid hydrolysis of the reaction mixture gave a 6.1 g (63%) recovery of (I).

Two other runs of this reaction, employing 10 g (0.03 mole) of (I) and 6.2 g (0.03 mole) of phosphorus pentachloride in 200 ml of carbon tetrachloride, and in 150 ml of sym-tetrachloroethane, yielded a 5.8 g (60%) and a 6.1 g (63%) recovery of (I), respectively.

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## SUMMARY

Details are provided for the preparation of tetrakis(trimethylsilyl)silane, and a discussion of its properties and mechanisms of formation are presented. The unique physical and chemical properties associated with this compound have been attributed to its high degree of symmetry and its branched-chain structure.

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