Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PREPARATION OF CERTAIN BROMOMETHYL- AND IODOMETHYL-SUBSTITUTED DISILANES

KOHEI TAMAO AND MAKOTO KUMADA
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)

(Received March 1st, 1971)

SUMMARY

A very convenient route to bromomethyl-substituted organodisilanes involving reaction of the corresponding (methoxymethyl)disilanes with triphenyldibromophoshporane is described. (Iodomethyl)disilanes were best prepared by treatment of the (bromomethyl)disilanes with sodium iodide in acetone, although they could be made by the action of phosphoric acid and potassium iodide on the (methoxymethyl)disilanes, with yields and purities being much lower. 1,2-Bis(chloromethyl)-tetramethyldisilane was prepared pure, but in very low yield, by the action of diazomethane on *sym*-dimethyltetrachlorodisilane followed by methylation of the remaining silicon–chlorine bonds.

INTRODUCTION

In the course of an extended investigation into the organofunctional disilanes and trisilanes[1–4], it became necessary to prepare several halomethyl-substituted disilanes such as $(XCH_2)Me_2SiSiMe_2(CH_2X)$ and $Me_3SiSiPhMe(CH_2X)$, where X stands for a halogen atom. Many methods are available for making halomethylsilicon compounds[5], but none of them has turned out to be used satisfactorily for synthesis of relatively large quantities of such compounds.

A most satisfactory method for synthesis has been found to take advantage of the recently discovered[6] cleavage of aliphatic ethers by triphenyldibromophosphorane to give high yields of alkyl bromides. This paper is mainly concerned with the preparation of certain bromomethyl-substituted disilanes from the corresponding (methoxymethyl)disilanes by this new approach. Preparations of (iodomethyl)-disilanes and 1,2-bis(chloromethyl)tetramethyldisilane are also described.

PREPARATIVE METHODS

Formulas, some physical properties and analytical data for the new compounds prepared in this study are listed in Table 1, and ^1H NMR data for some of them in Table 2.

(Bromomethyl)disilanes

The very convenient synthesis of (bromomethyl)pentamethyldisilane (I),

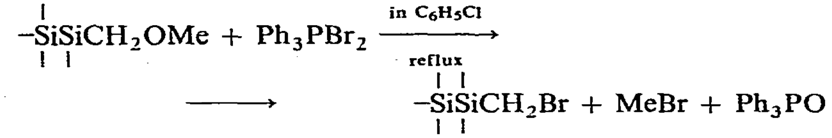
TABLE 1

SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR NEW COMPOUNDS

Compound		B.p. (°C/mm)	n_D^{20}	d_4^{20}	MR_D found (calcd.)	Analysis found (calcd.) (%)	
Formula	No.					C	H
$C_6H_{17}BrSi_2$	(I)	57/9	1.4782	1.0849	58.81 (58.59)	32.07 (31.99)	7.36 (7.61)
$C_6H_{16}Br_2Si_2$	(II)	115/13	1.5257	1.4143	65.98 (66.31)	23.70 (23.69)	5.15 (5.30)
$C_{11}H_{19}BrSi_2$	(III)	95–96/1.5	1.5457	1.1527	78.90 (78.80)	46.19 (45.98)	6.62 (6.66)
$C_{11}H_{19}BrSi_2$	(IV)	98–100/1.5	1.5450	1.1526	78.83 (78.80)	45.99 (45.98)	6.74 (6.66)
$C_8H_{22}O_2Si_2$	(VI)	81/26	1.4432	0.8518	64.38 (64.04)	46.76 (46.54)	10.91 (10.74)
$C_{12}H_{22}OSi_2$	(VII)	108–109.5/10	1.5076	0.9154	77.61 (77.52)	60.08 (60.43)	9.24 (9.30)
$C_{12}H_{22}OSi_2$	(VIII)	83/2	1.5090	0.9149	77.83 (77.52)	60.53 (60.43)	9.36 (9.30)
$C_5H_{14}BrClSi_2$	(IX)	69–70/13[a]				24.78 (24.44)	5.79 (5.74)[b]
$C_5H_{14}BrClSi_2$	(X)	98–99/33	1.4971	1.2429	57.86 (58.20)	24.82 (24.44)	6.15 (5.74)[c]
$C_6H_{16}I_2Si_2$	(XI)	103–105/1.5	1.5889	1.7451	76.88 (76.75)	17.95 (18.10)	4.19 (4.05)
$C_7H_{19}IOSi_2$	(XII)	104–106/14	1.5097	1.2744	70.91 (70.24)	28.28 (27.81)	6.60 (6.34)[d]
$C_6H_{16}Cl_2Si_2$	(XIII)	[e]				33.67 (33.47)	7.56 (7.49)
$C_{10}H_{17}ClSi_2$[f]		117–118/20	1.5191	0.9802	70.90 (70.80)	52.44 (52.48)	7.60 (7.49)[g]

[a] M.p., 25–26°. [b] For the determination of halogen contents, see text. [c] Found: Cl, 14.10. $C_5H_{14}BrClSi_2$ calcd.: Cl, 14.43%. [d] Slightly impure. [e] M.p., 37–39°. [f] $Me_3SiSiMePhCl$. [g] Found: Cl, 15.25. $C_{10}H_{17}ClSi_2$ calcd.: Cl, 15.49%.

1,2-bis(bromomethyl)tetramethyldisilane(II), 1-(bromomethyl)-1-phenyltetramethyldisilane (III), and 1-(bromomethyl)-2-phenyltetramethyldisilane (IV) has been accomplished by the action of triphenyldibromophosphorane in chlorobenzene[6] on the corresponding (methoxymethyl)disilanes, *i.e.*, (methoxymethyl)pentamethyldisilane (V)[2], 1,2-bis(methoxymethyl)tetramethyldisilane (VI), 1-(methoxymethyl)-1-phenyltetramethyldisilane (VII) and 1-(methoxymethyl)-2-phenyltetramethyldisilane (VIII), respectively. The reaction conditions and yields are given in Table 3.



$$-SiSiCH_2OMe + Ph_3PBr_2 \xrightarrow[\text{reflux}]{\text{in } C_6H_5Cl} -SiSiCH_2Br + MeBr + Ph_3PO$$

It is interesting to note that (VI) is much more reactive than (V) toward the phosphorane reagent. Monitoring the progress of the reaction by GLC revealed

TABLE 2

^{1}H NMR DATA FOR (METHOXYMETHYL)- AND (HALOMETHYL)-DISILANES, $RMe_2Si^{\beta}Si^{\alpha}MeR'(CH_2X)$ (τ VALUES)[a]

Compound		CH_3Si^{α}	CH_3Si^{β}	CH_2X
(I)	$Me_3SiSiMe_2(CH_2Br)$	9.83	9.87	7.47 (X=Br)
(II)	$[(BrCH_2)Me_2Si\text{-}]_2$	9.72		7.42 (X=Br)
(III)	$Me_3SiSiMePh(CH_2Br)$[b]	9.53	9.86	7.28 (X=Br)
(IV)	$PhMe_2SiSiMe_2(CH_2Br)$[c]	9.86	9.61	7.53 (X=Br)
(V)	$Me_3SiSiMe_2(CH_2OCH_3)$	9.93[d]		6.90 (X=OMe)[e]
(VI)	$[(MeOCH_2)Me_2Si\text{-}]_2$	9.92		6.90 (X=OMe)[f]
(VII)	$Me_3SiSiMePh(CH_2OMe)$[g]	9.63	9.86	6.68 (X=OMe)[h]
(VIII)	$PhMe_2SiSiMe_2(CH_2OMe)$[i]	9.96	9.65	6.91 (X=OMe)[j]
(IX)	$Me_3SiSiMeCl(CH_2Br)$	9.42	9.76	7.30 (X=Br)
(X)	$ClMe_2SiSiMe_2(CH_2Br)$	9.75	9.48	7.42 (X=Br)
(XI)	$[(ICH_2)Me_2Si\text{-}]_2$	9.76		7.89 (X=I)
(XII)	$(MeOCH_2)Me_2Si^{\beta}Si^{\alpha}Me_2(CH_2I)$	9.83	9.87	7.91 (X=I) 6.85 (X=OMe)[k]
(XIII)	$[(ClCH_2)Me_2Si\text{-}]_2$	9.82		7.10 (X=Cl)

[a] Measured on a JEOL Model C-60H in carbon tetrachloride. [b] Aromatic protons: 2.6–3.2. [c] Aromatic protons: 2.4–2.8. [d] Protons of five methyl groups appear in a single resonance. [e] OCH_3: 6.73. [f] $OC\underline{H}_3$: 6.73. [g] Aromatic protons: 2.4–2.8. [h] OCH_3: 6.74. [i] Aromatic protons: 2.4–2.9. [j] OCH_3: 6.73. [k] OCH_3: 6.71.

TABLE 3

PREPARATION OF (BROMOMETHYL)DISILANES

Starting Material		Reaction time[a]	Product		
No.	Weight (g)	(h)	No.	Weight (g)	Yield (%)[b]
(V)	17.6 (0.1 mole)	20	(I)	13.0	58
(VI)	10.3 (0.05 mole)	4	(II)	7.0	46
	33 (0.16 mole)	3		34.5	71
(VII)	23.9 (0.1 mole)	55	(III)	12.5	43.5
(VIII)	67 (0.28 mole)	24	(IV)	34	42

[a] At reflux temperature of the reaction mixture (ca. 130°). [b] Isolated yield.

that the former was consumed in 4 h, whilst the latter disappeared completely only after 20 h heating. (VII) and (VIII) were still less reactive, as seen from Table 3.

The (methoxymethyl)disilanes employed here were prepared by the known method which involves the reaction of the appropriate chlorodisilanes with chloromethyl methyl ether in the presence of magnesium in tetrahydrofuran[7,*]. 1-Chloro-1-phenyltetramethyldisilane for synthesis of (VII) was prepared in 85% yield by aluminum chloride catalyzed chlorodephenylation of 1,1-diphenyltetramethyldisilane by hydrogen chloride in chloroform at room temperature[11]. This reaction proceeded with cleavage of only one phenyl group.

$$Me_3SiSiMePh_2 + HCl \xrightarrow[\text{in } CHCl_3]{AlCl_3} Me_3SiSiMePhCl + PhH$$

---

* In place of magnesium, sodium[8] or lithium[9,10] may be used.

Chlorodephenylation of (III) and (IV)

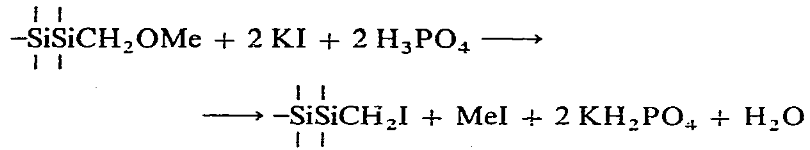
The silicon–phenyl bond in (III) and (IV) could readily be converted into the silicon–chlorine bond by treatment of these compounds with concentrated sulfuric acid in the cold and then with ammonium chloride. 1-(Bromomethyl)-1-chlorotetramethyldisilane (IX) (in 72% yield) and 1-(bromomethyl)-2-chlorotetramethyldisilane (X) (in 65% yield), respectively, were thus obtained.

$$\underset{\text{(III)}}{Me_3SiSiMePh(CH_2Br)} \xrightarrow[\text{2. } NH_4Cl]{\text{1. } H_2SO_4} \underset{\text{(IX)}}{Me_3SiSiMe(Cl)(CH_2Br)} + PhH$$

$$\underset{\text{(IV)}}{PhMe_2SiSiMe_2(CH_2Br)} \xrightarrow[\text{2. } NH_4Cl]{\text{1. } H_2SO_4} \underset{\text{(X)}}{ClMe_2SiSiMe_2(CH_2Br)} + PhH$$

(Iodomethyl)disilanes

The most frequently used procedure for cleaving ethers into iodides, which involves the use of either gaseous or aqueous hydrogen iodide, proved to be inapplicable to the synthesis of (iodomethyl)disilanes. No desired products were isolated at all. On the other hand, an application of the method reported by Stone and Shechter[12] to the methoxymethyl-substituted disilanes (V) and (VI), using excess orthophosphoric acid and potassium iodide as the ether cleaving reagent, afforded the expected (iodomethyl)pentamethyldisilane[1] in 58% yield and 1,2-bis(iodomethyl)tetramethyldisilane (XI) in 30% yield. In the latter case, the reaction was incomplete under the conditions used and 1-(methoxymethyl)-2-(iodomethyl)tetramethyldisilane (XII) was also obtained in 18% yield.



$$-\overset{|}{\underset{|}{Si}}\overset{|}{\underset{|}{Si}}CH_2OMe + 2\,KI + 2\,H_3PO_4 \longrightarrow -\overset{|}{\underset{|}{Si}}\overset{|}{\underset{|}{Si}}CH_2I + MeI + 2\,KH_2PO_4 + H_2O$$

A more convenient preparative method of the (iodomethyl)disilanes comprises the action of sodium iodide on the (bromomethyl)disilanes in acetone[13]. Thus (XI) could be obtained from (II) in a highly pure state and in substantially quantitative yield.

$$\underset{\text{(II)}}{(BrCH_2)Me_2SiSiMe_2(CH_2Br)} + 2\,NaI \longrightarrow \underset{\text{(XI)}}{(ICH_2)Me_2SiSiMe_2(CH_2I)} + 2\,NaBr$$

In the course of this preparation we noticed by GLC analysis that the previously reported "1,2-bis(chloromethyl)tetramethyldisilane", which had been obtained through peroxide catalyzed chlorination of (chloromethyl)pentamethyldisilane with sulfuryl chloride[1], and also the "1,2-bis(iodomethyl)tetramethyldisilane" derived from it[1] were in fact a mixture of the respective 1,1- and 1,2-bis(halomethyl) isomers. Comparison of the retention time on GLC of a pure sample of the 1,2-bis(iodomethyl)-disilane (XI) here obtained with that of the previous sample showed that the isomer with a longer retention time corresponded to the 1,2-isomer.

(Chloromethyl)disilanes

In an effort to obtain a pure sample of 1,2-bis(chloromethyl)tetramethyldisilane (XIII), we carried out the reaction of 1,2-dimethyltetrachlorodisilane with diazomethane by use of the techniques described in the literature[14-16]. Although attempts to isolate the product in the form of *sym*-bis(chloromethyl)dimethyldichlorodisilane were unsuccessful, subsequent treatment of the methylenation product with methylmagnesium bromide gave gas chromatographically homogeneous (XIII), though only in 3% yield.

$$Cl_2MeSiSiMeCl_2 + 2\,CH_2N_2 \longrightarrow$$

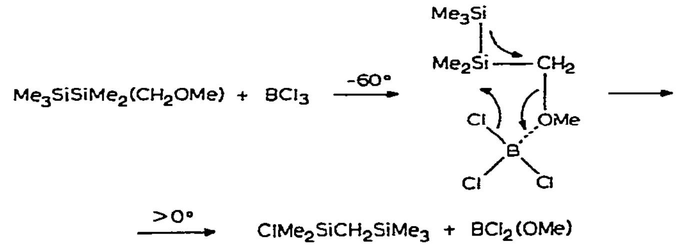
$$\longrightarrow [(ClCH_2)ClMeSiSiMeCl(CH_2Cl)] + 2\,N_2$$

$$\Big\downarrow {\scriptstyle MeMgBr}$$

$$(ClCH_2)Me_2SiSiMe_2(CH_2Cl)$$

$$\text{(XIII)}$$

In order to learn whether it would be possible or not to transform the (methoxymethyl)disilanes into the corresponding (chloromethyl)disilanes, we treated (V) with boron trichloride[17] at −60°. Immediately, a white crystalline mass believed to be an ether–boron chloride complex was formed. However, when it was allowed to warm up to room temperature it changed completely into (chlorodimethylsilyl)-(trimethylsilyl)methane, probably via a mechanism as shown below.



EXPERIMENTAL

1-*Chloro-1-phenyltetramethyldisilane*

In a 300-ml three-necked flask, provided with an air-tight stirrer, a gas-inlet tube the stem of which extended into the liquid nearly the bottom of the flask, and a reflux condenser was placed a mixture of 182 g (0.65 mole) of 1,1-diphenyltetramethyldisilane[18], 450 ml of chloroform and 2.0 g of aluminum chloride. Into the stirred mixture was passed dry hydrogen chloride at room temperature and the extent of the reaction was monitored by GLC analysis of small samples extracted periodically from the reaction mixture. After about 7 h, the starting substance disappeared with the formation of a single product homogeneous by GLC. At that time the introduction of hydrogen chloride was discontinued and ca. 10 ml of acetone was added to the mixture for the purpose of deactivating the catalyst. Removal by distillation of the solvent and benzene produced as a result of reaction, followed by fractional distillation of the residue gave 126 g (85%) of 1-chloro-1-phenyltetramethyldisilane.

1,2-Bis(methoxymethyl)tetramethyldisilane (VI)

In a 2-l three-necked flask was placed a mixture of 62.2 g (2.56 g-atoms) of magnesium, a small amount of mercuric chloride, 60 g (0.32 mole) of 1,2-dichlorotetramethyldisilane[19] and 500 ml of dry tetrahydrofuran. To this mixture was added with stirring and external cooling in an ice bath a solution of 206 g (2.56 moles) of chloromethyl methyl ether in 300 ml of tetrahydrofuran. The reaction mixture was allowed to stand overnight, and then refluxed for 5 h. About 550 ml of the solvent was removed by distillation over a 4-h period, the mixture was decomposed with a saturated solution of ammonium chloride with cooling in an ice bath. The organic layer was separated, dried over potassium carbonate and fractionally distilled to give 33 g (50% yield) of 1,2-bis(methoxymethyl)tetramethyldisilane.

1-(Methoxymethyl)-1-phenyltetramethyldisilane (VII) and 1-(methoxymethyl)-2-phenyltetramethyldisilane (VIII)

Similarly, (VII) was prepared in 67% yield from 1-chloro-1-phenyltetramethyldisilane and (VIII) in 73% yield from 1-chloro-2-phenyltetramethyldisilane[11].

Bromomethyl-substituted disilanes

The four bromomethyl-substituted disilanes (I)–(IV) were prepared in essentially the same manner. The following detailed description of the synthesis of (bromomethyl)pentamethyldisilane (I) is typical.

In a 300-ml three-necked flask fitted with an air-tight stirrer, a dropping funnel and a reflux condenser, a suspension of triphenyldibromophosphorane was prepared by adding dropwise with cooling 17.6 g (0.11 mole) of bromine diluted with 20 ml of chlorobenzene to a solution of 28.8 g (0.11 mole) of triphenylphosphine in 100 ml of chlorobenzene[6]. Disappearance of red color of bromine and precipitation of light yellow crystalline mass occurred immediately. To this mixture was added at a time, with stirring, a solution of 17.6 g (0.10 mole) of (methoxymethyl) pentamethyldisilane (V)[2] in 50 ml of chlorobenzene. The mixture was then heated to reflux with intermittent stirring for 20 h. The progress of the reaction was monitored by GLC. Most of the chlorobenzene was then removed by distillation under reduced pressure. To the residue in the flask was added ca. 250 ml of n-hexane and the precipitates (triphenylphosphine oxide) were filtered and washed with several small portions of n-hexane. The filtrate and washings were combined, washed with saturated $NaHCO_3$ solution and dried over $CaCl_2$. Fractional distillation gave the desired product.

1-(Bromomethyl)-1-chlorotetramethyldisilane (IX)

To vigorously stirred 98 g (1.0 mole) of concentrated sulfuric acid was added dropwise 10.5 g (0.037 mole) of 1-(bromomethyl)-1-phenyltetramethyldisilane with external cooling in an ice bath over a 20-min period. After the addition was completed, the reaction mixture was stirred for an additional 1 h. To it was then added with cooling 17 g (0.32 mole) of ammonium chloride in several portions. The acid layer was extracted with about 60 ml of benzene and the extract was fractionally distilled to give 6.5 g (72% yield) of a crystalline product. Titration of a weighed sample with 0.1 *N* alkali under cooling with an ice bath gave a neutral equivalent (Found: 245; calcd.: 246) corresponding to the quantitative hydrolysis of only the Si–Cl bond, while back titration gave a neutral equivalent (Found: 124; calcd.: 123) corresponding to the total halogens (Cl plus Br).

1-(*Bromomethyl*)-*2-chlorotetramethyldisilane* (*X*)

In a similar manner to that above, 1-(bromomethyl)-2-phenyltetramethyldisilane was converted in 65% yield to 1-(bromomethyl)-2-chlorotetramethyldisilane.

(*Iodomethyl*)*pentamethyldisilane*

To a cooled mixture of 43.3 g of 95% phosphoric acid (0.42 mole as H_3PO_4) and 12.3 g (0.07 mole) of (methoxymethyl)pentamethyldisilane (V) was added 46.5 g (0.28 mole) of potassium iodide in several portions with stirring. The reaction mixture was allowed to stand at room temperature overnight and then heated at 90±10° with vigorous stirring for 20 h. The progress of the reaction was monitored by GLC. The mixture was then hydrolyzed and the aqueous layer was extracted with 200 ml of ether. The organic layer and the extracts were combined and washed with sodium bicarbonate solution and then water, and dried over calcium chloride. Ether was removed by distillation and the remaining oil was fractionally distilled to give 11 g (58% yield) of (iodomethyl)pentamethyldisilane, b.p. 77–78°/11 mm[1].

1,2-*Bis*-(*iodomethyl*)*tetramethyldisilane* (*XI*)

(*a*). In a similar manner to that above, 10.3 g (0.05 mole) of 1,2-bis(methoxymethyl)tetramethyldisilane, 61.1 g of phosphoric acid and 66.5 g (0.40 mole) of potassium iodide were allowed to react, and the reaction mixture was worked up to give 2.7 g (18% yield) of slightly impure 1-(methoxymethyl)-2-(iodomethyl)tetramethyldisilane (XII), b.p. 104–106°/14 mm, and 6.0 g (30% yield) of 1,2-bis(iodomethyl)tetramethyldisilane (XI), b.p. 102–108°/1 mm, also in a slight pure state.

(*b*). A solution of 4.5 g (0.015 mole) of 1,2-bis(bromomethyl)tetramethyldisilane (II), and 5.6 g (0.037 mole) of sodium iodide in 60 ml of dry acetone was refluxed for 4 h. Since GLC analysis indicated that the reaction was complete at this point, acetone was removed by distillation and water was added to the residue. The organic layer and ether extracts from the aqueous layer were combined, washed with dilute sodium thiosulfate solution, then with water, and dried over potassium carbonate. Distillation gave very pure (XI) as a colorless liquid, in 93% yield.

1,2-*Bis*(*chloromethyl*)*tetramethyldisilane* (*XIII*)*

In a 2-l three-necked flask, equipped with a stirrer, dropping funnel and reflux condenser the exit of which was protected by a drying tube, there was placed 34 g (0.15 mole) of *sym*-tetrachlorodimethyldisilane[19], 150 ml of absolute ether and 0.5 g

---

* This preparation was carried out by Y. Hiromoto and A. Noro in this laboratory.

of copper powder, prepared freshly from cupric chloride and zinc. To the mixture cooled to −30 to −40° in an acetone/Dry Ice-bath was added dropwise a solution of diazomethane (0.45 mole) in about 1.2 l of ether with vigorous stirring. During the addition, considerable deposition of a white mass (probably polymethylene) occurred on the vessel wall and catalyst surface and so an additional 2 g of copper powder was introduced in 0.5 g portions. The reaction mixture was stirred for 1.5 h at the same temperature and then allowed to stand overnight at room temperature. To the mixture was then added an ethereal solution of 0.8 mole of methylmagnesium bromide. The reaction mixture was worked up in the usual way. After removal of ether, the residue was flash-distilled to give 10 g of a liquid boiling over the range of 56–200°/23 mm, along with 5 g of residue. Fractional distillation of the distillate gave 2.9 g of impure (XIII), largely boiling at 111–120°/30 mm. Preparative GLC (180°, Apiezon-L, Varian Model 90-P) from this fraction gave 1.2 g (3.1% yield) of the pure product. Several runs carried out in similar ways did not improve yields of the product.

Reaction of (methoxymethyl)pentamethyldisilane with boron trichloride

To 9 g (0.077 mole) of boron trichloride placed in a 50-ml three-necked flask, fitted with a Dry Ice-acetone condenser, gas inlet tube and serum cap, and cooled to −60° was added dropwise 8.8 g (0.05 mole) of (methoxymethyl)pentamethyldisilane[2] through the serum cap by means of a syringe. Immediately, the formation of white crystalline substance was observed, which was believed to be an ether–boron chloride complex because none of the reactants nor the product described below solidified under the same conditions. When the reaction mixture was allowed to warm to room temperature it turned clear. It was then stirred at room temperature for 2 h, during which period of time the progress of reaction was monitored by GLC. After standing overnight, the reaction mixture was distilled to give 8.8 g (98% yield) of (chlorodimethylsilyl)(trimethylsilyl)methane, b.p. 84–86°/91 mm, n_D^{20} 1.4330 (reported[20]: b.p. 154–155°, n_D^{20} 1.4320) (Found: Cl, 20.08. $C_6H_{17}ClSi_2$ calcd.: Cl, 19.61%), along with 1 g of a fore-run, boiling at 40–48°. This major product did not react with bromine (evidence for the absence of the Si–Si bond) and its retention time on GLC coincided completely with that of an authentic sample.

ACKNOWLEDGEMENT

The cost of this research was defrayed in part from the Grant-in-Aid for Scientific Research of the Ministry of Education, to which the authors' thanks are due. The authors are also greatly indebted to Tokyo-Shibaura Electric Co., Ltd. and Nitto Electric Industrial Co., Ltd. for support of this work.

REFERENCES

1 M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, 1 (1964) 411.
2 M. Kumada, M. Ishikawa and K. Tamao, *J. Organometal. Chem.*, 5 (1966) 226.
3 M. Kumada, K. Tamao, M. Ishikawa and M. Matsuno, *Chem. Commun.*, (1968) 614.
4 H. Sakurai, H. Yamamori and M. Kumada, *J. Org. Chem.*, 33 (1968) 1827.
5 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, p. 404.
6 A. G. Anderson, Jr. and F. J. Freenor, *J. Amer. Chem. Soc.*, 86 (1964) 5037.
7 M. Lefort (Rhone-Poulenc S.A.), *Fr. Pat.*, 1,303,195 (1962); *Chem. Abstr.*, 58 (1963) 7975.

8 J. L. SPEIER, JR., *U. S. Pat.*, 2,572,402 (1951); *Chem. Abstr.*, 46 (1952) 4560.
9 U. SCHOLLKOPF AND H. KUPPERS, *Tetrahedron Lett.*, (1964) 1503.
10 U. SCHOLLKOPF, H. KUPPERS, H.-J. TRAENCKNER AND W. PITTEROFF, *Justus Liebigs Ann. Chem.*, 704 (1967) 120.
11 M. KUMADA, M. ISHIKAWA AND S. MAEDA, *J. Organometal. Chem.*, 2 (1964) 478.
12 H. STONE AND H. SHECHTER, *J. Org. Chem.*, 15 (1950) 491.
13 H. FINKELSTEIN, *Ber.*, 43 (1910) 1528.
14 A. Y. YAKUBOVICH, S. P. MAMAROV, V. A. GINSBURG, G. I. GAVRILOV AND E. N. MERKULOVA, *Dokl. Akad. Nauk SSSR*, 72 (1950) 69; *Chem. Abstr.*, 45 (1951) 2856.
15 D. SEYFERTH AND E. G. ROCHOW, *J. Amer. Chem. Soc.*, 77 (1955) 907.
16 K. KRAMER AND N. WRIGHT, *Ber.*, 96 (1963) 1877.
17 W. GERRARD AND M. F. LAPPERT, *J. Chem. Soc.*, (1952) 1486 and references cited therein.
18 (a) H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, *J. Organometal. Chem.*, 2 (1964) 3690;
(b) H. GILMAN AND G. D. LICHTENWALTER, *J. Amer. Chem. Soc.*, 86 (1958) 608.
19 (a) M. KUMADA, M. YAMAGUCHI, Y. YAMAMOTO, J. NAKAJIMA AND K. SHIINA, *J. Org. Chem.*, 21 (1954) 1264;
(b) H. SAKURAI, T. WATANABE AND M. KUMADA, *J. Organometal. Chem.*, 7 (1967) P15.
20 I. HIZAWA AND E. NOJIMOTO, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, 59 (1956) 1359.