ALKALINE CLEAVAGE OF CERTAIN PHENYL- AND CHLORINE-SUBSTITUTED (HALOMETHYL)DISILANES*

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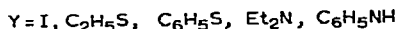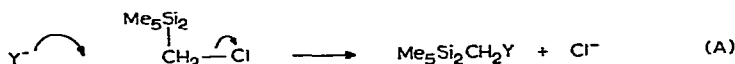*Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)*

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SUMMARY

The action of sodium ethoxide in ethanol on a number of (halomethyl)disilanes containing phenyl groups or chlorine atoms on silicon has been studied. The reaction proceeds in three directions: intramolecular rearrangement involving migration of a silyl group from silicon to carbon, cleavage of the silicon–silicon bond with concomitant reduction of the halomethyl group to methyl, without evolution of hydrogen, and cleavage of the silicon–silicon bond with evolution of hydrogen. The rearrangement/cleavage proportions depend upon the nature and the position of the substituents. Possible mechanisms are discussed.

INTRODUCTION

Previously, we reported that the reaction of (chloromethyl)pentamethyldisilane with various nucleophilic reagents proceeds in three directions, depending upon the nature of the reagent used[2,3]. Thus, substitution of the chlorine atom exclusively takes place by sodium iodide in acetone, by sodium mercaptides in mercaptans or by amines (Course A); only silicon–carbon cleavage occurs with sodium (or potassium) cyanide in alcohols (Course B); while only intramolecular rearrangement of a silyl group from silicon to carbon proceeds with sodium alkoxides in alcohols (Course C).

$$Y^- + \underset{\underset{CH_2-Cl}{|}}{Me_5Si_2} \longrightarrow Me_5Si_2CH_2Y + Cl^- \qquad (A)$$

$$Y = I, C_2H_5S, C_6H_5S, Et_2N, C_6H_5NH$$

$$CN^- + Me_5Si_2CH_2Cl \xrightarrow{ROH} Me_5Si_2OR + CH_3CN + Cl^- \qquad (B)$$

The chemistry of (halomethyl)disilanes containing group(s) other than methyl on a silicon atom, however, has received little attention so far, whereas a variety of reactions have been reported for monosilane analogs[4]. It has been well recognized

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* For a preliminary communication of some of this work see ref. 1.

that a phenyl group in (chloromethyl)dimethylphenylsilane migrates from silicon to carbon under the influence of a sodium alkoxide in alcohol, affording finally a dimethyl-dialkoxysilane and toluene[5]. We were interested in determining the relative migratory aptitude of trimethylsilyl and phenyl group from silicon to carbon by base, and in elucidating the recently observed unusual high reactivity, upon titration with alkali, of the carbon–halogen bond in certain (halomethyl)disilanes, such as $Me_3SiSiMeCl$-(CH_2Br) (VII)[6], $ClMe_2SiSiMeCl(CH_2Cl)$ (IX)[7], and $Cl_2MeSiSiCl_2(CH_2Cl)$ (X)[7]. Therefore, we investigated the action of sodium ethoxide in ethanol on phenyl- and chlorine-substituted (halomethyl)disilanes.

RESULTS AND DISCUSSION

We have now found that, in addition to the rearrangement (C), the reaction proceeds in two more directions: cleavage of the silicon–silicon bond without evolution of hydrogen but with concomitant reduction of the halomethyl to methyl group (Course D), and cleavage of the silicon–silicon bond with evolution of hydrogen keeping the halomethyl group intact (Course E)*.
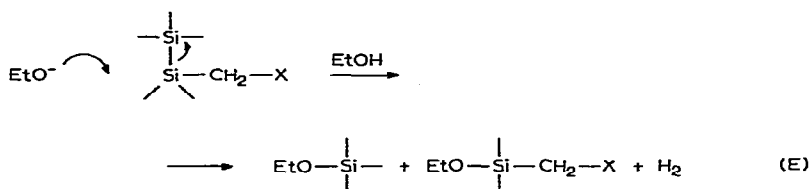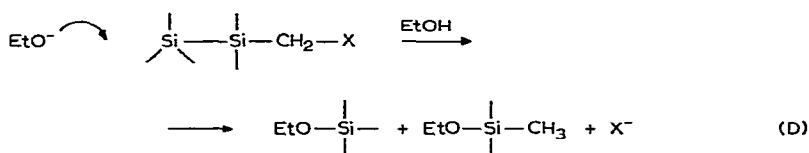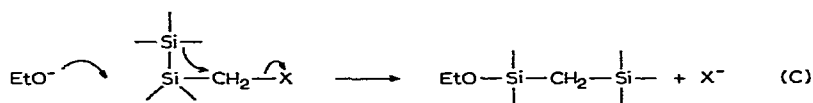
These three modes of reaction are represented in terms of synchronous processes, but such descriptions are intended for the sake of simplicity and not for any realistic meachanism; a two-step process may be more likely which involves a penta-covalent silicon intermediate being formed reversibly as a result of coordination by a nucleophile, followed by its decomposition in the rate-determining step to products[9]. Which course the reaction preferentially takes may mainly depend on the substituents on the silicon atoms. The most important for determining the reaction course may be

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* The base-catalyzed cleavage of polysilanes with evolution of an equivalent of hydrogen for each silicon–silicon bond is well known[8].

the nature of a leaving anionic silyl group, although the relative concentrations of the pentacovalent α- and β-silicon* intermediates in the prior equilibrium step will be none the less important.

The reaction conditions, amounts of products determined by GLC and rearrangement/cleavage proportions are given in Table 1. The products were isolated by preparative GLC, after neutralization with dry hydrogen chloride, filtration and subsequent distillation, and identified mainly on the basis of IR and NMR spectra and elementary analyses.

In all cases examined, except only for compound (XI) whose reaction took courses (C) and (E) (see below), no evolution of hydrogen occurred and the reaction proceeded according to courses (C) and (D).

(Halomethyl)pentamethyldisilanes

In the present work we have found that the silicon–silicon bond in (chloromethyl)pentamethyldisilane (I), for which we previously reported the exclusive rearrangement to occur based on product isolation experiments[2,3], in fact, undergoes cleavage up to 30 % with the chloromethyl group being reduced to methyl (Course D). The analogous rearrangement and reduction of a halomethyl group were also found to occur with compounds (II)[6] and (III)[2,6]. In the series of (halomethyl)pentamethyldisilanes, $Me_3SiSiMe_2(CH_2X)$, (I)–(III), the rearrangement/cleavage proportion increases in the order of $X = Cl \sim I < Br$, which is the same order as observed by Schott et al.[10] for the rearrangement/solvolysis ratio of (halomethyl)dimethylsilanes, HMe_2SiCH_2X ($X = Cl$, Br, I), under similar conditions. This may suggest that the rearrangement in both series proceeds by a similar mechanism.

Phenyl-substituted (halomethyl)disilanes

In marked contrast to (I)–(III), 1-(bromomethyl)-1-phenyltetramethyldisilane (IV)[6], under similar conditions, underwent cleavage up to 90 % without evolution of hydrogen but with concomitant replacement of the bromine atom by hydrogen to give trimethylethoxysilane and ethoxydimethylphenylsilane, with the remaining 10 % of the reaction proceeding via an intramolecular rearrangement to (ethoxymethylphenylsilyl)(trimethylsilyl)methane. An analogous result, (C) : (D) $\simeq 25 : 75$, was obtained with 1-(chloromethyl)-1,2-diphenyltrimethyldisilane (VI). On the contrary, the reaction with 1-(chloromethyl)-2-phenyltetramethyldisilane (V) led to only about 26 % cleavage, with 74 % intramolecular rearrangement. This rearrangement/cleavage proportion is comparable to that for (chloromethyl)pentamethyldisilane, indicating that the reaction course is little affected by replacement of one methyl by a phenyl group on β-silicon.

For the formation of $PhMe_2SiOEt$ from the cleavage of (IV) and (VI), one might conceive a pathway involving initial formation of hydride $HSiPhMe(CH_2X)$ as an intermediate, which subsequently undergoes nucleophilic intramolecular rearrangement involving the migration of hydrogen from silicon to carbon (Scheme 1).

However, this can be ruled out, since evolution of hydrogen would result from the simultaneous ethanolysis of the silicon–hydrogen bond. Indeed, Sommer et al.[11] reported that the action of potassium hydroxide in 95 % ethanol on (chloromethyl)dimethylsilane, HMe_2SiCH_2Cl, gave 31 % of the silicon–hydrogen solvolysis product,

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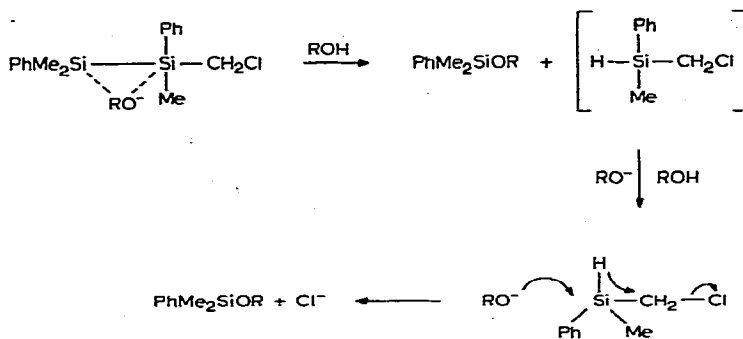* The silicon atom bearing a halomethyl group is designated the α-silicon, and the other is the β-silicon.

TABLE 1

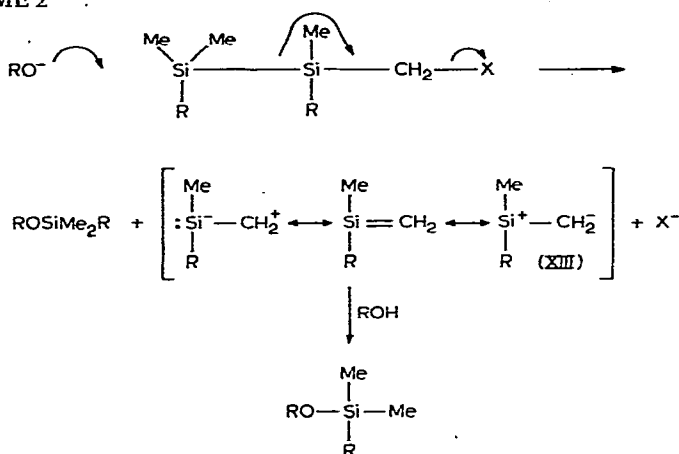REACTION OF (HALOMETHYL)DISILANES WITH SODIUM ETHOXIDE IN ETHANOL

No.	Compound (mmole)	Reaction conditions Temp.	Time (h)[b]	Products Rearrangement (mmole)[yield(%)]	Products Cleavage (mmole)[yield(%)]	Reaction proportions (%)[a] Rearrangement[c]	Cleavage[d]
(I)	Me$_3$SiSiMe$_2$(CH$_2$Cl) 30.0	R.t. Additional reflux	7 days[e]	Me$_3$SiCH$_2$SiMe$_2$(OEt) 11.4 (38)	Me$_3$SiOEt 8.6 (14)	73	27
(II)	Me$_3$SiSiMe$_2$(CH$_2$Br) 5.1	R.t.	7	Me$_3$SiCH$_2$SiMe$_2$(OEt) 18.9 (63)	Me$_3$SiOEt 21.8 (36)	63	37
(III)	Me$_3$SiSiMe$_2$(CH$_2$I) 10.2	R.t.	50	Me$_3$SiCH$_2$SiMe$_2$(OEt) 3.5 (68)	Me$_3$SiOEt 1.3 (13)	84	16
(IV)	Me$_3$SiSiMePh(CH$_2$Br) 10.5	R.t.	1	Me$_3$SiCH$_2$SiMePh(OEt) 5.3 (52)	Me$_3$SiOEt 5.2 (26)	67	33
(V)	PhMe$_2$SiSiMe$_2$(CH$_2$Cl) 9.95	R.t.	26	PhMe$_2$SiCH$_2$SiMe$_2$(OEt) 0.91 (9)	Me$_3$SiOEt, PhMe$_2$SiOEt 8.66 (83) 9.5 (91)	10	90
(VI)	PhMe$_2$SiSiMePh(CH$_2$Cl) 10.0	R.t.	20	PhMe$_2$SiCH$_2$SiMePh(OEt) 6.64 (67)	Me$_3$SiOEt, PhMe$_2$SiOEt 1.53 (15) 2.25 (23)	73	26
(VII)	Me$_3$SiSiMeCl(CH$_2$Br) 10.4	0°	5	Me$_3$SiCH$_2$SiMe(OEt)$_2$ 2.30 (23)	PhMe$_2$SiOEt 13.6 (68)	25	75
(VIII)	ClMe$_2$SiSiMe$_2$(CH$_2$Cl) 9.9	0°–r.t.	24	(EtO)Me$_2$SiCH$_2$SiMe$_2$(OEt) 9.5 (91)	Me$_3$SiOEt, Me$_2$Si(OEt)$_2$ 0.3 (3) 0.3 (3)	97	3
(IX)	ClMe$_2$SiSiMeCl(CH$_2$Cl) 9.9	0°–r.t.	50	(EtO)$_2$MeSiCH$_2$SiMe$_2$(OEt) 1.75 (18)	Me$_3$SiOEt, Me$_2$Si(OEt)$_2$ 5.9 (60) 3.9 (39)	23	77
				9.1 (92)	Me$_2$Si(OEt)$_2$ 2.2 (10)	90	10
(X)	Cl$_2$MeSiSiCl$_2$(CH$_2$Cl) 10.8	0°	12	(EtO)$_3$SiCH$_2$SiMe(OEt)$_2$ 3.8 (36)	MeSi(OEt)$_3$ 8.5 (40)	47	53
(XI)	Cl$_3$SiSiMe$_2$(CH$_2$Cl) 9.8	0°	1	(EtO)$_3$SiCH$_2$SiMe$_2$(OEt) 2.9 (29)	(EtO)$_4$Si, (EtO)Me$_2$Si(CH$_2$Cl)[f] 7.2 (73) 6.8 (68)	28	72[g]

[a] The percentage adjusted to add to 100. [b] The time when GLC analysis was carried out; by that time the reaction had been complete. [c] Course (C). [d] Unless otherwise noted, Course (D). [e] Conversion 55%. [f] Hydrogen 75%. [g] Course (E).

SCHEME 1

$$PhMe_2Si\text{---}Si(RO^-)(Me)(Ph)\text{---}CH_2Cl \xrightarrow{ROH} PhMe_2SiOR + \left[H\text{---}Si(Ph)(Me)\text{---}CH_2Cl \right]$$

$$\downarrow RO^- \;\; ROH$$

$$PhMe_2SiOR + Cl^- \longleftarrow RO^- \;\; Si(Ph)(Me)(H)\text{---}CH_2\text{---}Cl$$

SCHEME 2

$$RO^- \;\; Si(Me)(R)\text{---}Si(Me)(Me)(R)\text{---}CH_2\text{---}X \longrightarrow$$

$$ROSiMe_2R + \left[:\overset{Me}{\underset{R}{Si^-}}\text{---}CH_2^+ \longleftrightarrow \overset{Me}{\underset{R}{Si}}=CH_2 \longleftrightarrow \overset{Me}{\underset{R}{Si^+}}\text{---}CH_2^- \right] + X^-$$
$$(XIII)$$

$$\downarrow ROH$$

$$RO\text{---}\overset{Me}{\underset{R}{Si}}\text{---}Me$$

(HO)Me$_2$SiCH$_2$Cl, with evolution of hydrogen, as well as 69% of the rearrangement product, Me$_3$SiOH. Similar results were described by Schott et al.[10]. Further, we find that (chloromethyl)methylphenylsilane, HPhMeSiCH$_2$Cl, underwent 24% solvolysis with hydrogen evolution, in addition to 76% intramolecular rearrangement, on treatment with 2.2 N sodium ethoxide in ethanol at room temperature.

In a previous communication[1], we postulated a mechanism of synchronously proceeding β-elimination involving silicon. Thus, as the first step, an intermediate (XIII) is formed and solvent ethanol then adds to this unstable species to give the observed ethoxydimethylphenylsilane (Scheme 2).

Although several publications have recently appeared concerning the possible formation of methylenedimethylsilane, Me$_2$Si=CH$_2$, as an intermediate[12], a more acceptable mechanism would be described as a two step process rather than a synchronous "β-elimination" (Scheme 3). The first, probably rate-determining, step involves a nucleophilic substitution at the β-silicon atom, where the (halomethyl)silyl group as a whole is a leaving group. The presence of a phenyl group on the α-silicon atom may greatly favor the silicon–silicon cleavage of this type over the intramolecular rearrangement, possibly by stabilization of the leaving silyl anion[13]. The second step is a rapid carbon–halogen bond breaking process with simultaneous addition of
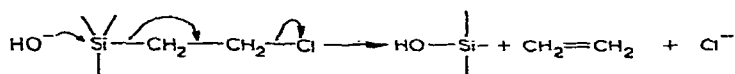
SCHEME 3

X = Cl, Br
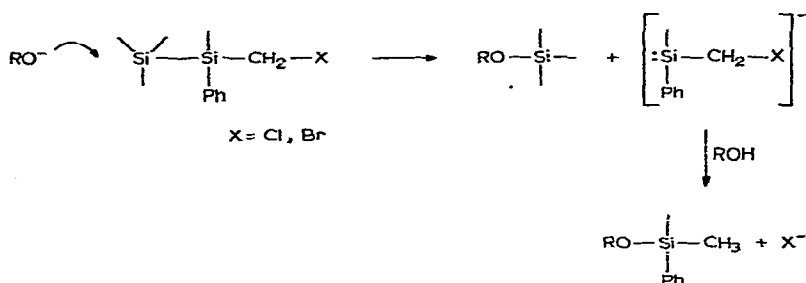
solvent ethanol, without intervention of such an intermediate species as (XIII).

Be that as it may, it can well be said that, unlike the intramolecular rearrangement (C) and the silicon–silicon cleavage with hydrogen evolution (E), the cleavage of the silicon–silicon bond with concomitant reduction of a halomethyl group proceeds by initial attack by an alkoxide ion on the β-silicon atom (D).

From the reaction of compound (IV) and (VI) bearing a phenyl group on α-silicon, no trace of toluene was detected by GLC, which might result from the migration of a phenyl group from silicon to carbon followed by cleavage of the silicon-benzyl bond by alkali[5]. It follows that, under the influence of base, both trimethylsilyl and phenyldimethylsilyl groups migrate from silicon to carbon much more easily than does a phenyl group.

Chlorine-substituted (halomethyl)disilanes

Previously we observed[7] that titration of $Cl_2MeSiSiCl_2(CH_2Cl)$ (X) with 0.1 N alkali at room temperature gives a neutral equivalent corresponding to the total chlorine content whereas other similar compounds such as $Cl_3SiSiMe_2(CH_2Cl)$ (XI) and $MeCl_2SiSiCl_2(CHCl_2)$ (XII) give neutral equivalents corresponding to the quantitative hydrolysis of only the Si–Cl bonds under the same conditions. This unusual reactivity of the C–Cl bond in (X) upon titration with base is reminiscent of the extremely facile cleavage of the C–Cl bond in (β-chloroethyl)trichlorosilane under the comparable conditions[14]. The cleavage in the latter case has been formulated as a β-elimination involving silicon:

The formal analogy in unusual reactivity of the C–Cl bond between these two cases may suggest a resemblance of reaction mechanism and the base cleavage of the C–Cl bond in (X) to proceed according to Scheme 2 (apart from the problem of whether the realistic mechanism involves a synchronous, one-step or a two-step process). However, the C–Cl bond breaking in (X) by base may also, in part, be accounted for in terms of the nucleophilic intramolecular rearrangement. Indeed, the results, given in Table I, of the reaction of (X) and other related (halomethyl)disilanes indicate that all these compounds except for (XI) undergo, without evolution of hydrogen, both types of reaction, intramolecular rearrangement (C) and silicon–silicon cleavage with concomitant reduction of the halomethyl group (D), with the

(C)/(D) proportion decreasing in the following order:

$$Me_3SiSiMeCl(CH_2Br) > ClMe_2SiSiMeCl(CH_2Cl) > Me_3SiSiMe_2(CH_2Br) >$$
$$\quad\text{(VII)} \qquad\qquad\qquad \text{(IX)} \qquad\qquad\qquad \text{(II)}$$

$$Me_3SiSiMe_2(CH_2Cl) \sim Me_3SiSiMe_2(CH_2I) > Cl_2MeSiSiCl_2(CH_2Cl) >$$
$$\quad\text{(I)} \qquad\qquad\qquad \text{(III)} \qquad\qquad\qquad \text{(X)}$$

$$ClMe_2SiSiMe_2(CH_2Cl)$$
$$\text{(VIII)}$$

It is very interesting to note that compound (VII) is most liable to the intramolecular rearrangement relative to the "elimination-type" cleavage on the one hand and the reverse is true for (VIII) on the other. A great difference in the value of the rearrangement/cleavage proportion between (VII) and (VIII) is much more than might be expected by considering the fact that the bromomethyl group favors intramolecular rearrangement over cleavage [compare the corresponding values for (I) and (II)]. Consequently, the difference in the position of chlorine attached to silicon between (VII) and (VIII) should be responsible for such a remarkable difference in the rearrangement/cleavage proportion value. Possibly, in the case of (VII) the attack of ethoxide ion on the α-silicon atom is favored over that on the β-silicon atom because an electronegative group (probably ethoxy group replaced for the original chlorine) is present apart from the halomethyl group, whilst the reverse is true for the case of (VIII) leading to displacement of $[:SiMe_2(CH_2Cl)]^-$ (not necessarily free but solvated), which is then rapidly converted into Me_3SiOEt and Cl^-. Rather unexpectedly, a relatively high value of the rearrangement/cleavage proportion was obtained from the reaction of (X) with ethoxide ion although the α-silyl group would be considered to become a good leaving group while the β-silyl group a rather poor migrating group.

The C–Cl bond in $Cl_3SiSiMe_2(CH_2Cl)$ (XI) is, as previously reported[7], extremely stable under the conditions of alkaline titration. This can be ascribed to the fact that the X_3Si group (where X stands for Cl, OH and/or OR) is so good a leaving group relative to $SiMe_2(CH_2Cl)$ group and can be stabilized as an anion* that the attack of base will preferentially lead to the silicon–silicon cleavage (Course E) in the fashion depicted by Scheme 4. This view is supported by the observation that, upon

SCHEME 4

$$Cl_3SiSiMe_2(CH_2Cl) \xrightarrow{RO^-} [X_3Si:]^- + ROSiMe_2(CH_2Cl)$$
$$\quad\text{(XI)} \qquad\qquad\qquad \downarrow 2\,ROH$$
$$Si(OR)_4 + H_2 + RO^-$$

treatment of (XI) with sodium ethoxide in ethanol, 75% of the theoretical amount of hydrogen was evolved and (chloromethyl)dimethylethoxysilane and tetraethoxysilane were formed in the amount corresponding to the gas evolution. The remaining part

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* A variety of characteristic reactions in which trichlorosilyl anion is believed to be involved are currently reported. See, e.g., ref. 15.

of the reaction took course (C) to give (triethoxysilyl)(ethoxydimethylsilyl)methane and only traces of trimethylethoxysilane, expected from course (D), were detected by GLC.

Under the conditions of alkaline titration, however, the reaction should proceed only via course (E), because if course (C) were also involved, titration would give an excess neutral equivalent over the quantity corresponding to the Si–Cl bonds only.

The fact that titration of 1-(dichloromethyl)-2-methyltetrachlorodisilane (XII) with alkali gives a neutral equivalent corresponding to the hydrolysis of only the Si–Cl bonds[7], despite two chlorine atoms are bonded to the silicon atom bearing the dichloromethyl group, can be understood if one accepts that this group is cleaved as a whole from silicon by base to give dichloromethane[2,16], which is unreactive to alkaline titration under the conditions used. Indeed, upon treatment with sodium ethoxide in ethanol, (XII) gave methyltriethoxysilane, tetraethoxysilane and dichloromethane with evolution of an almost quantitative amount of hydrogen.

$$Cl_2MeSiSiCl_2(CHCl_2) \xrightarrow[ROH]{RO^-} MeSi(OR)_3 + (RO)_4Si + CH_2Cl_2 + H_2$$
$$(XII)$$
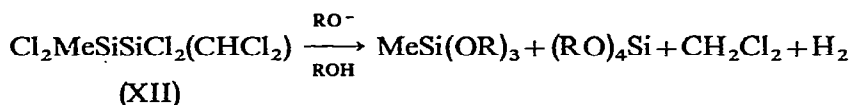
EXPERIMENTAL

NMR spectra were measured on a JEOL Model C-60H in carbon tetrachloride and the data are given in τ values. IR spectra were determined on a Hitachi Model EPI-G3 Grating Infrared Spectrophotometer.

Compounds (I)[2], (II)[6], (III)[2], (IV)[6], (VII)[6], (VIII)[17], (IX)[7], (X)[7], (XI)[7] and (XII)[7] are known and were prepared by known methods, the references given after the compounds being to them.

1-(Chloromethyl)-2-phenyltetramethyldisilane (V)

To phenylmagnesium chloride (0.082 mole) in 100 ml of THF, 15.1 g (0.075 mole) of 1-(chloromethyl)-2-chlorotetramethyldisilane[17] was added dropwise over a period of 40 min. The reaction mixture was heated to reflux with stirring for 10 h. After hydrolysis with a saturated solution of ammonium chloride, the organic layer was combined with the ether extracts from the aqueous layer, and dried over potassium carbonate. Flash distillation and subsequent fractionation gave 13 g (73% yield) of (V), b.p. 89–90°/4 mm, n_D^{20} 1.5321, d_4^{20} 0.9904, MR_D 76.01. (calcd. 76.17.). (Found: C, 54.50; H, 7.84. $C_{11}H_{19}ClSi_2$ calcd.: C, 54.39; H, 7.88%.)

1-(Chloromethyl)-1,2-diphenyltrimethyldisilane (VI)

By a similar procedure to that described above, 35 g (0.155 mole) of 1-(chloromethyl)-1,2-dichlorotrimethyldisilane[7] was reacted with excess phenylmagnesium chloride (0.50 mole) in 200 ml of THF. After 10 h reflux and subsequent work-up, the organic layer was fractionally distilled to afford 38 g (81% yield) of (VI), b.p. 170–175°/4 mm, n_D^{20} 1.5806, d_4^{20} 1.0555, MR_D 96.24 (calcd. 96.11). (Found: C, 62.92; H, 6.73. $C_{16}H_{21}ClSi_2$ calcd.: C, 62.69; H, 6.94%.)

(Chloromethyl)methylphenylchlorosilane

A Grignard solution, prepared from 50 g (0.44 mole) of chlorobenzene and 12.2 g (0.50 g-atom) of magnesium in 300 ml of THF and filtered for the purpose of being free from excess magnesium, was added to a solution of 65.5 g (0.40 mole) of (chloromethyl)methyldichlorosilane in 100 ml of THF at room temperature over a period of 30 min. Reflux for 2 h, removal of solvent and filtration were followed by distillation, which gave 55 g (67% yield) of (chloromethyl)methylphenylchlorosilane, b.p. 119–121°/17 mm (lit.[18] b.p. 136°/24 mm), n_D^{20} 1.5366, d_4^{20} 1.1798, MR_D 54.27 (calcd. 54.86).

(Chloromethyl)methylphenylsilane

To a suspension of 3.8 g (0.10 mole) of lithium aluminum hydride in 100 ml of ether was added dropwise a solution of (chloromethyl)methylphenylchlorosilane (20.5 g; 0.10 mole) in 50 ml of ether at room temperature with stirring over a period of 1 h. The mixture was then refluxed for 2 h and decomposed with water and then with ca. 5 N hydrochloric acid. The organic layer and extracts from the aqueous layer were combined, washed with water and then dried over sodium sulfate. Fractionation gave, in addition to 4 g of phenyldimethylsilane, 9.5 g (56% yield) of (chloromethyl)methylphenylsilane, b.p. 97°/17 mm, n_D^{20} 1.5308, d_4^{20} 1.0449. MR_D 50.56 (calcd. 50.71.). (Found: C, 56.48; H, 6.47. $C_8H_{11}ClSi$ calcd.: C, 56.25; H, 6.49%.) NMR: 9.52 [d, $SiCH_3$; $J(HSi–CH_3)$ 3.5 Hz], 7.05 [d, CH_2Cl; $J(HSi–CH_2Cl)$ 3.0 Hz], 5.47 (m, SiH), 2.35–2.85 (m, aromatic).

Reaction with sodium ethoxide in ethanol

General procedure. The reaction was carried out in a two-necked round-bottom flask, fitted with a serum cap and a condenser the top of which was connected to a gas buret for the purpose of measurements of the volume of hydrogen which might be evolved during the reaction. In the flask a solution of sodium ethoxide in ethanol was prepared by adding sodium or sodium ethoxide to ethanol. A (halomethyl)disilane was added through the serum cap by means of a syringe in the cold, except for (halomethyl)pentamethyldisilanes the reaction of which was carried out at room temperature. The reaction mixture was stirred magnetically for a given period of time. Dry hydrogen chloride was then passed through the reaction mixture in order to neutralize an excess of sodium ethoxide using phenolphthalein as an indicator. The yields of products (Table 1) were determined by GLC (at the outset, an appropriate hydrocarbon was added as an internal standard to the starting material). The identity of products was established as follows. The formed salt was filtered and the filtrate was flash-distilled under reduced pressure. Each product was isolated by fractional distillation or preparative GLC and identified on the basis of elemental analyses, IR and ^{1}H NMR spectra. On the IR spectra, characteristic absorption bands near 1160 and 960 cm^{-1} for ethoxysilanes[19,20], near 1050 cm^{-1} for the $SiCH_2Si$ structure assignable to the deformation vibration of the methylene group[21,22] and in the region of 1050–1100 cm^{-1} due to the Si–O stretching vibration[20] were diagnostic of the identification of the reaction product.

The PEG-20M column packing (20% on Cerite, 8 ft, 60–70°) was the only one of the several tried that was effective for the satisfactory resolution of trimethylethoxysilane from ethanol.

Compound (I)–(III)

In addition to (ethoxydimethylsilyl)(trimethylsilyl)methane, which has been previously reported as an only product from the reaction of (I)[2], trimethylethoxysilane could be isolated by preparative GLC and identified by comparison of its retention time on GLC and IR spectrum with those of an authentic sample.

Compound (IV)

To a solution of sodium ethoxide (75 mmole) in 40 ml of ethanol was added dropwise 14.4 g (50 mmole) of (IV) at room temperature with stirring. An exothermic reaction immediately occurred with white salt precipitating. After 1-h stirring, GLC analysis showed that the starting material was no longer present. No gas evolution was observed during the reaction. Trimethylethoxysilane and phenyldimethylethoxy-silane were characterized by complete coincidence of retention times on GLC and IR spectra with those of authentic samples. A minor product was identified as (phenyl-methylethoxysilyl)(trimethylsilyl)methane, n_D^{20} 1.4826. (Found: C, 61.86; H, 9.66. $C_{13}H_{24}OSi_2$ calcd.: C, 61.85; H, 9.58 %.) NMR: 10.02 [s, $Si(CH_3)_3$], 9.96 (s, $SiCH_2Si$), 9.65 (s, $SiCH_3$), 8.85 (t, $OCCH_3$), 6.38 (q, OCH_2C), 2.35–2.9 (m, aromatic). GLC analysis of the reaction mixture did not show even traces of toluene.

Compound (V)

Reaction of 6 g (25 mmole) of (V) with sodium ethoxide (30 mmole) in 20 ml of ethanol at room temperature for 26 h formed trimethylethoxysilane and phenyldi-methylethoxysilane, besides (phenyldimethylsilyl)(dimethylethoxysilyl)methane: n_D^{20} 1.4890, d_4^{20} 0.9199, MR_D 79.22 (calcd. 79.04). (Found: C, 62.70; H, 9.54. $C_{13}H_{24}OSi_2$ calcd.: C, 61.85; H, 9.58 %.) NMR: 10.02 [s, $Si(CH_3)_2O$], 9.95 (s, $SiCH_2Si$), 9.70 [s, $Si(CH_3)_2Ph$], 8.87 (t, $OCCH_3$), 6.44 (q, OCH_2C), 2.35–2.9 (m, aromatic).

Compound (VI)

Similarly, 9.1 g (30 mmole) of (VI) was added to a solution of sodium ethoxide 45 mmole) in 25 ml of ethanol over 1 h. The mixture was then heated gently for 3 h. Fractional distillation gave 5 g of phenyldimethylethoxysilane and preparative GLC afforded (phenylmethylethoxysilyl)(phenyldimethylsilyl)methane. (Found: C, 68.71; H, 8.23. $C_{18}H_{26}OSi_2$ calcd.: C, 68.73; H, 8.23 %.) NMR: 9.71 (s, $SiCH_3$ and $SiCH_2Si$), 8.87 (t, $OCCH_3$), 6.46 (q, OCH_2C), 2.4–2.95 (m, aromatic).

(Chloromethyl)methylphenylsilane

With cooling in an ice bath, 5.4 g (31.6 mmole) of (chloromethyl)methylphenyl-silane was reacted with 2.2 N sodium ethoxide in ethanol (38 mmole). Immediate evolution of hydrogen resulted. After 20 min, the gas evolution ceased and 185 ml (at 20°) of hydrogen was collected, which indicates the occurrence of 24 % solvolysis of the silicon–hydrogen bond. Work-up in the usual way followed by isolation by preparative GLC afforded, in addition to phenyldimethylethoxysilane, (chloro-methyl)methylphenylethoxysilane, (EtO)PhMeSiCH₂Cl. (Found: C, 55.69; H, 7.17. $C_{10}H_{15}ClOSi$ calcd.: C, 55.92; H, 7.04 %.) NMR: 9.53 (s, $SiCH_3$), 8.80 (t, $OCCH_3$), 7.11 (s, CH_2Cl), 6.24 (q, OCH_2C), 2.3–2.9 (m, aromatic). None of methyltriethoxy-silane and toluene, expected from migration of phenyl from silicon to carbon followed by cleavage of the silicon–carbon bond, was detected by GLC.

Compound (VII)

Reaction of 3.5 g (14.2 mmole) of (VII) with 34 mmole of sodium ethoxide in 40 ml of ethanol was carried out with cooling in an ice bath. Isolation by preparative GLC gave (diethoxymethylsilyl)(trimethylsilyl)methane, $(EtO)_2MeSiCH_2SiMe_3$. (Found: C, 48.04; H, 10.67. $C_9H_{24}O_2Si_2$ calcd.: C, 49.03; H, 10.97%.) NMR: 10.23 (s, $SiCH_2Si$), 9.96 (s, $SiCH_3$), 8.82 (t, $OCCH_3$), 6.27 (q, OCH_2C). Trimethylethoxysilane and dimethyldiethoxysilane were identified by GLC.

Compound (VIII)

Compound (VIII) (2.0 g; 9.9 mmole) was treated with 30 mmole of sodium ethoxide in ethanol to form trimethylethoxysilane, dimethyldiethoxysilane and bis-(ethoxydimethylsilyl)methane. All the products were identified by GLC and IR spectra.

Compound (IX)

Treatment of 2.2 g (10 mmole) of (IX) with 40 mmole of sodium ethoxide in 50 ml of ethanol at $0°$ for 2 h and at room temperature for 10 h afforded dimethyldiethoxysilane, and (diethoxymethylsilyl)(ethoxydimethylsilyl)methane, $(EtO)_2MeSiCH_2SiMe_2(OEt)$. (Found: C, 47.78; H, 10.34. $C_{10}H_{26}O_3Si_2$ calcd.: C, 47.95; H, 10.47%.) NMR: 10.14 (s, $SiCH_2Si$), 9.95 (s, $SiCH_3$), 9.92 [s, $Si(CH_3)_2$], 8.87 (t, SiOC-CH_3), 8.83 [t, $Si(OCCH_3)_2$], 6.40 (q, $SiOCH_2C$), 6.31 [q, $Si(OCH_2C)_2$].

Compound (X)

To a solution of sodium ethoxide (0.20 mole) in ethanol (150 ml) was added 6.6 g (0.025 mole) of (X) in the cold over a 10-min period. After the addition was completed, the reaction mixture was stirred at room temperature for 5 h. No gas evolution was observed during the reaction. Neutralization, filtration and subsequent distillation gave a liquid boiling up to 115°/12 mm, which was collected in a flask cooled in an acetone-Dry Ice bath. Fractionation through a column packed with glass helices afforded 5.2 g of methyltriethoxysilane boiling at mainly 140–141°; n_D^{20} 1.3840 (lit.[23] b.p. 140–145° n_D^{20} 1.3821). (Found: C, 47.05; H, 10.05. $C_7H_{18}O_3Si$ calcd.: C, 47.15; H, 10.18%.)

The higher boiling product was isolated by preparative GLC and verified as (triethoxysilyl)(diethoxymethylsilyl)methane, $(EtO)_3SiCH_2SiMe(OEt)_2$. (Found: C, 46.56; H, 9.82. $C_{12}H_{30}O_5Si_2$ calcd.: C, 46.42; H, 9.74%.) NMR: 10.18 (s, $SiCH_2Si$), 9.92 (s, $SiCH_3$), 8.83 [t, $Si(OCCH_3)_2$], 8.81 [t, $Si(OCCH_3)_3$], 6.30 [q, $Si(OCH_2C)_2$], 6.24 [q, $Si(OCH_2C)_3$].

Compound (XI)

To a solution of 44 mmole of sodium ethoxide in 70 ml of ethanol was added 2.0 g (8.3 mmole) of compound (XI) with external cooling over a 3-min period. Immediately, a rapid evolution of hydrogen was observed. After 1 h stirring in the cold, the volume of hydrogen amounted to 143 ml (at STP), 75% of that expected if all the reaction proceeded via Scheme 4. The reaction mixture was then worked up and distilled to give a liquid boiling up to 125°/65 mm, consisting of three main products. They were isolated by preparative GLC, and identified as (chloromethyl)dimethylethoxysilane, tetraethoxysilane (by comparison of retention times on GLC and IR spectra with those of the authentic samples), and (triethoxysilyl)(ethoxydimethylsilyl)methane,

$(EtO)_3SiCH_2SiMe_2(OEt)$. (Found: C, 46.33; H, 10.07. $C_{11}H_{28}O_4Si_2$ calcd.: C, 47.10; H, 10.17%.) NMR: 10.17 (s, $SiCH_2Si$), 9.90 [s, $Si(CH_3)_2$], 8.86 (t, $SiOCCH_3$), 8.81 [t, $Si(OCCH_3)_3$], 6.40 (q, $SiOCH_2C$), 6.25 [q, $Si(OCH_2C)_3$].

Compound (XII)

A solution of 6.0 g (20.0 mmole) of (XII) in 5 ml of dry benzene was added to a solution of sodium ethoxide (140 mmole) in ethanol (70 ml) in the cold with stirring over 1 min. Immediately, rapid evolution of hydrogen occurred and ceased just after the addition had been completed and 385 ml at STP (17.2 mmole; 85%) of the gas was collected. Analysis of the reaction mixture by GLC showed the only formation of methyltriethoxysilane and tetraethoxysilane in the ratio of about 1/1, and dichloromethane.

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