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PREPARATION OF SOME POLYSILICON HALIDES BY ALUMINUM HALIDE CATALYZED INTERCHANGE OF METHYL AND HALOGEN ON SILICON

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SUMMARY

The aluminum halide catalyzed interchange reaction of methyl and halogen on silicon has been found to afford a convenient and widely applicable method of preparing polysilicon compounds containing halodimethylsilyl groups. Thus by heating the corresponding poly(trimethylsilyl) compounds with excess trimethylhalosilane in the presence of an aluminum halide, $ClMe_2Si{-}(SiMe_2)_n{-}SiMe_2Cl$ ($n=0, 1$), $ClMe_2{-}Si(CH_2)_n{-}SiMe_2Cl$ ($n=1$–4), $ClMe_2Si{-}CHR{-}CH_2{-}SiMe_2Cl$ ($R=Me, Ph$), $(ClMe_2Si)_4E$ ($E=C, Si$), $BrMe_2Si{-}(CH_2)_n{-}SiMe_2Br$ ($n=0, 1$), and $XMe_2SiSiMe_3$ ($X=Cl, I$) have been prepared in excellent yields.

INTRODUCTION

During work directed toward the synthesis of organosilicon-bridged ferrocenes[1,2] and silicon-containing heterocyclic compounds[3] it became necessary to prepare relatively large quantities of polysilicon compounds containing $ClMe_2Si$ groups, such as (I)–(III). This paper is concerned with a new approach to synthesis of

$ClMe_2Si{-}(SiMe_2)_n{-}SiMe_2Cl$ $n=0, 1$ (I)
$ClMe_2Si{-}(CH_2)_n{-}SiMe_2Cl$ $n=1$–4 (II)
$ClMe_2Si{-}CHR{-}CH_2{-}SiMe_2Cl$ $R=Me, Ph$ (III)

these chlorosilanes and some other related halosilanes from the corresponding Me_3Si-substituted compounds, which is more convenient and widely applicable than earlier methods.

In previous papers from this Laboratory it was reported that 1,2-dichlorotetramethyldisilane (I, $n=0$) and 1,3-dichlorohexamethyltrisilane (I, $n=1$) can be prepared from hexamethyldisilane and octamethyltrisilane, respectively, by (1) demethylation with concentrated sulfuric acid followed by treatment with ammonium

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chloride[4,5], (2) chlorodemethylation with a 1/1 mixture of acetyl chloride and anhydrous aluminum chloride[6,*], or (3) chlorodemethylation by dry hydrogen chloride in the presence of aluminum chloride[6]. The first method gives the desired products in relatively low yields, (I, $n=0$) 55% and (I, $n=1$) 40%, because of oxidative cleavage of the silicon–silicon bond occurring to a significant extent, especially in the case of the trisilane. Although the second approach affords, in general, very satisfactory yields of the dichlorodisilane (87%) and -trisilane (84%), the use of large amounts of anhydrous aluminum chloride may be inconvenient. By the third method, it is possible to prepare (I, $n=0$) in 81% yield but this method requires special precautions to keep the reaction temperature in a rather narrow range (50–60°) and avoid an excess of hydrogen chloride introduced; otherwise more than one methyl group per silicon tends to be replaced by chlorine atoms.

The best way previously reported for the preparation of bis(chlorodimethylsilyl)methane (II, $n=1$) and 1,2-bis(chlorodimethylsilyl)ethane (II, $n=2$) involves chlorodemethylation of the respective bis(trimethylsilyl) compounds with an equimolar mixture of acetyl chloride and anhydrous aluminum chloride, which affords (II, $n=1$) in 70% yield and (II, $n=2$) in 95% yield[6]. However, this method cannot be extended to synthesis of the higher homologs (II, $n \geqslant 3$) because extensive cleavage of the silicon–methylene bonds occurs. A convenient method previously reported[3] for synthesis of (II, $n \geqslant 3$) involves reactions in two stages, *i.e.*, demethylation of α,ω-bis(trimethylsilyl)alkanes with concentrated sulfuric acid followed by treatment with ammonium hydrogen fluoride to produce the corresponding α,ω-bis(fluorodimethylsilyl)alkanes[7], and conversion of the latter into the desired chloro compounds by an aluminum chloride catalyzed fluorine/chlorine interchange by refluxing with excess trimethylchlorosilane[10]. Overall yields of (II, $n=3$) and (II, $n=4$) were about 60% in both cases.

RESULTS

We have now found that any one of the compounds of the formula (I)–(III) can successfully be prepared by an aluminum chloride catalyzed Si–Me/Si–Cl interchange reaction. Thus, when a mixture of an appropriate bis(trimethylsilyl) compound of the formula (IV)–(VI) with excess trimethylchlorosilane is boiled gently in the presence of a catalytic amount of aluminum chloride in a flask fitted with a suitable fractional distillation column, tetramethylsilane gradually distills out. The extent of the interchange is indicated by the amount of tetramethylsilane obtained. When no more tetramethylsilane is formed, most of excess of trimethylchlorosilane is removed by distillation, a small amount of acetone is then introduced into the flask for the purpose of deactivating the catalyst and finally the product is obtained by fractional distillation. The deactivation of catalyst seems necessary in order to avoid possible side reactions, such as further redistribution, skeletal rearrangement or decomposition, occurring during distillation at higher temperature. In most cases, the yields are excellent (see Table 1), which shows that no significant cleavage of the

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[*] Demethylation of hexamethyldisilane by a mixture of acetyl chloride and aluminum chloride was first described by Frainnet *et al.*[7,8], but their attention was focused on the ketones rather than the chlorodisilanes produced in this reaction.

TABLE 1

HALODIMETHYLSILYL-CONTAINING POLYSILICON COMPOUNDS PREPARED BY ALUMINUM HALIDE CATALYZED REDISTRIBUTION REACTION

Starting substance	(mmoles)	Me_3SiX (mmole)	AlX_3 (g)	Product	Yield[a] (%)
$Me_3SiSiMe_3$	68	460 (X=Cl)	0.5 (X=Cl)	$ClMe_2SiSiMe_2Cl$[b]	93
$Me_3SiSiMe_3$	68	320 (X=Br)	0.5 (X=Br)	$BrMe_2SiSiMe_2Br$[c]	82
$Me_3SiSiMe_3$	210	510 (X=Cl)	0.7 (X=Cl)	$ClMe_2SiSiMe_3$[d]	69
$Me_3SiSiMe_3$	100	250 (X=I)	2.4 (X=I)	$IMe_2SiSiMe_3$[e]	71
$Me_3SiSiMe_2SiMe_3$	49	460 (X=Cl)	0.5 (X=Cl)	$ClMe_2SiSiMe_2SiMeCl$[f]	91
$Me_3SiCH_2SiMe_3$	63	460 (X=Cl)	0.5 (X=Cl)	$ClMe_2SiCH_2SiMe_2Cl$[g]	89
$Me_3SiCH_2SiMe_3$	63	320 (X=Br)	0.5 (X=Br)	$BrMe_2SiCH_2SiMe_2Br$[h]	89
$Me_3Si(CH_2)_2SiMe_3$	57	460 (X=Cl)	0.5 (X=Cl)	$ClMe_2Si(CH_2)_2SiMe_2Cl$[i]	95
$Me_3Si(CH_2)_3SiMe_3$	53	460 (X=Cl)	0.5 (X=Cl)	$ClMe_2Si(CH_2)_3SiMe_2Cl$[j]	92
$Me_3Si(CH_2)_4SiMe_3$	49	460 (X=Cl)	0.5 (X=Cl)	$ClMe_2Si(CH_2)_4SiMe_2Cl$[k]	86
$Me_3SiCH(Me)CH_2SiMe_3$	53	460 (X=Cl)	0.5 (X=Cl)	$ClMe_2SiCH(Me)CH_2SiMe_2Cl$[l]	96
$Me_3SiCH(Ph)CH_2SiMe_3$	40	460 (X=Cl)	0.5 (X=Cl)	$ClMe_2SiCH(Ph)CH_2SiMe_2Cl$[m]	90
$(Me_3Si)_4C$	16	460 (X=Cl)	0.2 (X=Cl)	$(ClMe_2Si)_4C$[n]	88
$(Me_3Si)_4Si$	31	460 (X=Cl)	0.5 (X=Cl)	$(ClMe_2Si)_4Si$[o]	84

[a] Isolated yield.
[b] B.p. 63–64°/48 mm, n_D^{20} 1.4545 (ref. 4: b.p. 146–148°, n_D^{20} 1.4545); Found: Cl, 37.36 (calcd. 37.88%).
[c] B.p. 79–80°/37 mm, m.p. 63–64° (ref. 37: b.p. 79–82°/30 mm, m.p. ca. 40°); Found: Br, 57.98 (calcd. 57.88%).
[d] B.p. 133–135°, n_D^{20} 1.4429 (ref. 4: b.p. 134–135.6°, n_D^{20} 1.4430); Found: Cl, 21.09 (calcd. 21.25%).
[e] B.p. 80–85°/55 mm, m.p. 51–53° (ref. 24: b.p. 78°/71 mm, m.p. 53°).
[f] B.p. 69–70°/5 mm, n_D^{20} 1.4851 (ref. 5: b.p. 82–83°/11 mm, n_D^{20} 1.4852); Found: Cl, 28.56 (calcd. 28.89%).
[g] B.p. 56–58°/11 mm, n_D^{20} 1.4490 (ref. 10: b.p. 177°, n_D^{20} 1.4480); Found: Cl, 35.03 (calcd. 35.24%).
[h] B.p. 79–81°/10 mm, n_D^{20} 1.4891; Found: Br, 54.99 (calcd. 55.08%).
[i] B.p. 64–67°/8 mm, m.p. 38–39° (ref. 36: b.p. 198°/734 mm, m.p. 37°); Found: Cl, 32.73 (calcd. 32.94%).
[j] B.p. 86–89°/11 mm, n_D^{20} 1.4495 (ref. 3: b.p. 103–104/21 mm, n_D^{20} 1.4497); Found: Cl, 30.18 (calcd. 30.92%).
[k] B.p. 70–72°/4 mm, n_D^{20} 1.4513 (ref. 3: b.p. 123–124°/24 mm, n_D^{20} 1.4509); Found: Cl, 28.96 (calcd. 29.14%).
[l] B.p. 104°/24 mm, n_D^{25} 1.4543; Found: Cl, 30.54 (calcd. 30.93%).
[m] B.p. 102–103°/3 mm, m.p. 63–64°; Found: Cl, 24.05 (calcd. 24.37%).
[n] Sublimes at 130–150°/2 mm, m.p. >300° (ref. 38: m.p. >300°); Found: C, 27.12; H, 6.07 (calcd.: C. 27.97; H, 6.26%).
[o] Sublimes at 135–150°/2 mm, m.p. >300° (ref. 38: no properties given); Found: Cl, 35.46 (calcd. 35.24%).

silicon–silicon or silicon–methylene linkages occurs and that no more than one methyl group per silicon atom is replaced by chlorine.

$$\begin{array}{l} Me_3Si{-}(SiMe_2)_n{-}SiMe_3 + 2\ Me_3SiCl \xrightarrow{AlCl_3} (I) + 2\ Me_4Si \\ (IV)\ n=0,\ 1 \end{array}$$

$$\begin{array}{l} Me_3Si{-}(CH_2)_n{-}SiMe_3 + 2\ Me_3SiCl \xrightarrow{AlCl_3} (II) + 2\ Me_4Si \\ (V)\ n=1\text{–}4 \end{array}$$

$$\begin{array}{l} Me_3Si{-}CHR{-}CH_2{-}SiMe_3 + 2\ Me_3SiCl \xrightarrow{AlCl_3} (III) + 2\ Me_4Si \\ (VI)\ R=Me,\ Ph \end{array}$$

The present method has been found to be also applicable to synthesis of some other types of polysilicon derivatives containing halodimethylsilyl groups. Thus, tetrakis(chlorodimethylsilyl)methane (VII, E=C) and -silane (VII, E=Si), 1,2-dibromotetramethyldisilane (VIII) and bis(bromodimethylsilyl)methane (IX) can be prepared in good yields from the corresponding poly(trimethylsilyl) derivatives in essentially the same manner, except that trimethylbromosilane and anhydrous aluminum bromide must, of course, be used in the last two cases.

$$\begin{array}{ccc} (ClMe_2Si)_4E & BrMe_2Si\text{–}SiMe_2Br & BrMe_2Si\text{–}CH_2\text{–}SiMe_2Br \\ \text{(VII) } E=C, Si & \text{(VIII)} & \text{(IX)} \end{array}$$

Preparation of monohalo derivatives of disilane can also be accomplished if the distillation is interrupted when about one molar equivalent of tetramethylsilane has been collected; the catalyst is deactivated by addition of a little acetone, and distillation is resumed to give the desired product. The point at which acetone should be added is best determined by monitoring the progress of reaction by VPC of the contents of the flask. Thus, chloro- and iodopentamethyldisilane were prepared in 69 and 71% yield, respectively, from hexamethyldisilane.

$$\begin{array}{l} Me_3Si\text{–}SiMe_3+\underset{X=Cl,\ I}{Me_3SiX} \xrightarrow{AlX_3} XMe_2Si\text{–}SiMe_3+Me_4Si \end{array}$$

DISCUSSION

The redistribution reaction of silicon compounds has received considerable attention and been the subject of recent reviews by Eaborn and Bott[11], by Moedritzer[12], by Lockhart[13], and by Weyenberg *et al.*[14]. As for the aluminum chloride catalyzed interchange of methyl and chlorine on silicon, the redistribution and disproportionation of methylchlorosilanes have been studied at high temperatures (250–450°) and pressures from the synthetic[15], equilibrium[16] and mechanistic[17] point of view. Russell[18,19] has indicated, on the basis of kinetic data on the aluminum bromide catalyzed disproportionation of compounds of the type Me_3SiR where R stands for H, C_6H_5, C_2H_5, Br, a mechanism involving electrophilic attack on R and nucleophilic attack on silicon. The rate of disproportionation varies greatly with the non-migrating groups on silicon as well as the nature of the migrating groups. Thus, electron-donating groups greatly favor, whilst electron-accepting groups retard, the reaction and the observed somewhat slower methyl/bromine interchange in bromotrimethylsilane than methyl/ethyl interchange in ethyltrimethylsilane can be explained in terms of a large effect of the non-migrating bromine on the reactivity of the migrating methyl group.

The findings that the aluminum chloride catalyzed redistribution and disproportionation of methylchlorosilanes require very drastic conditions as cited above whereas redistributions involving methyl/chlorine or aryl/chlorine interchange, as reported previously[20], occur much more readily with systems containing a chloromethyldisilane compound can also be well understood on the same basis, if one assumes that the highly methylated disilanyl and disilanylene groups are electron-donating (see *e.g.* ref. 21).

$$Me_3Si\text{–}SiMe_3+ClMe_2Si\text{–}SiMe_2Cl \overset{AlCl_3}{\rightleftharpoons} 2\ ClM_2Si\text{–}SiMe_3$$

$$ArSiMe_3+ClMe_2Si\text{–}SiMe_3 \xrightarrow{AlCl_3} ArMe_2Si\text{–}SiMe_3+Me_3SiCl$$

The method for synthesis of halodimethylsilyl-containing polysilicon compounds, which is described in the present paper, appears, for several reasons, to take full advantage of the known features of the aluminum halide catalyzed redistribution reactions. First, it is likely that the methyl groups on silicon in all the compounds employed here, $\mathrm{Me_3Si{-}(SiMe_2)_n{-}SiMe_3}$ (IV), $\mathrm{Me_3Si{-}(CH_2)_n{-}SiMe_3}$ (V), $\mathrm{Me_3Si{-}CH(R){-}CH_2{-}SiMe_3}$ (VI) and $\mathrm{(Me_3Si)_4E}$ (E = C, Si), readily undergo the electrophilic attack by the $\mathrm{Me_3Si}$ group from a trimethylhalosilane complexed with an aluminum halide[18,19]. Second, the halogen atom in a trimethylhalosilane may have a large migratory tendency because of being activated greatly by the three methyl groups on the silicon atom. Third, the continuous removal of the volatile tetramethylsilane from the reaction zone as it forms serves to shift the equilibrium completely towards the production of the halodimethylsilyl compounds. Fourth, if one methyl of $\mathrm{Me_3Si}$ group in the polysilicon compound has been replaced by the halogen atom, no further replacement occurs because the now introduced halogen atom deactivates toward electrophilic attack the remaining two methyl groups on the same silicon atom. Finally, if the electrophilic attack by the $\mathrm{Me_3Si}$ group from the trimethylhalosilane complexed with the catalyst occurs not at a methyl but at a methylene (or methyne) carbon atom linked to silicon in compounds (V) [or (VI)], no net reactions occur.

Further studies are in progress in an effort to extend the present method to synthesis of organopolysilicon halides with a variety of skeletal structures.

EXPERIMENTAL

Starting substances

All the $\mathrm{Me_3Si}$-containing polysilicon compounds (IV), (V), (VI) and $\mathrm{(Me_3Si)_4E}$ (E = C, Si) used here are known except for (VI, R = Me). This new compound and its phenyl analog (VI, R = Ph) were prepared by the method described below, although the latter has been synthesized by Weyenberg *et al.*[22] by an alternative method. In the following list, the references given after the compounds are to the source or method of preparation: (IV, $n=1$)[4,5,23,24]; (IV, $n=2$)[5,23,24]; (V, $n=1$)[25,26]; (V, $n=2$)[27,28]; (V, $n=3$)[29]; (V, $n=4$)[30]; $\mathrm{(Me_3Si)_4C}$[31]; and $\mathrm{(Me_3Si)_4Si}$[32].

1,2-*Bis(trimethylsilyl)propane* (*VI, R = Me*)

This compound was prepared via two steps as shown by the following sequence:

$$\mathrm{Me_3Si{-}C(Me){=}CH_2 + MeSiHCl_2 \xrightarrow{H_2PtCl_6} Me_3Si{-}CHMe{-}CH_2{-}SiMeCl_2}$$

(X)

$$\xrightarrow{\mathrm{MeMgBr}} \text{(VI, R = Me)}$$

A mixture of 24 g (0.21 mole) of isopropenyltrimethylsilane[33,34], 25 g (0.22 mole) of methyldichlorosilane and 0.4 ml of 0.1 *M* isopropyl alcohol solution of chloroplatinic acid[35] was heated in a sealed tube at 130–145° for 100 h. Fractional distillation of the reaction mixture gave 33 g (67%) of 1-(dichloromethylsilyl)-2-(trimethylsilyl)propane (X), b.p. 93°/23 mm, n_D^{20} 1.4508. (Found: Cl, 30.41. $\mathrm{C_7H_{18}Cl_2Si_2}$ calcd.: Cl, 30.93%.) This product (30 g, 0.13 mole) was added to a stirred methylmagnesium bromide made from 7.2 g (0.3 g-atom) of magnesium in the usual way.

After reflux for 10 h, the reaction mixture was hydrolyzed and worked up. Fractionation gave 22 g (92%) of (VI, R=Me), b.p. 70°/24 mm, n_D^{20} 1.4300. (Found: C, 57.98; H, 12.82. $C_9H_{24}Si_2$ calcd.: C, 57.35; H, 12.84%.)

1,2-Bis(trimethylsilyl)-1-phenylethane (IV, R=Ph)

A solution of α-(trimethylsilyl)benzyllithium, $Me_3SiCH(Li)Ph$, was prepared by adding 170 ml of 1.4 *M* n-hexane solution of n-butyllithium to a mixture of 33 g (0.2 mole) of benzyltrimethylsilane and 23 g (0.2 mole) of *N,N,N′,N′*-tetramethylethylenediamine. To this solution was added at room temperature 24 g (0.2 mole) of (chloromethyl)trimethylsilane admixed with 2 ml of n-hexane. After reflux for 4 h, the mixture was hydrolyzed and worked up in the usual way. Fractional distillation gave 28 g (60%) of (VI, R=Ph), b.p. 113–114°/15 mm, n_D^{25} 1.4895 (lit.[22] b.p. 93–97°/4–5 mm, $n_D^{26.5}$ 1.4882) (Found: C, 67.11; H, 10.25. $C_{14}H_{26}Si_2$ calcd.: C, 67.11; H, 10.46%.), in addition to 9 g of recovered benzyltrimethylsilane.

The methyl/halogen interchange reaction

All the halodimethylsilyl polysilicon compounds reported in this paper were prepared in essentially the same manner with slight modifications in the cases of production of crystalline substances and monohalo derivatives. The following detailed description of the synthesis of 1,2-bis(chlorodimethylsilyl)propane (III, R=Me) is typical.

In a 100-ml flask fitted with a 1.0 × 30 cm fractional distillation column, packed with glass helices and mounted with a heating jacket, was placed a mixture of 10 g (0.053 mole) of (VI, R=Me), 50 g (0.15 mole) of trimethylchlorosilane and 0.5 g of anhydrous aluminum chloride. The flask was heated to gentle reflux. Tetramethylsilane, b.p. 26–27°, soon began to distill. After ca. 4 h, 13 ml (ca. 90%) of tetramethylsilane was collected and no more of it appeared to be formed. The temperatures of the flask and jacket were then increased to distill about 30 ml of trimethylchlorosilane. At this point, ca. 5 ml of acetone was introduced into the flask and the residue in the flask was fractionally distilled under reduced pressure to give 33 g of gas-chromatographically homogeneous product of (III, R=Me).

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