HETEROGENEOUS REACTIONS

VII *. FURTHER STUDIES ON THE HETEROGENEOUS GAS/SOLID REACTIONS OF SOLID ALKOXIDE BASES WITH VAPORIZED CHLOROMETHYLDIMETHYLHALOSILANES

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Summary

The results of the heterogeneous gas/solid reactions of chloromethyldimethyl-chloro (and fluoro)silane with solid lithium, sodium and potassium methoxide in the temperature range from 80—160°C are presented and discussed. Reaction with lithium methoxide serves as a clean, efficient high yield synthesis of chloro-methyldimethylmethoxysilane without the complicating factors of side products or solvent to separate. The reactions of both the sodium and potassium methoxides lead to the displacement of halogen from silicon and to the displacement of the chloromethyl group. New evidence for the mechanism of the latter reaction is presented. With the potassium compound methylethyldimethoxy-silane also is formed and a carbene, sila-olefin addition mechanism is suggested. Surprisingly, lithium t-butoxide did not react with the chlorosilane but did react with the fluorosilane to produce chloromethyldimethyl-t-butoxysilane in high purity and excellent yield. The reaction with potassium t-butoxide was more complicated, giving substitution for halogen and the chloromethyl group at silicon as well as t-butyl methyl ether.
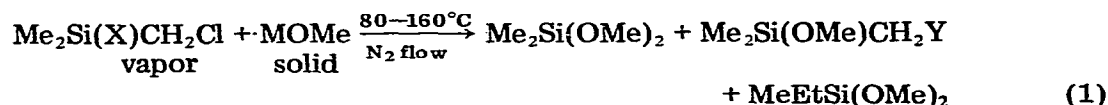
Introduction

Earlier papers in this series have presented the results of the heterogeneous gas/solid reactions of various solid alkoxide bases and vaporized organosilane [1—3] and alkyl halide [4—6] substrates. Tri- and dialkylchlorosilanes may be conveniently converted to tri- and dialkylalkoxysilanes under heterogeneous conditions [1]. The ease of reaction, generally good yields, and lack of solvent

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* For part VI see ref. 3.

to separate during the work-up procedure are obvious advantages of this new method of preparing alkoxysilanes. In another study with chloromethyldimethylsilane as the vaporized substrate and potassium t-butoxide as the solid reagent, the results were interpreted in terms of a 1, 2-hydride shift from silicon to carbon under heterogeneous conditions [2]. The analogous solution phase rearrangement was originally proposed in 1959 [7]. The considerable lattitude afforded by the heterogeneous system allowed some direct tests of the validity of this mechanism to be carried out. The work presented in this paper is an extension of our earlier work concerning the interaction of solid alkoxide bases with chloromethyldimethylhalosilanes [3].
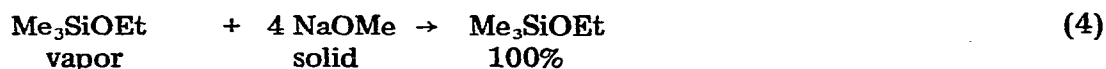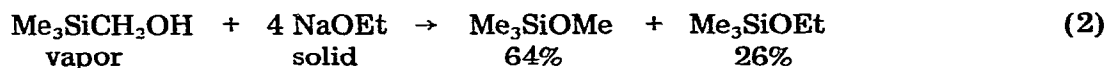
Results and discussion

Our earlier work [3] concerning the heterogeneous gas/solid reaction summarized in equation 1 has been repeated and extended to include the reactions of the fluorosilane substrate as well as the reactions of both substrates with lithium

$$Me_2Si(X)CH_2Cl + MOMe \xrightarrow[N_2 \, flow]{80-160^\circ C} Me_2Si(OMe)_2 + Me_2Si(OMe)CH_2Y$$
$$\text{vapor} \qquad \text{solid}$$
$$+ MeEtSi(OMe)_2 \qquad (1)$$

$$X = Cl \text{ and } F \qquad M = Li, Na, K \qquad Y = Cl \text{ and } OMe$$

and potassium methoxide. Since our initial work, modifications in the mode of packing the solid alkoxide base and improvement in the quality, i.e., lower hydroxide contamination, of the alkoxide bases have allowed both higher alkoxide incorporation and better overall yields.

Both the present and the earlier work on the interaction of chloromethyldimethylhalosilanes with sodium methoxide emphasize the role of trace hydroxides in the determination of the product distribution for this system. With higher hydroxide contamination the overall yield is lower and the amount of chloromethyl group displacement is higher. The former trend is likely due to hydroxide attack followed by proton transfer which converts the silane into a salt which remains in the furnace area. Two potential mechanisms have been suggested for the latter trend [3]. Both of these mechanisms involve initial displacement of chloride ion from carbon by hydroxide ion. Subsequent conversion of the alpha hydroxy silane to the alkoxysilane was suggested to occur, either by base catalyzed rearrangement [8,9] or via alkoxide attack at the silicon center. The results summarized in equations 2—4 are best accomodated in terms of both mechanisms operating for the sodium methoxide system. The relative

$$Me_3SiCH_2OH \; + \; 4\,NaOEt \; \rightarrow \; Me_3SiOMe \; + \; Me_3SiOEt \qquad (2)$$
$$\text{vapor} \qquad\qquad \text{solid} \qquad\quad 64\% \qquad\qquad 26\%$$

$$Me_3SiOMe \; + \; 4\,NaOEt \; \rightarrow \; Me_3SiOMe \; + \; Me_3SiOEt \qquad (3)$$
$$\text{vapor} \qquad\qquad \text{solid} \qquad\quad 84\% \qquad\qquad 12\%$$

$$Me_3SiOEt \; + \; 4\,NaOMe \; \rightarrow \; Me_3SiOEt \qquad (4)$$
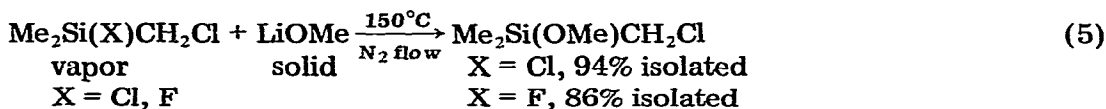$$\text{vapor} \qquad\qquad \text{solid} \qquad\quad 100\%$$

proportion of trimethylethoxysilane in equation 2 is higher than can be

accounted for by initial base catalyzed rearrangement followed by alkoxide—alkoxide exchange. If the latter mechanistic alternative were the only one in operation, the ratio of trimethylmethoxysilane to trimethylethoxysilane in equation 2 would be expected to be closer to 7 (eqn. 3) rather than the observed 2.5. Furthermore, a depression in the amount of trimethylethoxysilane in equation 3 due to alkoxide—alkoxide exchange is not likely on the basis of the results of equation 4.

Table 1 shows the results of the study of the reaction of chloromethyldimethylfluorosilane with sodium methoxide and includes two reactions of the corresponding chlorosilane for comparison. Table 2 shows the results of a repeated study of the reaction of the chlorosilane substrate with sodium methoxide. It should be noted that the differences in the results for the reaction of the chlorosilane in Tables 1 and 2 and in reference 3 are very likely due to the use of different samples of sodium methoxide. With a given sample of this base, our earlier suggestions and those set forth here are entirely consistent for each silane substrate. With sodium methoxide, the results of the reactions of the two halosilane substrates do not show a marked dependence on the nature of the halogen on silicon. As will be come evident later, this is likely due to the high reactivity of sodium methoxide toward these organosilicon substrates which masks the effect of halogen on silicon. The observations and suggestions of our earlier work with the chlorosilane likely apply to the reactions of the fluorosilane substrate as well.

Equation 5 summarizes the results of the reactions with lithium methoxide. In marked contrast to the two other methoxide bases studied, the reaction of

$$Me_2Si(X)CH_2Cl + LiOMe \xrightarrow[N_2\ flow]{150°C} Me_2Si(OMe)CH_2Cl \qquad (5)$$
$$\text{vapor} \qquad\qquad \text{solid} \qquad\qquad X = Cl, 94\% \text{ isolated}$$
$$X = Cl, F \qquad\qquad\qquad\qquad X = F, 86\% \text{ isolated}$$

lithium methoxide serves as a clean, convenient high yield synthesis of chloromethyldimethylmethoxysilane without the complicating factor of additional products. In addition the time consuming work-up procedure associated with the isolation of the product from the more traditional solution phase preparation [3] of this compound is avoided. Furthermore, as seen immediately follow-

TABLE 1

TEMPERATURE DEPENDENCE OF THE REACTION OF CHLOROMETHYLDIMETHYLHALO-SILANES WITH SODIUM METHOXIDE[a]

Silane	Temp. (°C)[b]	$Me_2Si(OMe)_2$[c]	$Me_2Si(OMe)CH_2Cl$[c]	$Me_2Si(OMe)CH_2OMe$[c]
$Me_2Si(F)CH_2Cl$	80	4	91	4
$Me_2Si(F)CH_2Cl$	100	6	91	5
$Me_3Si(Cl)CH_2Cl$	100	5	79	3
$Me_2Si(F)CH_2Cl$	120	12	61	8
$Me_2Si(F)CH_2Cl$	130	18	71	10
$Me_2Si(F)CH_2Cl$	150	30	53	11
$Me_2Si(Cl)CH_2Cl$	150	21	54	10

[a] All reactions utilized the general procedure described in the experimental section. [b] ±3°C. [c] As determined by internal standard yield analysis based on starting silane.
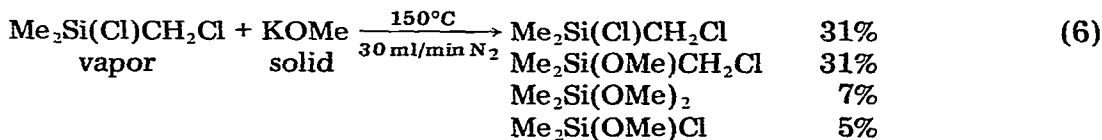
TABLE 2

TEMPERATURE DEPENDENCE OF THE REACTION OF CHLOROMETHYLDIMETHYLCHLORO-
SILANE WITH SODIUM METHOXIDE [a]

Temp. (°C) [b]	$Me_2Si(OMe)_2$ [c]	$Me_2Si(OMe)CH_2Cl$ [c]	$Me_2Si(OMe)CH_2OMe$ [c]
80	4	42	27
100	6	48	21
120	27	33	17
140	29	20	19
160	33	7	17

[a] All reactions utilized the general procedure described in the experimental section. [b] ±3°C. [c] As determined by internal standard yield analysis based on starting silane.

ing, the quality of the lithium methoxide is not so crucial to the observed chemistry as is the case for sodium and potassium methoxide. It could be argued that the sole production of chloromethyldimethylmethoxysilane in equation 5 was due to the lack of hydroxide contaminants in this base. To test this possibility lithium methoxide was deliberately contaminated with water prior to its reaction with the silane. Surprisingly, dimethyldimethoxysilane was produced in only 2% yield in this experiment. The reaction gave a 53% yield of the product of equation 5 with the remaining silicon products retained in the furnace area.
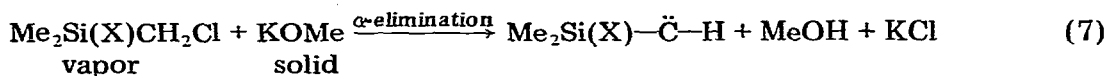
Unreacted starting material was observed in runs 3 and 4 of Table 3 in the reactions with potassium methoxide. Under comparable conditions no unreacted starting material has ever been observed in the reactions of lithium or sodium methoxide. Thus, in terms of the formation of chloromethyldimethyl-methoxysilane or dimethyldimethoxysilane, potassium methoxide is the least reactive of the three methoxide compounds. The chemistry of potassium methoxide also differs from that of sodium methoxide in that the distribution of products was not temperature dependent in the range of temperatures from 80—150°C. Under the conditions of run 5, no chloromethyldimethylmethoxy-silane has ever been observed in the reactions of chloromethylfluorosilane with potassium methoxide. When chloromethyldimethylmethoxysilane was subjected to the conditions of run 5, 9% of the starting material was found in the condensate. More methylethyldimethoxysilane is obtained in the reaction of the fluorosilane substrate than in the reaction with chloromethyldimethyl-methoxysilane, 59% versus 39%. Furthermore, when chloromethyldimethyl-chlorosilane was reacted under the conditions of run 5, the results summarized in equation 6 were obtained.

$$Me_2Si(Cl)CH_2Cl + KOMe \xrightarrow[30\ ml/min\ N_2]{150°C} \begin{array}{ll} Me_2Si(Cl)CH_2Cl & 31\% \\ Me_2Si(OMe)CH_2Cl & 31\% \\ Me_2Si(OMe)_2 & 7\% \\ Me_2Si(OMe)Cl & 5\% \end{array} \qquad (6)$$
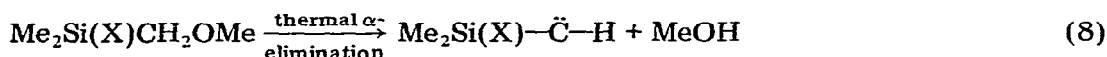
vapor   solid

These observations suggest that the substitution of methoxide or chloride for fluoride on the silicon substrate leads to a modulation of the various processes which lead to the observed distribution of products in the reactions of potassium methoxide. Apparently, a fairly electronegative substituent on the silicon

atom undergoing reaction activates the process which leads to the formation of methylethyldimethoxysilane; compare run 4 to equation 6. It should be noted that the contrasting amounts of methylethyldimethoxysilane production in runs 5 and 6 may reflect the operation of both electronic and steric factors. It is conceivable that the substitution of methoxide for fluoride at silicon activates, perhaps sterically, the process leading to chloromethyl group displacement relative to the process which leads to the formation of methylethyldimethoxysilane. In the reactions of potassium methoxide, it would appear that the factors which determine the observed distribution of products are rather easily modulated by electronic and/or steric considerations at the silicon center.

Two of the mechanistic pathways which lead to the formation of methylethyldimethoxysilane involve the initial formation of a carbene α to silicon either via a base-induced α-elimination of the elements of hydrogen chloride from the chloromethyl group or the thermal elimination of the elements of methanol from an originally formed methoxymethyl group, i.e., equations 7 and and 8.

$$Me_2Si(X)CH_2Cl + KOMe \xrightarrow{\alpha\text{-elimination}} Me_2Si(X)-\ddot{C}-H + MeOH + KCl \qquad (7)$$

$$\text{vapor} \qquad\qquad \text{solid}$$

X = F or OMe

$$Me_2Si(X)CH_2OMe \xrightarrow[\text{elimination}]{\text{thermal }\alpha\text{-}} Me_2Si(X)-\ddot{C}-H + MeOH \qquad (8)$$

X = F or OMe

The latter alternative seems less likely since methoxymethyldimethylmethoxysilane has been isolated and fully characterized from the reactions with sodium methoxide in the range of temperatures studied for the reactions with potassium methoxide [3]. The subsequent rearrangement of the carbene to a sila-olefin followed by the addition of methanol, equation 9, to give the observed

$$Me_2Si(X)-\ddot{C}-H \rightarrow MeSi(X)=CHCH_3 \xrightarrow{MeOH} Me\underset{|}{\overset{}{Si}}(X)CH_2CH_3 \qquad (9)$$
$$OMe$$
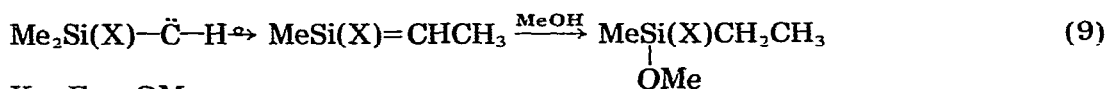
X = F or OMe

product have been documented previously [10,11]. If this product is produced via a base-induced α-elimination reaction, the fact that this process occurs with potassium methoxide and not sodium methoxide may be a reflection of our suggestion that the potassium compound is more basic than the sodium compound under the conditions of heterogeneous reaction [12]. The observed electronic effects are in accord with this mechanistic alternative and it is well known that silicon stabilizes carbanions α to itself [13].

Runs 7 and 8 of Table 3 show the results of the reactions of the two silane substrates with potassium t-butoxide. Apparently the relative reactivity of this base also masks the effects of halogen on silicon. The results of the reaction of chloromethyldimethylfluorosilane with this base closely parallel those of the corresponding chlorosilane in that there is little temperature dependence in the product distribution and the results of the reaction do depend on the nitrogen flow rate [3]. As noted earlier, increasing the contact time with the base charge

TABLE 3

REACTIONS OF CHLOROMETHYLDIMETHYLHALOSILANES WITH SOLID ALKOXIDE BASES[a]

Run	Silane	Base	Products	Yield[b]
1	$Me_2Si(Cl)CH_2Cl$	NaOMe	$Me_2Si(OMe)CH_2Cl$	54
			$Me_2Si(OMe)_2$	21
			$Me_2Si(OMe)CH_2OMe$	10
2	$Me_2Si(F)CH_2Cl$	NaOMe	$Me_2Si(OMe)CH_2Cl$	53
			$Me_2Si(OMe)_2$	30
			$Me_2Si(OMe)CH_2OMe$	11
3	$Me_2Si(Cl)CH_2Cl$	KOMe	$Me_2Si(Cl)CH_2Cl$	54
			$Me_2Si(OMe)CH_2Cl$	17
			$Me_2Si(OMe)_2$	4
			$Me_2Si(OMe)Cl$	6
4	$Me_2Si(F)CH_2Cl$	KOMe	$Me_2Si(F)CH_2Cl$	34
			$Me_2Si(OMe)CH_2Cl$	7
			$Me_2Si(OMe)_2$	19
			$MeEtSi(OMe)_2$	18
5	$Me_2Si(F)CH_2Cl$	KOMe[c]	$MeEtSi(OMe)_2$	59
			$Me_2Si(OMe)_2$	10
6	$Me_2Si(OMe)CH_2Cl$	KOMe[c]	$MeEtSi(OMe)_2$	39
			$Me_2Si(OMe)_2$	52
			$Me_2Si(OMe)CH_2Cl$	9
7	$Me_2Si(Cl)CH_2Cl$	t-BuOK	$t-BuOSi(CH_2Cl)Me_2$	26
			$(t-BuO)_2SiMe_2$	40
			$t-BuOMe$	24
8	$Me_2Si(F)CH_2Cl$	t-BuOK	$t-BuOSi(CH_2Cl)Me_2$	23
			$(t-BuO)_2SiMe_2$	32
			$t-BuOMe$	38
9	$Me_2Si(Cl)CH_2Cl$	t-BuOLi	$Me_2Si(Cl)CH_2Cl$	83[d]
10	$Me_2Si(F)CH_2Cl$	t-BuOLi	$t-BuOSi(CH_2Cl)Me_2$	80[d]

[a] All reactions utilized the general procedure described in the experimental section. [b] As determined by internal standard yield analysis based on starting silane. [c] Run at 30 ml/min with a tightly compressed base charge. [d] Isolated in greater than 95% purity.

can effect the observed results. For potassium t-butoxide increasing the contact time increased the amount of alkoxide incorporation. In addition to the products shown in run 7 in 28, 35 and 25% yields respectively, ca. 10% of t-butoxymethyldimethyl-t-butoxysilane was found in the condensate when the contact time was increased.

The results of the reactions with lithium t-butoxide, runs 9 and 10, are quite surprising. Chloromethyldimethylchlorosilane failed to react with this base. In contrast, the fluorosilane reacted smoothly and resulted in the formation of pure chloromethyldimethyl-t-butoxysilane in excellent yield. Efforts to prepare this latter compound by the more traditional solution phase reaction (t-BuOK in pentane in the presence of Et_3N) in these laboratories met with limited success (22% isolated yield) and required a long work-up procedure [3]. Thus the heterogeneous reaction between lithium t-butoxide and chloromethyldimethylfluorosilane is clearly the method of choice for the preparation of the corresponding butoxy derivative. As noted elsewhere in this paper and in other studies [12], it would appear that the lithium alkoxides are far more selective in their reac-

tions both at silicon and at carbon. Investigations into the generality of the selectivity of this class of reagents are currently underway.

At this point in the development of heterogeneous gas/solid chemistry several factors remain to be investigated before a consistent explanation for the comparisons and contrasts in the observed chemistry for the bases thus far investigated will become apparent. The relative basicities and nucleophilicities of these alkoxide bases under heterogeneous conditions are currently being investigated. The structure of lithium [14], sodium [15], and potassium [16] methoxide, as well as that of potassium t-butoxide [17], have been reported. We are exploring the possibility that there is a correlation between the crystalline structure of the solid alkoxide bases and their reactivity and/or selectivity. Finally, the thermodynamics of the overall process needs to be considered. Unfortunately, to our knowledge, few of the necessary thermodynamic parameters for the solid alkoxide bases are available and, hence, at this time it is difficult to precisely as ascertain the role of these factors in the observed chemistry. Our efforts to delineate the controlling factors, selective reactions and potential applications of heterogeneous gas/solid reactions are continuing and will be the subject of later reports.

Experimental

Product distributions were determined by the method of internal standard yield analysis. An F&M Model 700 gas chromatograph equipped with a six foot 15% SE-30 column was used for analytical and preparative work. A Varian T-60 NMR and EM 600 mass spectrometer were used for the determination of spectra. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Chloromethyldimethylchlorosilane and trimethylsilylmethanol were obtained from Petrarch Systems and used without further purification. Chloromethyldimethylfluorosilane was prepared by the method of Sommer [18]. The products mentioned in this work, save two, have all been previously characterized in these laboratories [1,3]. The two new compounds were fully characterized.

During the development of this series of studies, the quality of the alkoxide bases, in particular their relative hydroxide content, has been found to be an important factor in the observed chemistry under the conditions of heterogeneous gas/solid reactions. The bases used in this study were obtained from Aldrich (potassium t-butoxide and sodium methoxide) and Alfa Ventron (all others). With the exception of sodium ethoxide, both suppliers provide bases of good quality and relatively low hydroxide content. Several precautions are required in order to obtain consistent and reproducible results for these heterogeneous reactions. Larger batches of base were rebottled with the minimum of exposure into smaller bottles. The smaller bottles and smaller batches of base were stored over Drierite in a desiccator at all times between uses. All comparative studies, for example Tables 1 and 2, were performed with a given smaller batch of base over as short a time span as physically possible. Bottles were returned to their desiccator as soon as possible after samples were removed for a given reaction. Usually bottles were opened no more than five times for a given series of reactions. All glassware was oven dried at 110°C before use. The sam-

ples of base were charged into warm (CAUTION: some of these bases will inflame in air at temperatures above ca. 100°C) furnace tubes and placed under a nitrogen purge as soon as possible. These precautions are sufficient to provide consistent and meaningful results for a given smaller batch of base.

Several systems studied in this work are referred to as having a product distribution that was independent of temperature in a specified range of temperature. Where this statement is made the stated reaction was carried out at at least four intermediate temperatures between the extremes stated. The distribution of products from these series was found to be the same within the experimental error associated with the yield determination.

General procedure for the reaction of vaporized silanes with alkoxide bases

The reaction of chloromethyldimethylfluorosilane with sodium methoxide is representative of all of the reactions reported in this study. The equipment and apparatus have been previously described [1,2,4].

Sodium methoxide, 5.1 g (95 mmol, a four-fold molar excess over the silane used) was charged between two small glass wool plugs with the one nearest the exit of the tube being held in place by four small glass indentations in the furnace tube. The charge could be uniformly lightly packed by lowering a 250 g cylinder rod of diameter slightly less than that of the furnace tube gently onto the uppermost plug and then releasing the rod with the furnace tube in a vertical position. The weight of the rod would cause the base charge to contract slightly but uniformly from reaction to reaction. The tube was then equipped with the addition apparatus and the charge was "baked out" under a 60 ml/min flow of nitrogen at ca. 150°C for 0.5 hour. The exit of the tube was then equipped with a condensing trap immersed in Dry Ice/acetone. The fluorosilane, 3.05 g (24 mmol) was added to the addition apparatus and the addition apparatus was wrapped with a four foot heating tape. The heating tape was connected to a Variac and heated with a setting of 20 units of a 140 units maximum (for the chlorosilane reactions the setting was 40/140). In this manner the silane was vaporized into the furnace area over a period of 30 to 35 minutes. The furnace was then raised to 160°C and "blown out" for approximately 15 minutes to elute all volatile products. The condensate, 2.78 g, was shown by internal standard yield analysis to contain the distribution of products given in Table 3. The yield analysis accounted for 94% of the starting silane and 2.64 g (95%) of the mass of the condensate.

Reaction of chloromethyldimethylchlorosilane with "doped" lithium methoxide

Lithium methoxide, 3.98 g (105 mmol) was thoroughly mixed in a mortar with 0.38 g (21 mmol) of water over a period of two minutes. The base charge then was reacted by the general procedure with the exception that the "bake out" period was 1 hour. Analysis of the condensate from the reaction of 2.97 g (21 mmol) of the chlorosilane indicated the presence of 0.45 mmol (2%) of dimethyldimethoxysilane and 11.1 mmol (53%) of chloromethyldimethylmethoxysilane. This analysis accounted for 71% of the mass of the condensate, 2.23 g. The remainder of the condensate was methanol.

Reaction of chloromethyldimethylchlorosilane with a compressed charge of potassium t-butoxide

A charge of 9.4 g (84 mmol) of the title base was compressed to 70% of its original length. The reaction was carried out in the standard fashion. Analysis of the condensate, 3.6 g, indicated the presence of the following components: t-butylmethyl ether (25%), bis-t-butoxydimethylsilane (35%) and chloromethyldimethyl-t-butoxysilane (28%). A final higher boiling component of the reaction mixture was present in roughly 10% yield and was characterized as t-butoxymethyldimethyl-t-butoxysilane by the following data: NMR δ 3.15 (s, 2 H, —CH_2O—); 1.51 (s, 9 H, t-BuOCH_2—); 1.39 (s, 9 H, *t-BuO*Si) and 0.36 ppm (s, 6 H, *Me*$_2$Si). Anal. Found: C, 60.58; H, 12.04. $C_{11}H_{26}O_2Si$ calcd.: C, 60.49; H, 12.00%. The mass spectrum was in accord with the formulation of the product.

Reaction of potassium methoxide with chloromethyldimethylfluorosilane for maximum production of methylethyldimethoxysilane

The reaction was carried out in the usual fashion with two exceptions. After the potassium methoxide was charged into the furnace tube manual pressure was applied to the packing rod until the base would no longer contract and was tightly packed. The nitrogen flow rate was 30 ml/min rather than 60 ml/min. The reaction of 3.0 g (24 mmol) of the title silane and 6.7 g (98 mmol) of freshly opened potassium methoxide (previously opened samples gave slightly lower yields) at 150°C required one hour for complete addition at the lower flow rate. The condensate, 2.78 g, was examined by GLC and shown to contain 13.9 mmol (59%) of methylethyldimethoxysilane and 2.3 mmol of dimethyldimethoxysilane (10%). The latter lower boiling silane was removed by distillation through a short column to leave behind a 49% isolated yield of product that was at least 95% pure by GLC. The condensate from this reaction as well as those from three other similar reactions showed no trace of chloromethyldimethylmethoxysilane. The 60 MHz, NMR, IR, and mass spectra of the product were identical to those of an authentic sample of the product prepared by the heterogeneous reaction of methylethyldichlorosilane and lithium methoxide.
^{1}H NMR (CCl$_4$ with internal HCCl$_3$, 250 MHz): δ 3.402 (s, 6.2 H, Si(OMe)$_2$); 1.100 (t, 2.93 H, J 7.5 Hz, SiCH$_2$CH_3); 0.890 (q, 1.91 H, J 7.5 Hz, SiCH_2) and —0.20 ppm (s, 2.93 H, SiMe).
^{13}C NMR (DCCl$_3$ solvent and standard. Chemical shifts relative to TMS.): δ —50.0, —6.1, —4.7 and +6.7 ppm.
Mass spectra m/e: 134 (M)$^+$ (5%), 119 (M — Me)$^+$ (19%), 105 (M — Et)$^+$ (100%), 89 (M — Me — CH$_2$O)$^+$ (10%), 75 (M — Et — CH$_2$O)$^+$ (34%), 61 (MeOSiH$_2$)$^+$ (6%), 59 (EtSiH$_2$)$^+$ (15%).

Reaction of chloromethyldimethylmethoxysilane with potassium methoxide

In a manner identical to that described immediately above, the title silane (3.0 g, 22 mmol) and 6.7 g (98 mmol) of potassium methoxide were allowed to react. A setting of 90/140 on the heating tape caused complete addition in 1.25 hour. The condensate was found to contain the distribution of products given in run 6 of Table 3 and weighed 2.36 g.

Acknowledgement

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