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HETEROGENEOUS REACTIONS

VI *. REACTIONS OF TRIMETHYLCHLOROSILANE, DIMETHYLDICHLOROSILANE AND CHLOROMETHYLDIMETHYLCHLOROSILANE WITH POTASSIUM t-BUTOXIDE AND SODIUM METHOXIDE

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Summary

The heterogeneous gas-solid reaction of trimethylchlorosilane and an equal molar mixture of potassium t-butoxide and sodium methoxide gave exclusively trimethyl-t-butoxysilane. A similar reaction utilizing dimethyldichlorosilane as the vapor phase substrate gave predominant incorporation of butoxide. The heterogeneous reaction of chloromethyldimethylchlorosilane with these two bases was extensively studied. The parameters investigated for the latter system include the dependence of the product distribution on temperature, nitrogen flow rate and the relative hydroxide content of the solid alkoxide base. These studies allow the assessment of the relative reactivities of these bases under the conditions of heterogeneous gas/solid reaction. Under these conditions and with partially hydrolyzed bases a substantial amount of displacement of the chloromethyl group from chloromethyldimethylchlorosilane is observed. The role of hydroxide ion in this reaction is discussed. Convenient syntheses of t-butyl methyl ether and dimethylchloromethoxysilane are reported.

Results and discussion

Earlier reports in this series have disclosed the use of heterogeneous reaction conditions for the purpose of effecting dehydrohalogenation reactions at carbon centers [1,2] and substitution reactions at silicon centers [3]. Other studies have demonstrated that the interaction of solid alkoxide bases with vaporized

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* This paper is dedicated to the late Professor Edward L. Haenisch of Wabash College. His "chemical family" mourns the loss of an unexcelled undergraduate educator whose dedication to the discipline, love of teaching and impressive personage will not soon be forgotten.

TABLE 1

POTASSIUM t-BUTOXIDE. TEMPERATURE DEPENDENCE [a]

Temperature (°C)	t-BuOMe [b] (%)	$(t\text{-BuO})_2SiMe_2$ (A) [c] (%)	$t\text{-BuOSi}(CH_2Cl)Me_2$ (B) [c] (%)	A/B
50	39	27	19	1.5
80	36	46	30	1.6
90	27	41	27	1.6
100	35	48	21	2.3
110	30	40	19	2.6
120	24	56	26	2.1
130	26	40	18	2.3
140	26	46	18	2.6
150	28	49	15	3.2
160	20	44	14	2.9

[a] All reactions run with approximately 20 mmol of $ClCH_2Si(Cl)Me_2$ and a four fold molar excess of base. The nitrogen flow rate was 60 ml/min and the heating tape was set such that the addition required approximately 1/2 h. [b] As determined by internal standard yield analysis under the assumption that one mol of the ether is produced per mol of silane. [c] As determined by internal standard yield analysis.

substrates may proceed via a methoxide-induced radical process [4] or, in the case of potassium t-butoxide, a base induced 1,2-hydride shift from silicon to carbon [5]. As a way of learning more about the relative reactivities of these bases and the nature of the gas/solid interaction under these conditions, the studies of displacement reactions at silicon centers have been extended.

The results of a study of the temperature dependence of the reaction of chloromethyldimethylchlorosilane with potassium t-butoxide in the range from 50 to 150°C contrast sharply with a similar study with sodium methoxide (see Tables 1 and 2). With the butoxide the distribution of products was relatively constant, showing only a small break at about 100°C. For the reaction with sodium methoxide the ratio of chloromethyldimethylmethoxysilane to dimethyldimethoxysilane showed a marked temperature dependence (see Fig. 1). The

TABLE 2

SODIUM METHOXIDE. TEMPERATURE DEPENDENCE [a]

Temperature (°C)	$(MeO)_2SiMe_2$ (A) [b] (%)	$ClCH_2Si(OMe)Me_2$ (B) [b]	B/A
50	3.5	44.4	12.51
60	4.2	47.5	11.23
70	4.2	42.6	10.05
80	8.3	71.0	8.55
90	4.3	33.2	7.70
100	7.6	40.5	5.30
110	11.0	40.7	3.70
120	9.4	28.1	3.00
130	13.0	23.0	11.77
140	23.5	33.2	1.42
150	19.8	16.7	0.85

[a] All reactions utilized approximately 20 mmol of $ClCH_2Si(Cl)Me_2$ and a four fold molar excess of base. A nitrogen flow of 60 ml/min was used and the addition apparatus was heated such that the addition time was ca. 1/2 h. [b] As determined by internal standard yield analysis.

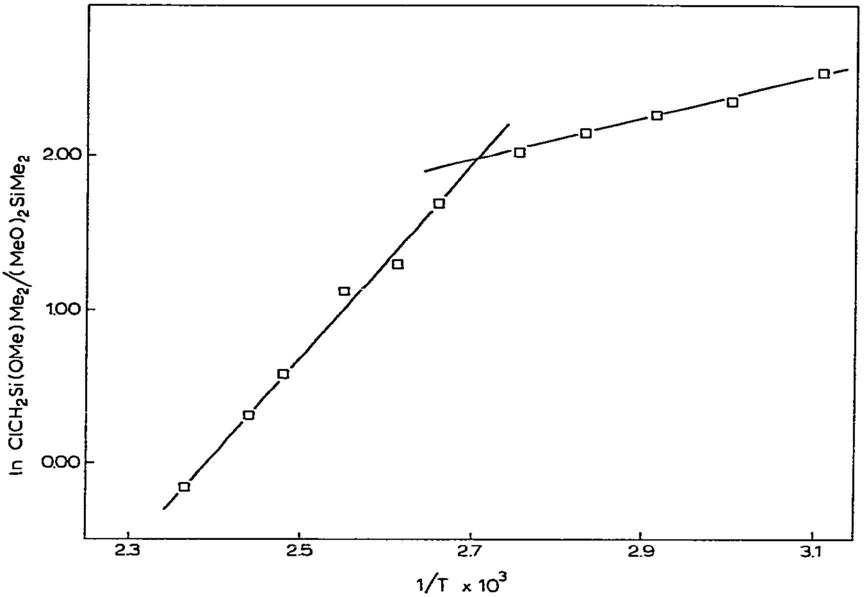

Fig. 1. $ClCH_2Si(Cl)Me_2$ + NaOMe, temperature dependance and product distribution.

basis for this contrast is likely the relative reactivities of these two bases under heterogeneous reaction conditions.

The control experiments 1 and 2 of Table 3 support the premise that potassium t-butoxide is more reactive than sodium methoxide in displacement reactions at silicon centers. Experiments 1 and 2 are remarkable in light of the fact that earlier work has shown that sodium methoxide reacts cleanly and in high yield with both of the halosilanes to give the corresponding alkoxysilanes [3]. Experiment 3 shows that a significant amount of exchange, butoxide for methoxide, occurs under the conditions of the reaction. Experiment 4 establishes that the reverse exchange does not occur to any great extent. Experiment 5 further emphasizes the difficulty of displacing butoxide once it is incorporated into the molecule since, under the conditions of the reaction, methoxide does displace ethoxide, 37%. Thus the exclusive incorporation of butoxide in experiment 1 and the predominant incorporation in experiment 2 may be attributed to its high reactivity toward displacing methoxide as well as its resistance toward being displaced. The incorporation of some methoxide in experiment 2 suggests a leveling of relative reactivities perhaps due to the activation of the silicon center by the initial substitution of the more electronegative oxygen group.

As a further example of the relative differences in reactivity, the dependence of the product distribution on the nitrogen flow rate was studied. At lower flow rates (15 and 30 ml/min) and a somewhat lower temperature (120 verses 150°C) in the reaction of chloromethyldimethylchlorosilane no monosubstituted product was found in the condensate from the reaction with the butoxide. At 60 ml/min the butoxide gave 44% di-t-butoxydimethylsilane and 15% chloromethyldimethyl-t-butoxysilane. On the other hand, with sodium methoxide, the ratio of monosubstituted to disubstituted product was constant, 0.85 ± 0.15, within

TABLE 3

HETEROGENEOUS REACTIONS OF ORGANOSILANES[a]

Experiment	Silane	Base (mol. ex)	Products	Yield (%)
1	Me_3SiCl	t-BuOK(4)	$t\text{-}BuOSiMe_3$	65
		NaOMe(4)	$(Me_3Si)_2O$	12
2	Me_2SiCl_2	t-BuOK(6)	$(t\text{-}BuO)_2SiMe_2$	54
		NaOMe(6)	$t\text{-}BuOSi(OMe)Me_2$	38
3	Me_3SiOMe	t-BuOK(3.5)	$t\text{-}BuOSiMe_3$	30
			starting material	32
4	$t\text{-}BuOSiMe_3$	NaOMe(3.5)	starting material	90
5	$ClCH_2Si(OEt)Me_2$	NaOMe(4)	$ClCH_2Si(OMe)Me_2$	37
			starting material	43
6	Me_3SiCH_2Cl	NaOMe(4)	starting material	78
7	Me_3SiCH_2Cl	t-BuOK(4)	starting material	90
8	$ClCH_2Si(OMe)Me_2$	NaOMe(4)	$Me_2Si(OMe)_2$	9
			starting material	59
9	$MeOSi(Cl)Me_2$	NaOMe(4)	$Me_2Si(OMe)_2$	57
			starting material	12
10	$t\text{-}BuOSi(CH_2Cl)Me_2$	t-BuOK(4)	$(t\text{-}BuO)_2SiMe_2$	22
	run at 120°C		t-BuOMe	27
			starting material	19
11	2.0 D_2O followed by			
	1.0 $ClCH_2Si(Cl)Me_2$	t-BuOK(5)	t-BuOMe	42
12	$t\text{-}BuOSiMe_3$	t-BuOK(4)	starting material	53
13	$t\text{-}BuOSiMe_3$	t-BuOK(4)+		
		0.5 H_2O	starting material	44
14	$ClCH_2Si(Cl)Me_2$	NaOMe(4)	$ClCH_2Si(OMe)Me_2$	67
	run at 50°C		$Me_2Si(OMe)_2$	3
15	$ClCH_2Si(Cl)Me_2$	NaOMe(4)	$ClCH_2Si(OMe)Me_2$	50
			$Me_2Si(OMe)_2$	5
			$MeOCH_2Si(X)Me_2$, X = Cl, OMe	25
16	$ClCH_2Si(Cl)Me_2$	NaOMe(4)	$ClCH_2Si(OMe)Me_2$	17
		1.0 H_2O	$Me_2Si(OMe)_2$	20
17	$ClCH_2Si(Cl)Me_2$	none	starting material	94

[a] All reactions were run at 150°C unless otherwise specified. The nitrogen flow rate was 60 ml/min and each reaction utilized 20—25 mmol of the vapor phase substrate. See experimental for the general procedure used for all of these reactions.

experimental error at all three flow rates. These observations are in accord with the butoxide being more reactive than the methoxide toward the displacement of the chloromethyl group.

The solution phase reaction of chloromethyldimethylchlorosilane with sodium methoxide in refluxing ether gave 92% chloromethyldimethylmethoxysilane and 7.5% dimethyldimethoxysilane. The corresponding reaction with potassium t-butoxide gave much lower yields of substitution products. The considerable latitude afforded by our heterogeneous system prompted us to investigate the details of the chloromethyl group displacement in the reactions of these two bases. Experiments 6 and 7 suggest that the chloromethyl group resists displacement without an additional electronegative group at the silicon center. Experiments 8, 9 and 10 show some patterns of reactivity of chlorine and chloromethyl groups under heterogeneous reaction conditions.

We have examined the possibility that the displaced chloromethyl group decomposes to give free methylene. With both bases under the conditions of maximum chloromethyl group displacement, reaction in the presence of large amounts of cyclohexene failed to give any detectable amounts of norcorane.

For the butoxide system the following observations and experiments shed some light on the details of the reaction involving chloromethyl group displacement. Older base (presumably partially hydrolyzed [6]) gives lower overall yields of silanes and higher yields of t-butyl methyl ether. In experiment 11, when deuterium oxide was bubbled into the furnace area prior to the addition of the silane, the ether and some t-butanol were the sole constituents of the condensate. In this experiment all of the silane remained in the furnace area. When the base charge from this reaction was hydrolyzed and subsequently acidified an insoluble silicon polymer which did not melt below 300°C was isolated in quantity. One rationale for these experiments and observations is as follows. The potassium hydroxide present in the base can react at the silicon center in analogy to the other two bases. If the hydroxide displaces chloride, for example, the resulting silanol could undergo reaction with the base to give a silanolate salt which remains in the furnace area. The t-butanol thus formed might well remain in the furnace area long enough to undergo subsequent reaction. If the reaction involving chloromethyl group displacement takes place near the t-butanol, the methylene group of the displaced chloromethyl moiety might insert into the hydroxyl bond of the alcohol giving the ether and potassium chloride. Experiment 10 lends some support to the premise if the 27% yield of ether is interpreted as hydroxide butoxide exchange, experiments 12 and 13, proton transfer forming butanol which intercepts the displaced chloromethyl group *.

The role of hydroxide in the sodium methoxide reactions would appear to be somewhat different. In none of the reactions with this base is there evidence for the formation of the analogous ether. However increasing hydroxide content increases chloromethyl group displacement for this system as well. Comparison of experiments 15 and 16, where the base charge was deliberately adulterated with water and throughly mixed before being placed in the furnace area, demonstrates this fact. In experiment 15, where very pure base was used, a substantial amount of methoxide displacement for chlorine at carbon is observed. With the less pure sodium methoxide, it is possible that the sodium hydroxide undergoes a similar reaction leading to the formation of a hydroxymethyl group. The α-hydroxysilane might give the corresponding alkoxysilane via base catalyzed rearrangement [7] or alternatively one could envision base attack at silicon leading, in principle, to the formation of formaldehyde and sodium hydride. That α-hydroxysilanes give the corresponding alkoxysilanes under the conditions of heterogeneous reaction is demonstrated in a control experiment (eq. 1).

$$Me_3SiCH_2OH + 3\ NaOMe \xrightarrow{150^\circ C} \underset{(93\%)}{Me_3SiOMe} \qquad (1)$$

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* Reference to Table 1 shows, except at the extremes of temperature, the amount of ether formed is relatively constant. This observation is consistant with the proposal since the degree to which the base is contaminated by hydroxide would correlate with the amount of butanol formed in the base charge.

Since the hydroxide content substantially effects the observed chemistry, all of the comparative studies in this work and the temperature-dependent studies were carried out in as short a time span as possible. The bases were stored in a dessicator over anhydrous calcium chloride when not in use. These precautions are sufficient to give reproducible results within the limits of the experimental error inherent to the internal standard yield analysis.

During the course of this work, dimethylhaloalkoxysilanes were required for control experiments and some independent syntheses. The published procedure for the preparation of dimethylethoxychlorosilane [8] could be modified for the preparation of dimethylmethoxychlorosilane. However, the direct reaction of dimethyldichlorosilane and dimethyldimethoxysilane catalyzed by aluminum trichloride is a much more convenient route to dimethylmethoxychlorosilane. The details of this reaction are reported in the experimental section and we are investigating the generality of this reaction in the context of a synthetically useful route to mixed alkoxyhalosilanes and mixed alkoxysilanes. Our efforts to delineate the controlling factors and potential applications of heterogeneous gas/solid reactions are continuing and will be the subject of later reports.

Experimental

The product distribution of all reactions was determined using the method of internal standard yield analysis with hexamethyldisiloxane or heptane as the standard except where noted. An F & M Model 700 gas chromatograph equipped with a six foot 15% SE-30 column was used for the analyses. Representative reactions were run in triplicate to test for reproducibility and found to give identical results, within experimental error, provided that the sample of base used was of consistent quality. As mentioned in the text, the hydroxide content of the base can affect the observed chemistry. The bases were stored over calcium chloride in a dessicator to minimize hydrolysis between runs. A Varian T-60 NMR and EM-600 mass spectrometer were used for the determination of spectra. Except where noted all products were identified by comparison of their spectra to those of independently synthesized samples [3]. Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Reaction of chloromethyldimethylchlorosilane with t-butanol and methanol in the presence of triethylamine in pentane solvent served to prepare chloromethyldimethyl-t-butoxysilane and chloromethyldimethylmethoxysilane in good isolated yields. Chloromethyldimethylchlorosilane, chloromethyltrimethylsilane and trimethylsilylmethanol were purchased from Petrarch Chemicals and used without further purification. The alkoxide bases used in this study were obtained from Aldrich.

In all studies, the yield analysis accounted for at least 75%, in most cases more, of the mass of the condensate from the reaction. For the butoxide reactions, under the assumption that one mol of silane is consumed per mol of ether produced, 75—100% of the silane was accounted for in the analysis. In the methoxide studies the analysis accounted for 55—75% of the starting silane as mono- or di-substituted products. In these reactions it is likely that the unaccounted silane remains in the furnace area as a salt.

Heterogeneous reaction of chloromethyldimethylchlorosilane and sodium methoxide at 125°C

The following procedure is typical of all of the heterogeneous reactions carried out in this work.

The apparatus used in this work has been previously described [1,3]. The furnace tube was charged with 4.50 g (83 mmol) of sodium methoxide, equipped with the bubbler addition apparatus and placed in a preheated oven at 125°C. The tube and its contents were allowed to come to thermal equilibrium under a nitrogen flow to purge the charge of any residual methanol. The addition apparatus was wrapped with a four foot heating tape and the tape was connected to a Variac with a setting of 40/140. The nitrogen flow was adjusted to 60 ml/min and the exit of the furnace tube was connected to a cylindrical trap emmersed in a Dry Ice/acetone trap. Chloromethyldimethylchlorosilane, 3.15 g (22 mmol) was added to the addition apparatus. The oven heat control was lowered by about 20% such that the exotherm of the reaction in conjuction with carefully monitoring the temperature maintained a constant temperature of 125 ± 2° C during the course of the 40 minute addition time. Upon the completion of the addition, the oven temperature was raised to 160°C and maintained at that temperature for 10 minutes to elute all volatile products. The Dry Ice/acetone was removed and the trap was allowed to warm to room temperature under nitrogen flow. The condensate, 2.50 g, was analyzed and found to contain 5.6 mmol (25.3%) of dimethyldimethoxysilane and 11.2 mmol (51%) of chloromethyldimethylmethoxysilane. The combined yields of the silanes accounted for 89% of the mass of the condensate from the reaction.

Reaction of trimethylchlorosilane with a mixture of potassium t-butoxide and sodium methoxide

Sodium methoxide, 4.32 g (80 mmol) and potassium t-butoxide, 8.96 g (80 mmol) were placed in a mortar and thoroughly mixed. The mixture was placed in a furnace tube and the charge was "baked out" at 150°C with a nitrogen flow of 60 ml/min for 30 minutes. The addition apparatus was wrapped with a four foot heating tape which was connected to a Variac set at 20/140. Trimethylchlorosilane, 2.20 g (20.3 mmol) was added to the addition apparatus and vaporized into the reaction area. The addition required 50 minutes. A total of 2.50 g of condensate was removed from the warmed trap and analyzed using toluene as the internal standard. The condensate contained 2.59 mmol of hexamethyldisiloxane (12.8%) and 13.1 mmol of trimethyl-t-butoxysilane (64.5%). The GLC trace showed a trace of t-butanol and no evidence for any other volatile products. The yield analysis accounted for 90% of the silicon added and 93% of the mass of the condensate.

Reaction of dimethyldichlorosilane with a mixture of potassium t-butoxide and sodium methoxide

A mixture of 13.4 g (120 mmol) of potassium t-butoxide and 6.50 g (120 mmol) of sodium methoxide was prepared as described for the previous reaction and "baked out" at 150°C for 30 minutes with a nitrogen flow of 60 ml/min. Dimethyldichlorosilane, 2.40 g (18.6 mmol) was added in the standard fashion over a period of 45 minutes. The resulting condensate, 3.45 g, was analyzed using toluene as the internal standard. The condensate contained 7.15 mmol of t-butoxydimethylmethoxysilane (38.4%) and 10.0 mmol of bis(t-butoxydimethyl)-silane (54.0%). The analysis accounted for 93% of the mass of the condensate and 92% of the silicon added. The mixed alkoxy product gave identical spectral properties to those of an independently synthesized (see later) sample as follows. NMR: δ 3.47, s, 3 H, OMe; 1.34, s, 9 H, t-BuO and 0.14 ppm, s, 6 H, Me_2Si. Mass spectrum (m/e, % abundance) 147(66.6, $M^+ - Me$), 91(97.6), 89(100, $M^+ -$ t-BuO), 77(9.3), 75(12.2), 61(21.1), and 59(32.1).

Reaction of chloromethyldimethylchlorosilane with sodium methoxide at 150°C. Substitution at carbon

Using the general procedure for heterogeneous reaction 4.50 g (83 mmol) of sodium methoxide and 2.95 g (20.6 mmol) of the title silane were allowed to react with a flow rate of 60 ml/min. Analysis of the resulting condensate, 2.62 g, indicated that it contained 1.01 mmol of dimethyldimethoxysilane (5%) and 10.3 mmol of chloromethyldimethylmethoxysilane (50%). An additional peak eluted between the peaks for the two substitution products. This peak was collected and shown by NMR and mass spectra to be methoxymethyldimethylmethoxysilane contaminated by a small amount of methoxymethyldimethylchlorosilane. Assuming a response factor for this peak to be intermediate between those for the two substitution products, the yield analysis gives 5.5 mmol (or roughly 25% based on starting silane) using the average molecular weight for the two products. A fairly pure sample of methoxymethyldimethylmethoxysilane could be obtained by selective collection of the earlier part of the mixture's peak. This slightly impure sample had NMR and mass spectra which were very similar to those of an authentic sample of the compound obtained from another system under study. The analysis and spectra for methoxymethyldimethylmethoxysilane were as follows. NMR: δ 3.25, 2 closely spaced singlets, 6 H, OMe; 3.06, s, 2 H, OCH_2Si; and -0.10 ppm, s, 6 H, Me_2Si. Mass spectrum (*m/e*, % abundance) 119(30.8, $M^+ - Me$), 105(71.0, $MeOCH_2Si(H)OMe^+$), 91 (21.9, $(MeO)_2SiH^+$), 89(100, $MeOCH_2Si(H)Me^+$ or Me_2SiOMe^+), 75 (49.7, $MeOCH_2SiH_2^+$ or $MeOSi(H)Me^+$), 61(21.3, $MeOSiH_2^+$), 59 (92.9, Me_2SiH^+), 45(12) and 43(14.2). Analysis Found: C, 47.71; H, 10.57. $C_5H_{14}O_2Si$ calcd.: C, 47.73; H, 10.51%.

Preparation of an authentic sample of t-butoxydimethylmethoxysilane

Dimethylmethoxychlorosilane was prepared by the reaction of 6.0 g (50 mmol) of dimethyldimethoxysilane and 6.4 g (50 mmol) of dimethyldichlorosilane catalyzed by 0.02 g of aluminum trichloride. The mixture was heated in a single necked flask equipped with a still head for 2 h at a gentle reflux. Fractional distillation yielded a fraction, 5.5 g (44%), with b.p. 78°C. This fraction gave essentially a single peak on GLC analysis and had a b.p. which agrees with the literature value for dimethylmethoxychlorosilane, b.p. 77°C [9]. The reaction of 6.2 g of dimethylmethoxychlorosilane prepared in the above fashion with 4.07 g of t-butanol in 75 ml of pentane solvent in the presence of 5.5 g of triethylamine served to prepare the title compound. Fifty mmol of each reagent was present and the butanol was added to the silane over a period of 20 minutes. After it had been stirred at room temperature for 14 h, the mixture was filtered from 6.5 g (95%) of amine salts. Fractional distillation yielded 3.36 g (43%) of the title compound with b.p. 110°C.

Synthesis of t-butyl methyl ether

The general procedure for heterogeneous reactions was used to effect reaction between 7.1 g (63 mmol) of potassium t-butoxide and 3.0 g (21 mmol) of methyl iodide at 100°C with a nitrogen flow rate of 60 ml/min. The addition apparatus was wrapped with a four foot heating tape set at 10/140 and the addition required 1 h. The condensate, 1.87 g. was GLC pure. The yield was quantitative. NMR: δ 3.00, s, 3 H, MeO and 1.04 ppm, s, 9 H, t-Bu.

Synthesis of bis(t-butoxydimethyl)silane

The general procedure for heterogeneous reactions utilized 9.0 g (80 mmol) of potassium t-butoxide and 2.95 g (22 mmol) of dimethyldichlorosilane with a reaction temperature of 150°C and a flow rate of 60 ml/min. The condensate was examined by GLC and found to contain traces of butanol. The condensate was extracted with four portions of 0.1 *M* NaOH, dried and filtered to give to give 1.96 g (66%) of GLC and NMR-pure product.

Reaction of chloromethyldimethylchlorosilane with sodium methoxide in refluxing ether solution

A round bottomed, three necked 100 ml flask equipped with a magnetic stirring unit, reflux condenser and a constant pressure addition funnel was charged with 4.48 g (80 mmol) of sodium methoxide and 50 ml of dry ether. The silane, 2.86 g (20 mmol), was added dropwise with stirring over a period of 10 minutes. The initial reaction was fairly exothermic and upon the completion of the addition the stirred mixture was maintained at reflux for 1 h. The cooled reaction mixture was trap-to-trap distilled (0.2 mmHg, 50°C) into a vessel chilled in Dry Ice/acetone. Internal standard yield analysis indicated the presence of 18.5 mmol of chloromethyldimethylmethoxysilane (92%) and 1.5 mmol of dimethyldimethoxysilane (7.5%). The products were identified by their GLC retention times and the NMR spectra of collected samples.

Reaction of chloromethyldimethylchlorosilane with potassium t-butoxide in refluxing ether solution

In a manner identical to that described for the previous reaction 8.96 g (80 mmol) of potassium t-butoxide and 2.86 g (20 mmol) of the silane in 50 ml of dry ether were reacted. A similar work-up and yield analysis indicated the presence of 4.3 mmol of chloromethyldimethyl-t-butoxysilane (22%) and a trace of bis(t-butoxydimethyl)silane. The GLC trace indicated complete consumption of the starting material and the trap-to-trap pot contained 10.9 g of semisolid.

Reaction between trimethylsilylmethanol and sodium methoxide

The general procedure for heterogeneous reactions was used to effect reaction between 4.70 g (88 mmol) of sodium methoxide and 2.96 g (28 mmol) of the title silane. The injection heating tape was set at 45/140, the addition time was 50 minutes with the flow rate set at 60 ml/min. The condensate, 2.96 g, was GLC and NMR pure trimethylmethoxysilane (93%). The product was identified by its GLC retention time and NMR and IR spectra, all of which were identical to those of an authentic sample [3].

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