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HETEROGENEOUS REACTIONS

III. EVIDENCE FOR AN ALKOXIDE INDUCED 1,2-HYDRIDE SHIFT FROM SILICON TO CARBON UNDER HETEROGENEOUS GAS/SOLID PHASE REACTION

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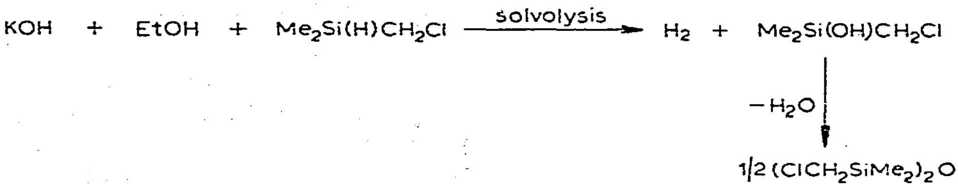
Summary

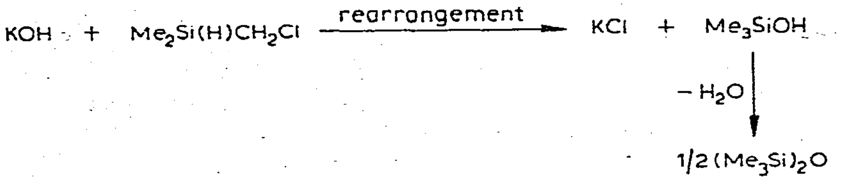
The interaction of solid alkoxide bases with chloromethyldialkylsilanes leads to the formation of products which may be formulated as arising via a 1,2-hydride shift from silicon to carbon. Other mechanisms for the formation of the rearranged product are considered and evidence for an intramolecular process is presented. The syntheses of chloromethyldimethyldeuteriosilane, chloromethyldiethylsilane and t-butoxydiethylmethylsilane are described.

Discussion

In 1959 Sommer published experimental results concerning the reaction of halomethyldimethylsilanes with alkaline ethanol [1]. These experiments established the operation of the two competing mechanisms summarized in eq. 1 and 2. The rearrangement mechanism was supported by three observations:



(1)



(2)

(1) the amount of KCl formed closely corresponded to the amount of hexamethyldisiloxane observed; (2) if the reaction was carried out in 70% dioxane/30% D_2O, the rearrangement product contained no deuterium as shown by infrared spectroscopy, and (3) the ratio of products was relatively insensitive to halogen, i.e., for Cl 1/2 = 2.16 and for I 1/2 = 8.09, as compared with the relative reactivity of 10^2 for the solvolysis rates of RI versus RCl in carbon systems [2]. As far as we have been able to ascertain, only one other paper directly related to this rearrangement has appeared [3]. In this paper we present evidence which is in accord with the mechanism involving a 1,2-hydride shift from silicon to carbon using alkoxide bases and demonstrate that the rearrangement is not intermolecular.

We have recently reported the use of heterogenous gas phase/solid phase reactions for the purpose of effecting dehydrohalogenation at carbon centers [4a] and substitution at silicon centers [4b]. Since, in this system, the complication of the solvolysis reaction is eliminated, it was of interest to test the possibility of observing a 1,2-hydride shift induced by solid alkoxide bases. Accordingly, we have carried out the reaction summarized in eq. 3.

$$\underset{\text{vapor}}{Me_2Si(H)CH_2Cl} + \underset{\text{solid}}{\text{t-BuOK}} \xrightarrow[N_2,\ \text{flow}]{100^\circ} \underset{(40\text{—}50\%)}{\text{t-BuOSiMe}_3} + \text{minor products} \qquad (3)$$

The major product of this reaction may be rationalized as being formed by a rearrangement similar to that of Sommer's work [1]. Several other mechanisms may be envisioned which also lead to the formation of t-butoxytrimethylsilane. These are intramolecular or intermolecular rearrangement prior to contact with the base, as well as an elimination-addition pathway. Our heterogeneous system allows some of these mechanisms to be tested directly and/or indirectly as follows.

The intramolecular rearrangement to trimethylchlorosilane followed by its reaction with the base [4b] must be considered. Sommer has shown that such a rearrangement is catalyzed by aluminum trichloride [5]. In 1957 Kaesz and Stone [6] reported the rearrangement of chloromethyldimethylsilane to trimethylchlorosilane when the former was distilled through a chromel spiral column. No rearrangement was observed when the silane was distilled through a glass column or stored in vacuo. In 1968 a mechanism for the rearrangement of R_3SiCH_2Cl to $R_2Si(Cl)CH_2R$ catalyzed by aluminum trichloride was proposed as involving the synchronous intramolecular migration of the organic group and the chloride ion [7]. An analogous non-catalytic rearrangement of alkyl and aryl groups from silicon to carbon has recently been shown to proceed through an "inverse ylid" of the form $R_3X\overset{+}{Si}\text{—}\overset{-}{C}HR'$ where X is halogen, OTos and OAc [8]. These intramolecular rearrangements in the absence of a catalyst occur at temperatures considerably higher than those of this work. With the exception of the fluoride and OTos at 150°C, all other rearrangements reported were observed at temperatures of 220°C or higher. In fact, in our system, the optimum yield of rearranged product is achieved when the reaction is carried out at room temperature. Thus, we feel that it is unlikely that the silane is rearranging prior to its contact with the base in our heterogeneous system.

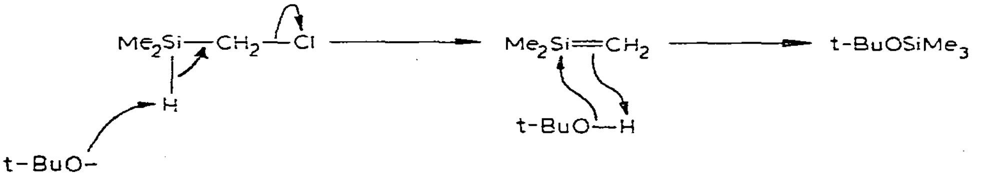
To demonstrate the intramolecular nature of this reaction, we have synthesized chloromethyldimethyldeuteriosilane and subjected it to the conditions of the reaction. The product from the reaction of the labeled silane was shown to be the expected t-$BuOSi(CH_2D)Me_2$ by mass spectral analysis. In addition to the assigned fragmentation pattern (see Experimental section), the following observations offer support for the formulation of the product. In the spectrum of t-butoxytrimethylsilane the *m/e* peak at 73 has a relative abundance of 94.3% and an *m/e* peak at 131 has 96.3% relative abundance. In the spectrum of the product from the labeled silane the relatively low abundance of $m/e = 73$ (5.6%), together with a significant $M^+ -16$ peak at $m/e = 131$(13.6%), suggests that this product contains only a small amount, if any, of undeuterated t-butoxytrimethylsilane. Hence, it would appear that under these conditions there has been a direct shift of hydrogen (deuterium) from silicon to carbon.

An intermolecular rearrangement to yield trimethylchlorosilane followed by its reaction with the base could also lead to the formation of t-butoxytrimethylsilane. In order to test for this possibility as well as to gain further evidence for the 1,2-hydride transfer, we have synthesized chloromethyldiethylsilane. When subjected to the conditions of heterogeneous reaction, this silane gave a 28% yield of "rearranged" product, namely t-butoxydiethylmethylsilane. The reaction with chloromethyldiethylsilane is somewhat more complicated than that with the dimethyl analog. We have tentatively identified one isomeric product which appears to be the result of substitution at carbon. However, this side reaction does not substantially effect the following control experiment. When a mixture of chloromethyldimethyldeuteriosilane and chloromethyldiethylsilane were contacted with solid potassium t-butoxide at 100°C, only two "rearranged" products were found in the condensate, as shown in eq. 4. If intermolecular exchange is a viable pathway under these conditions, one would expect to see

$$Et_2Si(H)CH_2Cl + Me_2Si(D)CH_2Cl \xrightarrow[100^\circ C,\, N_2]{t\text{-}BuOK} t\text{-}BuOSi(CH_2D)Me_2 + t\text{-}BuOSiEt_2Me \qquad (4)$$

a fair amount of t-$BuOSiMe_3$ and t-$BuOSi(CH_2D)Et_2$ in the condensate as well. The mass spectra of the observed products from this experiment were identical to those of authentic t-$BuOSi(CH_2D)Me_2$ and t-$BuOSiEt_2Me$. No evidence of deuterium-hydrogen exchange could be found within the limits of experimental detection. These observations militate against intermolecular exchange as a necessary requirement for the formation of the observed products.

In our system, an elimination-addition mechanism may be proposed to account for the formation of the observed products, e.g., eq. 5. Sommer's solution phase experiment employing the dioxane-D_2O solvent rules out this mechanism for



(5)

the reaction with alkali. We have run our heterogeneous reaction in the presence of reagents which might be expected to trap an intermediate silaethylene [9], i.e., cyclohexene, isoprene [10a], and 2,3-dimethyl-1,3-butadiene [10a,b]. When ethylene was used as a carrier gas, no 1,1-dimethyl-1-silacyclobutane could be detected in the condensate. Furthermore, no 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the dimerization product of such an intermediate, has been observed under our reaction conditions. The present experimental evidence does not allow a definitive exclusion of this mechanistic pathway in our system but we feel that it is not a likely mechanism under such mild conditions of temperature. Most of the known thermal routes to such intermediates occur at temperatures in excess of 500°C [12].

We feel that the weight of available evidence indicates that the interaction of solid alkoxide bases with chloromethyldialkylsilanes proceeds in close analogy to that found for ethanolic alkali. Utilizing the heterogeneous reaction system suppresses the complication of a competing solvolysis reaction and has allowed a direct experimental test of the inter- vs. intra- molecular nature of this reaction. In analogy to Sommer's earlier work, the mechanism for the formation of t-butoxytrimethylsilane and t-butoxydiethylmethylsilane under these conditions would appear to be a base-induced 1,2-hydride shift from silicon to carbon.

Several other products are formed in yields of less than 10% under these conditions. Some of these products may find their origin in the presence of trace hydroxides in the alkoxide base. In the reaction of the dimethylsilane the formation of hexamethyldisiloxane can be explained by a hydroxide-induced rearrangement reaction followed by the subsequent condensation of the silanol. The formation of 2-t-butoxy-2-methyl-2-silapropanol is also in accord with the presence of hydroxide. In some of our earlier work [4b] we have noted the extreme reactivity of silicon centers, compared with carbon centers, toward alkoxide bases under heterogeneous conditions. It would appear that the discrimination is not so sharp for hydroxide under these conditions. The 2-silapropanol could be formed via direct hydride displacement at silicon by alkoxide and reaction of hydroxide at the carbon center. Also in accord with our earlier work [4b] products from the displacement of the chloromethyl group are present, i.e., bis(t-butoxy)dimethylsilane. In all of these reactions, the remaining mass balance is found as a polymeric material which is retained in the solid alkoxide base.

Experimental

The furnace reactions were carried out as previously described [4] with a modification of the furnace to allow operation at lower temperatures and a modification of the inlet system (bubbling nitrogen through the heated liquid) to allow more dilute addition. A Varian A90-P3 gas chromatograph equipped with 6 and 12 foot 20% SE-30 columns was used for preparative and analytical work. The IR spectra were recorded on a Perkin—Elmer Model 167 spectrometer. A Varian T-60 NMR was used for recording NMR data. The mass spectra recorded here were obtained using a Varian E-60 mass spectrometer operating with ionization potential at 70 eV. All known compounds were characterized by comparison of their IR, NMR and mass spectra with those of independently synthesized compounds. The spectral data reported in this section refer to neat liquids for IR, solutions in carbon tetrachloride with chloroform as an internal standard for NMR, and the mass spectra are reported *m/e* (% abundance).

Preparation of chloromethyldimethyldeuteriosilane

A round bottomed, three necked 250 ml flask equipped with a magnetic stirring unit and a reflux condenser topped with a nitrogen inlet tube was "flamed out" and allowed to cool under nitrogen. The flask was charged with 28.6 g (0.20 mol) chloromethyldimethylchlorosilane and 150 ml dry ether. To the mixture was then added 2.1 g (0.05 mol) lithium tetradeuterioaluminate (Alfa-Ventron). The flask was fitted with a heating mantle and heated with stirring at a gentle reflux under nitrogen for 12 h. After cooling to room temperature and allowing the suspended solids to settle, the organic layer was decanted and trap-to-trap distilled (0.1 mmHg/24°C) into a receiver chilled in Dry Ice/ acetone. Fractional distillation of the volatiles through an 8" column packed with glass beads gave 15.0 g (69%) of the title compound, b.p. 82—85°C. The isolated compound was identified by its mass spectrum and the following spectral data: NMR δ 2.87, s, 2H, —CH_2Cl and δ 0.27, s, 6H, Me_2Si. IR 2960m, 2930w, 2900w, 1550(s, Si—D[12]), 1420w, 1395m, 1255s, 1175w, 1105w, 840s, 820s, 805s, 745w, 720w, 685m, 660m. Mass spectrum 111(3.7), 109(12.3), 107(5.7), 96(7.8), 95(3.6), 94(22.5), 81(4.9), 80(4.9), 79(13.5), 68(6.6), 67(11.3), 66(20.0), 65(27.6), 63(11.1), 62(5.7), 61(11.9), 60(100), 59(10.7).

Preparation of chloromethyldiethylsilane

A 1 l, round bottomed, three necked flask equipped with an overhead mechanical stirrer, constant pressure addition funnel and a reflux condenser topped with a nitrogen inlet tube was "flamed out" and charged with 60 g (0.33 mol) chloromethyltrichlorosilane (PCR Inc., freshly opened) and 200 ml dry ether. The mixture was heated to reflux under nitrogen. A solution of 0.66 mol ethylmagnesium bromide, prepared from 16.0 g (0.66 mol) magnesium and 72.0 g (0.66 mol) ethyl bromide in 500 ml dry ether, was added dropwise with stirring over a period of 6 h. The final mixture was heated at reflux under nitrogen overnight. To the reaction mixture was then added as a solid 3.1 g (82.5 mmol) of lithium aluminum hydride and the mixture was heated at reflux under nitrogen for an additional 24 h. After cooling to room temperature, the reaction mixture was treated with saturated ammonium chloride solution until the magnesium salts had been precipitated as rock-like salts. The organic layer was then extracted with water, dried over magnesium sulfate and fractionally distilled to yield 11 g (27%) of the title compound. The product was identified by its b.p. = 138—142°C (lit. [13], b.p. = 135—138°C) and the following spectral data. NMR δ 3.87, m, 1H, Si—H; 2.86, d, 2H, $J = 2$ Hz, —CH_2Cl; and 1.32—0.42, m, 10 H, Et_2Si. IR 2970s, 2930m, 2905w, 2105s, 1460m, 1415w, 1400w, 1235m, 1175w, 1015m, 970m, 840s, 815s, 700w. Mass spectrum 138(2.0), 136(4.4), 123(4.2), 121(8.6), 109(20.6), 107(57.6), 95(8.4), 93(23.2), 87(85.2), 86(22.6), 81(34.5), 79(94.1), 73(26.1), 67(9.4), 65(32.5), 59(100).

Preparation of an authentic sample of t-butoxydiethylmethylsilane

Methyltrichlorosilane was treated with a two-fold molar excess of ethylmagnesium bromide in ether and hydrolyzed in situ to give 1,3-dimethyl-1,1,3,3-

tetraethyldisiloxane. The disiloxane was isolated in 63% yield by vacuum fractional distillation, b.p. 78—82°C/15 mmHg (lit. [14], b.p. 90°C/20 mmHg). The spectral data for the product were as follows: NMR δ 1.27—0.42, m, 20 H, Et—Si; and δ 0.12, s, 6H, Me—Si. Mass spectrum 218(1.8), 203(4.7), 189(100), 161(80), 147(4.7), 133(44.1), 131(9.4), 105(25.9), 103(8.8), 91(4.7), 87(5.9), 80(47.1), 73(11.1), 66(16.5), 59(18.2).

Methyldiethylfluorosilane was prepared from the reaction of the disiloxane with boron trifluoride diethyletherate according to the method of Sommer [15] and isolated in 57% yield. The compound gave a b.p. 83—85°C (lit. [16], b.p. 80—85°C, impure) and the following spectral data. NMR δ 1.42—0.43, m, 10 H, Et—Si, and δ 0.27, d, 3 H, J(H—F) = 8 cps, Me—Si. Mass spectrum 120(16.1), 105(8.9), 101(5.8), 91(100), 77(15.7), 63(84.3), 47(16.6).

The title compound was prepared from the fluorosilane in 83% isolated yield utilizing the heterogeneous reaction system [4]. The following spectral data were recorded for t-butoxydiethylmethylsilane. NMR δ 1.32, s, 9 H, t-BuO, 1.22—0.42, m, 10 H, Et—Si and δ 0.17, s, 3 H, Me—Si. Mass spectrum 174(0.7), 159(12.2), 145(36.6), 133(5.1), 131(2.4), 103(9.1), 101(16.9), 89(100), 75(6.3), 73(12.6), 61(36.2).

Heterogeneous reaction between chloromethyldimethylsilane and potassium t-butoxide

The following represents a typical heterogeneous reaction carried out in this work. The furnace tube was charged with 4.0 g (55 mmol) of potassium t-butoxide fitted with the nitrogen inlet system and placed in a preheated (100°C) oven. The charge was "baked out" by allowing it to come to thermal equilibrium with the oven with a nitrogen flow rate of 60 ml/min. Caution! The heated base will inflame at 100° if not under nitrogen! After an additional 15 min, the end of the furnace tube was equipped with a cylindrical trap and the trap was cooled with a Dry Ice/acetone bath. The reservoir was then charged with 0.98 g (9.0 mmol) of chloromethyldimethylsilane and a heating tape was applied to the sample container. The nitrogen flow rate was adjusted to a slow rate of bubbling through the liquid and the tape was heated. In this fashion the addition of the silane usually required 30—45 min. Upon completion of the addition, the tube was blown out for 15 min with the flow rate again increased to 60 ml/min. From the trap was recovered 0.89 g (68% mass balance based upon replacement of one chlorine by one butoxide per mol of silane) of condensate. The condensate was examined by GLC and found to contain components both of shorter and longer retention times than that of the major component identified as trimethyl-t-butoxysilane. An internal standard yield analysis indicated that there were present in the condensate 4.537 mmol Me_3SiOt-Bu. This represents a yield of 51% based on the original amount of silane present.

The minor pdocuts formed in this reaction were identified by their IR, NMR, and mass spectra. They were, in order of their elution from a 20% SE-30 column, as follows: t-butanol, t-butylmethyl ether, hexamethyldisiloxane before the major product's peak and 2-t-butoxy-2-methyl-2-silapropanol and bis(t-butoxy)dimethylsilane after the major product's peak. Internal standard yield analysis indicated that the distribution of these products varied slightly with temperature ranging between 3 and 10% each.

Heterogeneous reaction between chloromethyldimethyldeuteriosilane and potassium t-butoxide

The reaction was carried out in an identical fashion to that described above. The GLC trace of the crude condensate could be superimposed upon that of a reaction of unlabeled silane with the base. The peak corresponding to that of t-butoxytrimethylsilane in the labeled reaction was collected and identified as t-butoxytrimethyl(D1)silane by mass spectra. The mass spectra of the unlabeled and labeled product are given here for comparison. t-BuOSiMe$_3$: 146(3.3, M^+, $C_7H_{18}SiO$), 133(4.3), 132(11.9), 131(96.3, M^+ — Me, $C_6H_{15}SiO$), 77(5.7), 76(11.5), 75(100, $Me_2Si{=}OH^+$), 74(11.5), 73(94.3, Me_3Si^+). t-BuOSi(CH_2D)Me$_2$: 147(5.6, M^+, $C_7H_{17}DSiO$), 134(4.8), 133(13.0), 132(100, M^+ — Me, $C_6H_{14}DSiO$), 131(13.6, M^+ — CH_2D, $C_6H_{15}SiO$), 78(3.4), 77(7.9), 76(86.4, $CH_2DSiMe{=}OH^+$), 75(48.9, $Me_2Si{=}OH^+$), 74(77.4, $Me_2SiCH_2D^+$), 73(5.6).

Heterogeneous reaction between chloromethyldimethyldeuteriosilane chloromethyldiethylsilane and potassium t-butoxide

This reaction was run in an identical fashion to those described above with the exception of the mode of addition. Since the two silanes have quite different boiling points, the mixture was added via syringe to insure intimate mixing of their vapors in the reaction zone. The reaction utilized 1.0 g (9.1 mmol) of chloromethyldimethyldeuteriosilane, 1.0 g (7.3 mmol) of chloromethyldiethylsilane and 2.4 g (32.8 mmol) of potassium t-butoxide. The silane mixture was added in small portions over a period of 1 h. The resulting condensate, 2.4 g (92% mass balance for the replacement of one chlorine by one butoxide per mol of silane), was examined by GLC. The condensate's trace was superimposed upon those of reactions of each of the silanes separately. The peaks corresponding to t-BuOSi(CH_2D)Me$_2$ and t-BuOSiEt$_2$Me were collected and the mass spectrum of each product was recorded. Comparison of these spectra with those of authentic samples yielded no evidence for deuterium—hydrogen exchange within the limits of experimental error.

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