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Procedures for the preparation of silanols

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Abstract

Two procedures are described for the preparation of silanols and silanediols from the corresponding chlorosilanes. The first procedure, a two-phase hydrolysis–extraction process, is particularly convenient and suited to the preparation of a wide range of mono-silanols. Hydrolysis of dichlorosilanes by this procedure gives varied results depending on the structure of the dichlorosilane and specific reaction conditions. The second procedure, a modification of a published procedure, is especially beneficial for the preparation of silanols and silanediols prone to undergo self-condensation.

Key words: Silicon; Hydrolysis; Self-condensation; Silanols

1. Introduction

Low molecular weight silanols and silanediols are important intermediates in organosilicon chemistry. The lower homologues such as trimethylsilanol, 1,1-dimethylsilanediol, 1,1,3,3-tetramethyldisiloxane-1,3-diol and 1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diol are particularly important as water-soluble environmental breakdown products of silicones [1]. The lower members of this series have a propensity to undergo self-condensation. This tendency depends on the nature and size of the substituents attached to silicon. For example, the relative rates of condensation of trimethylsilanol, triethylsilanol and triphenylsilanol are $1 : 1.7 \times 10^{-3} : 2.0 \times 10^{-6}$ [2]. The silane-1,1-diols exhibit similar behavior, dimethylsilane-1,1-diol being the most reactive. Preparation of the more sensitive silanols requires conditions that ensure a neutral medium throughout the course of preparation and isolation of the product. Additional complications are associated with the water solubility of some of the lower homologues. Reported methods for preparation of silanols have employed various means of fulfilling this criterion of neutrality by hydrolysis of alkoxy silanes [3], acetoxysilanes [4], silazanes [5] and chlorosilanes in the presence of various acid acceptors, such as sodium, potassium or ammonium bicarbonates [6] or aniline [7]. The aim of this investigation was to modify existing procedures and/or to develop new procedures that would be both convenient and general for the preparation of a variety of labile, low molecular weight silanols and silanediols from the corresponding chlorosilanes. Two procedures are described: a two-phase hydrolysis employing ammonium carbonate as an acid acceptor and a homogeneous hydrolysis using triethylamine as the acceptor.

2. Results and discussion

In the two-phase hydrolysis procedure, a chlorosilane dissolved in diethyl ether is added slowly (preferably via a syringe pump) to a chilled, rapidly stirred two-phase mixture of diethylether and water saturated with NaCl containing a slight excess of $(NH_4)_2CO_3$. The silanol is extracted as it forms and is isolated simply by decanting the ether layer at the end of the reaction. This procedure is convenient for the preparation of a wide range of mono-silanols. Table 1 lists the yields for a number of silanols that have been prepared by this two-phase hydrolysis–extraction procedure.

Hydrolysis of dihalosilanes by this procedure affords mixtures of products depending on the structure of the dihalosilane and/or the specific reaction conditions employed (rate of addition, rate of stirring, concentra-

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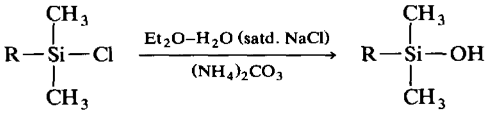
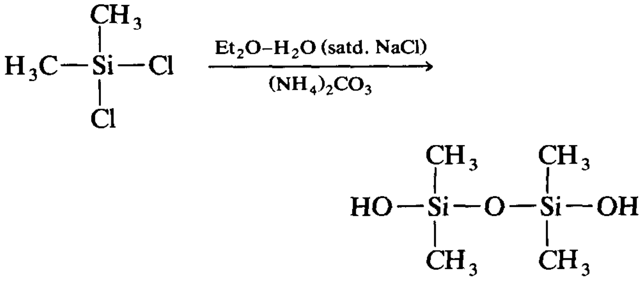
TABLE 1. Preparation of mono-silanols via the two-phase hydrolysis-extraction procedure

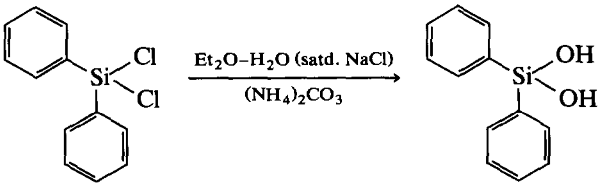


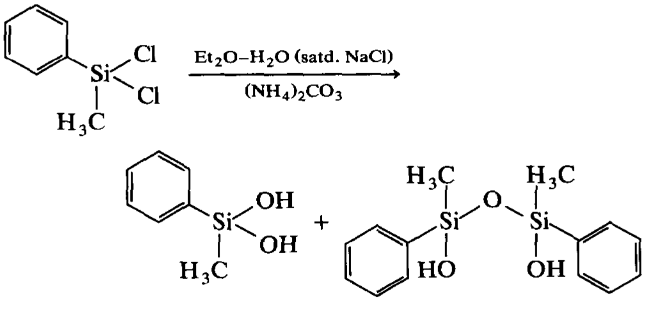
R	Yield (%)	Reference
$CF_3(CH_2)_2$-	98	[8]
$CF_3(CF_2)_5(CH_2)_2$-	70	[9]
$CF_3(CF_2)_7(CH_2)$-	95	[9]
CH_3-	78	[5]
C_6H_5-	92	[10]
$ClCH_2$-	95	[11]
$BrCH_2$-	79	[12]
-$(Me_2SiO)_3$-	99	[13]
$(CH_3)_3Si(Me_2SiO)_2$-	95 (65)	[14]

tion of reagents etc.). For example, hydrolysis of dimethyldichlorosilane under these two-phase conditions affords only traces of dimethylsilanediol but good to excellent yields of 1,1,3,3-tetramethyldisiloxane-1,3-diol. Hydrolysis of diphenyldichlorosilane under identical conditions produces diphenylsilane-1,1-diol exclusively and hydrolysis of phenylmethyldichlorosilane produces a mixture of monomer and dimer diols.



91% yield

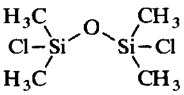
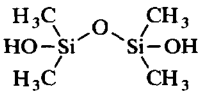
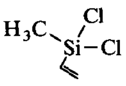
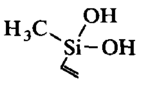
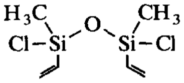
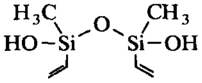




The products obtained using this method appear to depend on a subtle balance between the rates of hydrolysis, condensation and extraction of the intermediates, a balance affected by concentration, stir rates etc.

The second procedure, a modification of a procedure reported by Takiguchi [7] for preparation of dimethylsilane-1,1-diol, was found to be effective for obtaining diols particularly sensitive to condensation. In the Takiguchi procedure, the appropriate chlorosilane dissolved in ether is added at 0°C to a mixture of ether, aniline (1.0 equivalents per SiCl), water (1.0 equivalents per SiCl) and enough acetone to make the mixture homogeneous. The desired silanol products are then isolated by filtration to remove aniline hydrochloride, followed by evaporation of the ether and rinsing of the products with pentane to remove any higher oligomers formed during the hydrolysis. Although the Takiguchi procedure provides good yields of sensitive silanols and silanediols, the products are often unstable to storage when trace amounts of residual aniline are present. The immiscibility of aniline and pentane precludes its removal during the washing step. Therefore, when employing this method, exact stoichiometry is critical. Triethylamine offers a number of advantages over aniline as an HCl acceptor in this procedure. Its volatility and solubility in pentane ensure its complete removal from the silanol products during work-up. It can thus be used in a slight excess during the hydrolysis step, avoiding any possibility of excess acid at the end of the reaction. Silanols and silanediols obtained using this modified procedure were found to be stable to storage for prolonged periods even at room temperature. Dimethylsilanediol was repeatedly obtained in 80–90% yield by this procedure and stored for months in the freezer without deterioration. Details of this procedure are described in the experimental section. Table 2 lists a number of silane-

TABLE 2. Silanediols prepared using triethylamine as an acid scavenger in the Takiguchi procedure

Dichlorosilane	Silanediol	Yield (%)	Reference
$(CH_3)_2SiCl_2$	$(CH_3)_2Si(OH)_2$	83	[3a]
		92	[3a]
		85	[13]
		85	13

diols obtained from the corresponding dichlorosilanes using the triethylamine modification of the Takiguchi procedure.

The two procedures described in this paper make possible easy preparation of a wide range of silanols and silanediols from the corresponding chlorosilanes. The two-phase procedure has the advantage of simplicity and ease of work-up while the triethylamine process is particularly suited to the preparation of diols prone to self-condensation.

3. Experimental section

3.1. Reagents

Chlorosilanes were obtained from Huls–Petrarch and were distilled just prior to use. Triethylamine was obtained from Aldrich and used without further purification or drying.

3.2. Analysis

High pressure liquid chromatography was carried out on a Perkin–Elmer series 410 high performance liquid chromatography pump interfaced to a Perkin–Elmer LC 30-RI refractive index detector or an LC-95 UV–visible detector. A Whatman Partisil 10 ODS-3 column was employed with isocratic 80% acetonitrile–20% water as the eluant at a flow rate of 1.5 ml min^{-1}. NMR spectra were determined on a GE NMR Instruments QE-300 instrument operating at a frequency of 75.4 MHz for ^{13}C spectra and 300 MHz for proton spectra. IR spectra were determined using a Mattson Instruments Galaxy series FT-IR model 6020 instrument.

3.3. Preparation of silanols using a two-phase method

A typical procedure is outlined for the preparation of 1,1,3,3,5,5,7,7,7-nonamethyltrisiloxan-1-ol (MD_3OH).

MD_3OH: 1-chloro-1,1,3,3,5,5,7,7,7-nonamethyltrisiloxane (MD_3Cl) was prepared by reaction of trimethylchlorosilane with hexamethylcyclotrisiloxane [15]. MD3Cl (13.9 g, 0.042 mol) in diethylether (20 ml) was added dropwise via a syringe pump over about 30 min into a rapidly stirred two-phase system consisting of 100 ml of water, 100 ml of ether, 2.4 g (0.025 mol) of freshly titrated ammonium carbonate and enough sodium chloride to saturate the aqueous phase (about 350 mg ml^{-1}). When the addition was complete, the aqueous layer was extracted three times with ether and the combined ether fractions were dried over anhydrous sodium sulfate and concentrated to afford 12.4 g of MD_3OH which was purified by column chromatography on silica gel using hexane–ethyl acetate as eluant. This process afforded 8.3 g of purified MD_3OH. ^{1}H NMR (dimethylsulfoxide (DMSO)-d_6): δ 6.12 (s, 1, OH); 0.07 (s, 9, $Si(CH_3)_3$); 0.03 (s, 6, $Si(CH_3)_2$); 0.02 (s, 6, $Si(CH_3)_2$); -0.02 (s, 6, $Si(CH_3)_2$) ppm. ^{13}C NMR (DMSO-d_6): δ 1.83; 1.2; 1.18; and 0.80 ppm.

In a similar manner to that described, the following silanols were prepared.

$PhSi(CH_3)_2OH$: obtained as an oil. ^{1}H NMR ($CDCl_3$): δ 7.7 (m, 2, ArH); 7.49 (m, 3, ArH); 4.0 (br-s, 1, OH); 0.40 (s, 6, $SiCH_3$) ppm.

$(CH_3)_3SiOH$: purified by distillation; b.p., 90°C at 760 Torr. ^{1}H NMR ($CDCl_3$): δ 0.0 (s, 9, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 1.0 (CH_3) ppm.

$CF_3(CF_2)_5(CH_2)_2Si(CH_3)_2OH$: purified by distillation; b.p., 65°C at 1.4 Torr. ^{1}H NMR ($CDCl_3$): δ 2.1 (m, 2, CH_2–CH_2Si); 0.83 (pent., 2, $SiCH_2$–); 0.2 (s, 6, $SiCH_3$) ppm.

$CF_3(CH_2)_2Si(CH_3)_2OH$: oil. ^{1}H NMR (DMSO-d_6): δ 5.57 (s, 1, OH); 2.15 (m, 2, CF_3CH_2); 0.61 (m, 2, CH_2Si); 0.01 (s, 6, $SiCH_3$) ppm.

$BrCH_2Si(CH_3)_2OH$: purified by distillation; b.p., 55°C at 9 Torr. ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 2, $SiCH_2Br$); 0.26 (s, 6, $SiCH_3$) ppm.

$ClCH_2Si(CH_3)_2OH$: purified by distillation; b.p., 65°C at 20 Torr. ^{1}H NMR ($CDCl_3$): δ 2.79 (s, 2, $SiCH_2$); 0.26 (s, 6, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 30.37 ($ClCH_2$); -2.01 ppm (CH_3) ppm.

$CF_3(CF_2)_7CH_2CH_2Si(CH_3)_2OH$: obtained as an oil. ^{1}H NMR ($CDCl_3$): δ 2.1 (m, 2, CH_2CH_2Si); 0.79 (m, 2, CH_2CH_2Si); 0.15 (s, 6, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 121.9–110.35 (8-carbons F-coupled); 14.84 (CH_2CH_2Si); 7.08 (CH_2CH_2Si); -1.13 ($SiCH_3$) ppm. IR: (neat) ν(OH) 3280 cm^{-1}.

3.4. Preparation of silanols using triethylamine as acid scavenger

A typical procedure is outlined for preparation of dimethylsilanediol.

Dimethylsilanediol: Dichlorodimethylsilane (30.0 g, 0.23 mol) in 300 ml of ethyl ether was added dropwise with stirring to a 0°C solution consisting of 47.4 g of triethylamine (0.47 mol, 2.01 equivalents), 9.0 g of water (0.5 mol, 2.15 equivalents), 700 ml of ethyl ether and enough acetone (about 70 ml) to provide homogeneity. Addition of chlorosilane was complete in 1.0 h. Following addition the solution was allowed to stir for an additional 30 min at 0°C. The triethylamine hydrochloride was removed by vacuum filtration and the filtrate was concentrated to one tenth of its volume by rotary evaporation. At this point an excess of pentane was added to the flask and rotary evaporation continued. The solid was collected by filtration and washed with cold pentane to remove any residual triethylamine. Crude dimethylsilanediol (17.3 g (83%)) was obtained (m.p. 93–96°C). Recrystallization from pentane–ethyl ether afforded white plates (m.p., 98–100°C), ^{1}H NMR (DMSO-d_6): δ 5.76 (s, 2, OH); -0.08 (s, 6, CH_3) ppm. In an analogous way the following were prepared.

Tetramethyldisiloxane 1,3-diol: crude yield, 92%; white needles; m.p., 63–64°C; recrystallized from pentane–ethyl ether. ^{1}H NMR ((DMSO-d_6): δ 6.06 (s, 2, OH); -0.02 (s, 3, CH_3) ppm.

Methylvinylsilanediol: crude yield, 85%; m.p., 67–69°C; recrystallized from pentane–ethyl ether. ^{1}H NMR (DMSO-d_6): δ 6.06 (s, 2, OH); 5.88 (m, 3, vinyl-H); -0.02 (s, 3, CH_3) ppm.

meso / rac-1,3-Dimethyl-1,3-divinyldisiloxane-1,3-diol: (mixture of isomers); crude yield, 85%; b.p. 85°C at 0.5 Torr. ^{1}H NMR ($CDCl_3$): δ 6.0 (m, 6, Vi–H); 4.5 ppm (brs, 2, OH); 0.23, 0.22 (s, 3, CH_3) ppm.

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