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The recycling of organosilyl protecting species used in organic synthesis and the water binding ability of the silanol $^tBuMe_2SiOH$

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Abstract

The silanols formed on the cleavage of organosilyl protecting groups from organic compounds can be efficiently reconverted into the chlorosilanes used in the initial silylation reaction by treatment with $SOCl_2$. The silanol $^tBuMe_2SiOH$ is very readily removed from organic reaction mixtures as its remarkably volatile hemihydrate $[^tBuMe_2SiOH]_2 \cdot H_2O$.

Introduction

The use of organosilyl protecting groups has undergone great growth in the last 15 years and they are now likely to be used in any synthesis of reasonable complexity. The first group to be used extensively was Me_3Si, but recently bulkier groups such as $^tBuMe_2Si$, (t-hexyl)Me_2Si [(t-hexyl) = 1,1,2-trimethylpropyl] and $^tBuPh_2Si$, which form more stable silylated products, have come into fairly widespread use.

Deprotection of compounds containing bulky silyl groups is usually achieved by treatment with fluoride ion (often derived from $^nBu_4NF$) and the silicon-containing product thus formed is a silanol (Si–OH species) or silanol/silyl fluoride mixture. After isolation of the required organic material, the organosilicon by-product is normally disposed of as waste, even on an industrial scale. We have found that the silanols formed in such deprotection reactions can easily be reconverted into the chlorosilanes that are often the initial source of the protecting group, and that in the case of the probably most widely used group, $^tBuMe_2Si$, the silanol can be efficiently removed from reaction mixtures as its hemihydrate $[^tBuMe_2SiOH]_2 \cdot H_2O$.

Results and discussion

The silanols $^iPrMe_2SiOH$, $^tBuMe_2SiOH$, (t-hexyl)Me_2SiOH and $^tBuPh_2SiOH$ were prepared by hydrolysis of the corresponding chlorides with $KOH/H_2O/MeOH$ as described by Sommer and Tyler [1]. The chlorosilanes were reformed by treating the silanol with $SOCl_2$ in $CHCl_3$, and isolated by removing the chloroform by distillation at room temperature. It should be noted that the conversion of silanols to chlorosilanes by treatment with $SOCl_2$ has been known for some time [3], and that the conversion of $^tBuPh_2SiOH$ to $^tBuPh_2SiCl$ by oxalyl chloride in 4-(dimethylamino)pyridine has been described [4]. In spite of this, the potential for this type of reaction in the recycling of protecting groups in organic chemistry seems to have been overlooked.

The isolated yields of chlorosilanes derived from $^iPrMe_2SiOH$, (t-hexyl)Me_2SiOH, and $^tBuPh_2SiOH$ were very good (90, 82, and 81% respectively) but for $^tBuMe_2SiCl$ only 39% was isolated. This lower yield is probably caused by losses during distillation, and a more careful fractionation would no doubt lead to a much higher yield, and a yield of 95% for the reaction has been reported in a patent [2].

A problem inherent in the recycling of waste products is their isolation from other materials in the product mixture. This was achieved for the silanols described above by distillation under reduced pressure, but a much easier method has been found in the case of the most commonly encountered $^tBuMe_2SiOH$ that makes use of its remarkable ability to bind water.

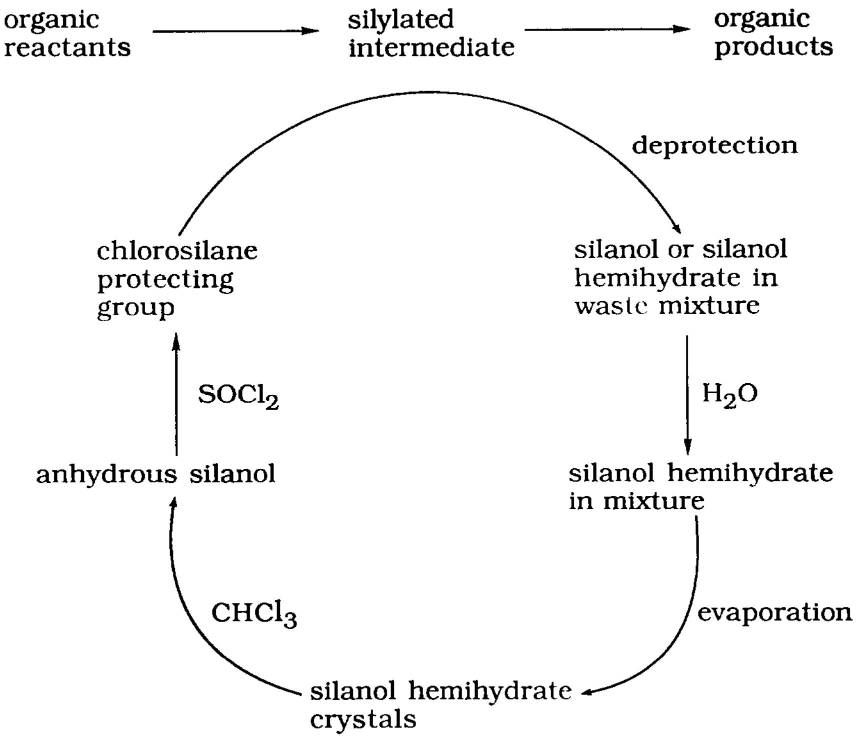
Anhydrous $^tBuMe_2SiOH$ is a liquid (b.p. 139 °C/739 mmHg) but it readily forms a solid hemihydrate $[^tBuMe_2SiOH]_2 \cdot H_2O$ when in contact with moist air or in a solution containing water. The hemihydrate (m.p. 68–70 °C) sublimes very readily at room temperature and pressure to form long, needle-like crystals [1]. Thus, $^tBuMe_2SiOH$ may readily be removed from a reaction mixture as its hemihydrate by evaporation with the solvent in, for example, a rotary evaporator. The hemihydrate is readily broken down by addition to chlorinated solvents such as CH_2Cl_2 or CCl_4, after which water separates and can be isolated by decantation of the solvent. After it has been dried with $MgSO_4$, the solution can be used for the chlorination step of the recycling process, as shown in Scheme 1.

The solid state structure of $[^tBuMe_2SiOH]_2 \cdot H_2O$ has been found [5] to comprise hydrogen bonded chains as shown diagrammatically in Fig. 1, and is very similar to that of the carbon analogue $[^tBuMe_2COH]_2 \cdot H_2O$ [6]. The unusually high volatility of the silanol hemihydrate compared with that of other silanols and of anhydrous $^tBuMe_2SiOH$ may therefore be due to the fact that in the hemihydrate the only hydrogen bonds present are between silanol and water molecules, whereas in anhydrous silanols only silanol–silanol interactions (which are stronger due to the greater acidity of silanols) are possible. The steric requirements for the formation of a chain structure of the type shown in Fig. 1 seem to be met particularly well for $^tBuMe_2SiOH$, since none of the other silanols discussed above seem to form simple adducts with water.

In conclusion it can be seen that silyl protecting species can readily be recycled, and that this is particularly simple for the very widely used $^tBuMe_2Si$ group. In the light of the high cost of many silyl protecting groups and the current concern with waste product disposal, the process described should be of widespread use.

Experimental

Infrared spectra were recorded as liquid films or nujol mulls between KBr plates on a Perkin Elmer 1710 Fourier transform instrument. NMR spectra were recorded as $CDCl_3$ solutions at 90 MHz.



Scheme 1. Recycling of ^{t}BuMe$_2$SiCl.

Preparation of silanols

[^{t}BuMe$_2$SiOH]$_2$ · H$_2$O. Sommer and Tyler's method was used [1]. Thus 95 g of ^{t}BuMe$_2$SiCl gave 72.8 g (87%) of the hemihydrate, m.p. 68–70 ° C, as long needles. Crystals several centimetres in length can be readily prepared by slow sublimation at room temperature and pressure.

(t-hexyl)Me$_2$SiOH. The same method starting from 25 g of (t-hexyl)Me$_2$SiCl gave 21.9 g (89%) of (t-hexyl)Me$_2$SiOH as a colourless liquid, ν(OH) 3583 (free) and 3338 cm^{-1} (hydrogen bonded). ^{1}H NMR: δ 0.14 (s, 6H, SiMe$_2$), 0.87 (s, 6H, SiCMe$_2$), 0.92 (d, $J = 8$ Hz, 6H, CH*Me*$_2$), 1.60 (d, 1H, C*H*Me$_2$), 2.06 (bs, 1H, OH).

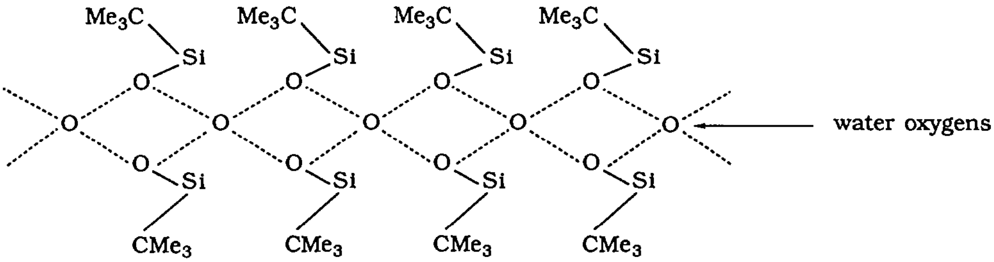


Fig. 1. Hydrogen bonded arrangement found in [^{t}BuMe$_2$SiOH]$_2$·H$_2$O. The methyl groups on silicon and the hydroxylic protons are omitted for clarity and dashed lines represent hydrogen bonds.

^{t}BuPh$_2$SiOH. The same method starting from 19.2 g of ^{t}BuPh$_2$SiCl gave 17.1 g (95%) of ^{t}BuPh$_2$SiOH as a colourless liquid, ν(OH) 3583 (free) and 3391 cm^{-1} (hydrogen bonded). ^{1}H NMR: δ 1.00 (s, 9H, CMe$_3$), 2.20 (s, 1H, OH), 7.15–7.30 and 7.50–7.70 (m, 10H, Ph).

^{i}PrMe$_2$SiOH. The same method starting from 5 g of ^{i}PrMe$_2$SiCl gave 3.3 g (77%) of ^{i}PrMe$_2$SiOH as a colourless liquid, ν(OH) 3674 (free) and 3303 cm^{-1} (hydrogen bonded). ^{1}H NMR: δ 0.10 (s, 6H, SiMe$_2$), 0.90 (m, 1H, CHMe$_2$), 0.99 (d, $J = 6$ Hz, 6H, CHMe_2).

Chlorination of silanols

Anhydrous ^{t}BuMe$_2$SiOH was obtained by pouring the hemihydrate into chloroform, upon which the water separated out and could be isolated by decantation of the solution, which was then dried (MgSO$_4$). The chloroform solution thus prepared was then used for the chlorination step, which was carried out by a modification of that used by George et al. [7]. For example, a solution of SOCl$_2$, 100 g (0.84 mol) in CHCl$_3$ (100 ml), was added dropwise during 1 h to a solution of ^{t}BuMe$_2$SiOH, 72 g (0.55 mol) in CHCl$_3$ (150 ml). The mixture was then stirred for a further 30 min, after which ^{1}H NMR spectroscopy indicated complete conversion of the silanol into ^{t}BuMe$_2$SiCl. The CHCl$_3$ was removed by distillation under dry nitrogen to give the chlorosilane in 39% isolated yield as a volatile solid. Isolated yields of chlorosilanes derived similarly from ^{i}PrMe$_2$SiOH, (t-hexyl)Me$_2$SiOH and ^{t}BuPh$_2$SiOH were 90, 82, and 81%, respectively.

Acknowledgement

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