SILYLATION OF NITROGEN-CONTAINING COMPOUNDS USING TRIMETHYLSILYLIMIDAZOLE IN THE ACTIVE MEDIUM OF HEXAMETHYLDISILAZANE

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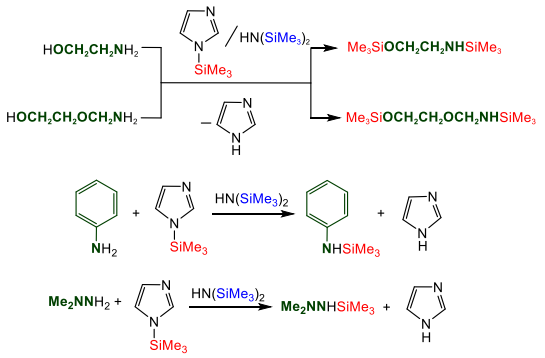
Abstract

A new silylating system is suggested based on trimethylsilylimidazole in the active medium of hexamethyldisilazane, which allows for the introduction of trimethylsilyl units both at the OH and NH_2 groups. The use of this system ensures the synthesis of trimethylsilyl derivatives of amino alcohols in one stage, and, in the case of aniline and *N,N*-dimethylhydrazine, significantly reduces the reaction time and increases the product yields.



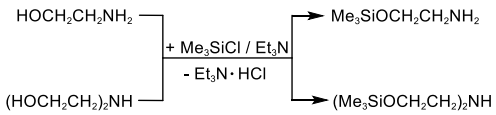
Key words: silylating system, trimethylsilylimidazole, hexamethyldisilazane, amino alcohols, *N,N*-dimethylhydrazine, aniline.

Introduction

Nitrogen-containing organosilicon compounds are widely used as silylating and finishing agents, as well as starting substances for the production of pharmaceuticals, ureas, and semicarbazides [1–4].

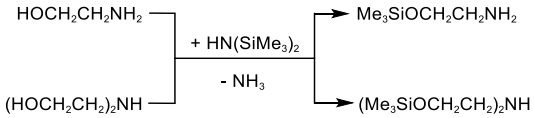
Earlier it has been shown [5] that the use of hexamethyldisilazane or a trimethylchlorosilane/triethylamine mixture, as a rule, does not allow simultaneous silylation at the hydroxy and amine groups in amino alcohols.

Usually, the silylation with chlorosilanes occurs exclusively at the OH group, requiring the use of solvents and acceptors of released hydrogen chloride (ammonia, triethylamine, pyridine or an excess of the amino alcohol itself) (Scheme 1).



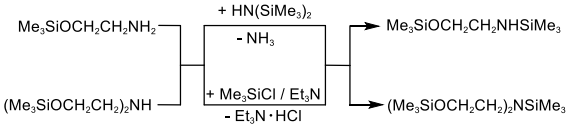
Scheme 1. Silylation of amino alcohols with trimethylchlorosilane in the presence of triethylamine.

The interaction of hexamethyldisilazane with amino alcohols proceeds similarly, but in this case the use of solvents and the filtration stage are not required (Scheme 2).



Scheme 2. Silylation of amino alcohols with trimethylchlorosilane in the presence of hexamethyldisilazane.

For the synthesis of silicon derivatives of amino alcohols containing both Si–O and Si–N bonds, the best results can be obtained with the silylation of the amino group of preformed individual aminoalkoxysilanes (Scheme 3).

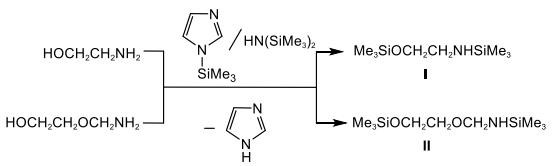


Scheme 3. Silylation of the *O*-trimethylsilyl derivatives of amino alcohols.

Results and discussion

We have developed a previously unknown silylating system without the use of organochlorosilanes: trimethylsilylimidazole in the active medium of hexamethyldisilazane.

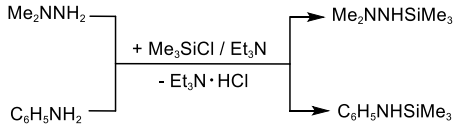
It was established that, in some cases, this silylating system allows for the simultaneous introduction of trimethylsilyl groups at both reaction centers. For example, in the case of monoethanolamine and 2,2-aminoethoxyethanol, at the hydroxy and amine groups (Scheme 4).



Scheme 4. Synthesis of (trimethylsilyl){2-[(trimethylsilyl)oxy]-ethyl}amine (**I**) and (trimethylsilyl)(2-{2-[(trimethylsilyl)oxy]ethoxy}ethyl)amine (**II**).

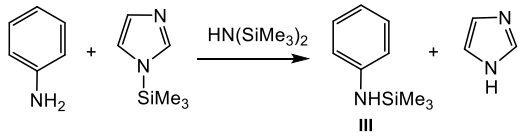
The reactions were carried out by adding a 1:1 mixture of trimethylsilylimidazole/hexamethyldisilazane to the starting amino alcohols, followed by the filtration of precipitated imidazole and isolation of the target products by fractional distillation under vacuum. The yields of target products **I** and **II** were 98 and 92%, respectively.

When passing from amino alcohols to aniline and *N,N*-dimethylhydrazine [6], it should be noted that their silylation is also complicated, as is the case with amino alcohols and their derivatives. Therefore, trimethylchlorosilane with a hydrogen chloride acceptor, namely, triethylamine is usually used as a silylating agent for them (Scheme 5). Therewith, the yields of the target products range within 70–80%.

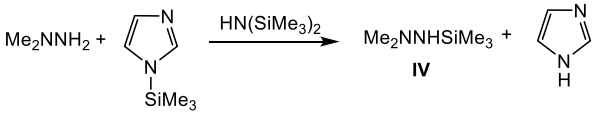


Scheme 5. Silylation of aniline and *N,N*-dimethylhydrazine with trimethylchlorosilane in the presence of triethylamine.

It was found that, in this case, the use of the silylating system based on trimethylsilylimidazole in the active medium of hexamethyldisilazane significantly reduces the time of the silylation process and increases the yield of target products *N*-phenyl-*N*-(trimethylsilyl)amine (**III**) and 1,1-dimethyl-2-(trimethylsilyl)hydrazine (**IV**) to 88% and 87%, respectively (Schemes 6 and 7).



Scheme 6. Synthesis of *N*-phenyl-*N*-(trimethylsilyl)amine.



Scheme 7. Synthesis of 1,1-dimethyl-2-(trimethylsilyl)hydrazine.

Experimental section

The ^{1}H NMR spectra were recorded on a Bruker WP-300 spectrometer with an operating frequency of 400 MHz. The solvent was trichloromethane-D.

All manipulations with the substances were carried out in a dry nitrogen atmosphere.

Synthesis of (trimethylsilyl){2-[(trimethylsilyl)oxy]-ethyl}amine (I). Hexamethyldisilazane (34.3 g, 0.204 mol) and trimethylsilylimidazole (27.0 g, 0.192 mol) were added to monoethanolamine (5.9 g, 0.096 mol). The fractionation afforded 19.3 g of compound **I**. Yield: 98%. Bp: 174.5 °C/20 mm Hg; n_D^{20}: 1.4124. ^{1}H NMR: δ 0.01 s (9H, $OSiMe_3$), 0.08 s (9H, $NSiMe_3$), 2.77 s (2H, NCH_2), 3.46 s (2H, OCH_2) ppm.

Synthesis of (trimethylsilyl)(2-{2-[(trimethylsilyl)oxy]ethoxy}ethyl)amine (II). Hexamethyldisilazane (22.0 g, 0.114 mol) and trimethylsilylimidazole (16.0 g, 0.114 mol) were added to 2,2-aminoethoxyethanol (6.0 g, 0.057 mol). The fractionation afforded 26.0 g of compound **II**. Yield: 92%. Bp: 80–82 °C/1 mm Hg; n_D^{20}: 1.4274. ^{1}H NMR: δ 0.03 s (9H, $OSiMe_3$), 0.04 s (9H, $NSiMe_3$), 2.79 s (2H, NCH_2), 3.46 s (2H, NCH_2), 3.66 s (2H, OCH_2) ppm.

Synthesis of *N*-phenyl-*N*-(trimethylsilyl)amine (III). A mixture of aniline (10.0 g, 0.108 mol), hexamethyldisilazane (25.0 g, 0.108 mol), and trimethylsilylimidazole (15.0 g, 0.108 mol) was heated at 70–75 °C for 28 h. The fractionation afforded 19.5 g of compound **III**. Yield: 88%. Bp: 59–64 °C/2 mm Hg; n_D^{20}: 1.5219. ^{1}H NMR: δ 0.06 s (9H, $SiMe_3$), 6.34 s (2H, CH), 6.80 s (2H, CH) ppm.

Synthesis of 1,1-dimethyl-2-(trimethylsilyl)hydrazine (IV). A mixture of *N,N*-dimethylhydrazine (4.0 g, 0.068 mol), hexamethyldisilazane (13.5 g, 0.084 mol), and trimethylsilylimidazole (9.5 g, 0.068 mol) was heated at 55 °C for 16 h. The fractionation afforded 7.83 g of compound **IV**. Yield: 87%. Bp: 126–130 °C; n_D^{20}: 1.4001. ^{1}H NMR: δ 0.04 s (9H, $SiMe_3$), 2.36 s (6H, CH_3) ppm.

Conclusions

Hence, the method for obtaining organosilicon derivatives of amino alcohols, aniline and *N,N*-dimethylhydrazine was described. The previously unknown highly active silylating system was discovered: trimethylsilylimidazole in the active medium of hexamethyldisilazane. It was found that the use of this silylating system significantly simplifies the process of introducing trimethysilyl groups at hydroxy, amine, and hydrazine groups and also increases the yields of target products.

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