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Novel nucleophilic addition to the N=C bond of silicon isocyanates: conversion of some sterically hindered organosilicon isocyanates into aminosilanes

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Abstract

Treatment of the sterically hindered organosilicon isocyanates $(Me_3Si)_3CSiMe_2NCO$, $(PhMe_2Si)_3CSiMe_2NCO$ and $(Me_3Si)_2C(SiMePh_2)(SiMe_2NCO)$ with 2 M NaOH in 1/1 v/v $MeOH/CH_2Cl_2$ at room temperature gives the aminosilanes $(Me_3Si)_3CSiMe_2NH_2$, $(PhMe_2Si)_3CSiMe_2NH_2$ and $(Me_3Si)_2C(SiMePh_2)(SiMe_2NH_2)$ respectively. Treatment of $(Me_3Si)_3CSiMe_2NCO$ with 0.5 M NaOMe in 1/1 v/v $MeOH/CH_2Cl_2$ gives the urethane $(Me_3Si)_3CSiMe_2NHCOOMe$.

Keywords: Silicon; Nucleophilic addition; Isocyanates

1. Introduction

The severe steric hindrance to direct nucleophilic attack at functional silicon centres bearing the bulky 'trisyl' group $(Me_3Si)_3C$, denoted here by Tsi, or a related group, has allowed observation of reactions and mechanisms which would otherwise be obscured [1–9]. Hydrolysis of organic isocyanates is a common method for the preparation of primary amines [10], but no example of nucleophilic addition to the nitrogen carbon double bond of silicon isocyanate which would presumably be required for the corresponding conversion to aminosilane has been reported, displacement of the NCO by the nucleophile being favoured [11]. The study described below has shown that when such displacement is inhibited on silicon by the presence of a Tsi or related bulky group, conversion to the aminosilane proceeds very satisfactorily.

2. Results and discussion

The organosilicon isocyanate $TsiMe_2NCO$ was recovered unchanged when its solution in MeOH, alone or containing 5 vol.% H_2O, was stirred under reflux for 24 h. However, it was found to react with 2 M NaOH in 1/1 v/v $MeOH/CH_2Cl_2$ (the CH_2Cl_2 being required to increase the solubility of the substrate) to give exclusively the corresponding aminosilane $TsiSiMe_2NH_2$. The product gave spectra identical with those of an authentic sample obtained by reaction of $TsiSiMe_2OClO_3$ with liquid ammonia in CH_2Cl_2 [9]. The formation of the aminosilane $TsiSiMe_2NH_2$ rather than the hydroxide $TsiSiMe_2OH$ that would be expected from direct nucleophilic attack at the functional silicon centre is presumably attributed to the very large steric hindrance caused by the Tsi ligand. The course of the reaction is diverted towards nucleophilic attachment of the hydroxide ion to the carbon of the isocyanate group to give an unstable carbamate ion, which undergoes spontaneous decarboxylation to give the observed aminosilane (Scheme 1), possibly via a mechanism analogous to that postulated for the hydrolysis of organic isocyanates [10].

In contrast to the isocyanate, the isothiocyanate $TsiSiMe_2NCS$ was recovered unchanged on treatment with NaOH under similar conditions. The low reactivity of the organosilicon isothiocyanate towards nucleophilic addition is consistent with that observed for organic isothiocyanates [10].

The closely related isocyanates $TpsiSiMe_2NCO$ (Tpsi = $(PhMe_2Si)_3C$) and $(Me_3Si)_2C(SiMePh_2)(SiMe_2NCO)$ were likewise converted in high yield by the same method into the corresponding aminosilanes

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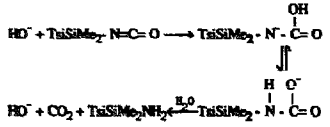

Scheme 1.

$TpsiSiMe_2NH_2$ and $(Me_3Si)_2C(SiMePh_2)(SiMe_2NH_2)$. Since such sterically hindered organosilicon isocyanates are readily obtained from the reactions between the corresponding halogenosilanes and KOCN [12] or (via the cyanates) from the iodides and AgOCN [4], this new procedure provides a more convenient route to the bulky aminosilanes than that previously used [9,13]. Less sterically hindered silylisocyanates can be expected to undergo direct nucleophilic displacement and, indeed, the secondary organosilicon isocyanate TsiSiMeHNCO was found to undergo hydrolysis even in refluxing H_2O/MeCN to give the corresponding (known) silanol TsiSiMeH(OH) [14].

The reaction of $TsiSiMe_2NCO$ with 0.5 M NaOMe in 1/1 v/v $MeOH/CH_2Cl_2$ was briefly examined. It proceeded fairly slowly to give after 24 h of stirring at room temperature and aqueous work-up a solid that was shown by ^1H NMR spectroscopy and GLC-MS to contain unchanged isocyanate, $TsiSiMe_2NH_2$ and the urethane $TsiSiMe_2NHCOOMe$ in 35:25:40 ratio. The formation of the urethane presumably involves initial attack of the methoxide ion on the carbon at the isocyanate group in a mechanism similar to that proposed for the corresponding reactions of organic isocyanates [15]. The formation of aminosilane can be attributed to the hydrolysis of the initially formed urethane by aqueous NaOH during work-up to give the unstable carbamate ion, which undergoes spontaneous decarboxylation, as shown in Scheme 1. This assumption was confirmed by the absence of the aminosilane $TsiSiMe_2NH_2$ from the reaction mixture when the experiment was repeated but without addition of water during work-up. The solid isolated was shown by its ^1H NMR spectrum to contain only unchanged isocyanate and $TsiSiMe_2NHCOOMe$ in 40:60 ratio. TLC gave $TsiSiMe_2NHCO_2Me$ in 32% yield.

3. Experimental

The ^1H NMR spectra were recorded at 100 MHz on a JEOL FT-NMR spectrometer for solution in $CDCl_3$. The IR spectra were recorded as KBr pellets on a Perkin–Elmer 883 spectrophotometer. Mass spectra were obtained by electron impact at 70 eV. For gas–liquid chromatography a column of 12 m × 0.321 mm, HP-1 at 250 °C was used with a Pye Unicam GCG chromatograph. Kieselgel GF_{254} was used for TLC, with n-hexane as eluant. Elemental analyses were carried out by the Research Institute at the King Fahd University of Petroleum & Minerals. Melting points were determined with an 'Electrothermal' apparatus with samples in open tubes.

The following compounds were prepared by published methods: $TsiSiMe_2NCO$ [4], $TpsiSiMe_2NCO$ [5], $(Me_2Si)_2C(SiMePh_2)(SiMe_2NCO)$ [4] and $TsiSiMe_2NCS$ [8].

Methanol was refluxed over and distilled from $Mg(OMe)_2$ immediately before use. Methylene chloride was refluxed with $CaCl_2$ then distilled and kept over 4 Å molecular sieves. n-Hexane was stored over Na wire.

3.1. Attempted solvolysis of $TsiSiMe_2NCO$

(i) A solution of $TsiSiMe_2NCO$ (0.1 g, 0.3 mmol) in MeOH (10 cm^3) was stirred at room temperature for 24 h. Removal of the solvent on a rotary evaporator gave a white solid, which was shown by its ^1H NMR spectrum to be unchanged starting material.

(ii) The process described under (i) was repeated but in 5 vol.% H_2O/MeOH to give the same result.

3.2. Preparation of $TsiSiMe_2NH_2$

A mixture of $TsiSiMe_2NCO$ (0.5 g, 1.5 mmol), NaOH (1.6 g, 40 mol), MeOH (10 cm^3) and CH_2Cl_2 (10 cm^3) was stirred at room temperature for 24 h. Removal of the solvent under vacuum gave a solid, which was dissolved in a mixture of CCl_4/H_2O. The organic layer was separated, washed several times with water and dried ($MgSO_4$). Removal of the solvent on a rotary evaporator gave a white solid, which was recrystallized from MeOH to give $TsiSiMe_2NH_2$ (0.39 g, 85%), m.p. 296–297 °C (Lit. m.p. 296 °C [9]). ^1H NMR spectrum, δ ($CDCl_3$): 0.23 (27H, s) and 0.29 (6H, s). IR: 3680 w, 3480 w, 3405 m, 2980 s, 2960 s, 2890 s, 1540 m cm^{-1}. m/z 290 (70%, $[M-Me]^+$) 274 (33%, $[M-Me-NH_2]^+$) 202 (21), 186 (14), 130 (18), 93 (20) and 73 (100).

3.3. Preparation of $TpsiSiMe_2NH_2$

A mixture of $TpsiSiMe_2NCO$ (0.5 g, 0.97 mmol), NaOH (1.6 g, 40 mmol), MeOH (10 cm^3) and CH_2Cl_2 (10 cm^3) was stirred at room temperature for 24 h. Work-up as above gave a solid, which was recrystallized from MeOH to give $TpsiSiMe_2NH_2$ (0.43 g, 90%), m.p. 138 °C. δ_H ($CDCl_3$): 0.28 (6H, s, $SiMe_2NH_2$), 0.63 (18H, s, $SiMe_2Ph$) and 7.0–7.5 (15H, m, Ph). IR: 3480, 3410 w, 2980 s, 2960 s, 2895 s, 1540 m and 1430 s. m/z 491 (59%, $[M]^+$), 476 (44, $[M-Me]^+$), 414 (45), 381 (100), 326 (22), 309 (35) and 135 (70). Anal.

Found: C, 66.1; H, 8.5; N, 2.8. $C_{27}H_{41}Si_4N$ Calc.: C, 66.0; H, 8.4; N, 2.9%.

3.4. Preparation of $(Me_3Si)_2C(SiMePh_2)(SiMe_2NH_2)$

A mixture of $(Me_3Si)_2C(SiMePh_2)(SiMe_2NCO)$ (0.5 g, 1.1 mmol), NaOH (1.6 g, 40 mmol), MeOH (10 cm^3) and CH_2Cl_2 (10 cm^3) was stirred at room temperature for 24 h. Work-up as before gave a solid, which was recrystallized twice from MeOH to give $(Me_3Si)_2C(SiMePh_2)(SiMe_2NH_2)$ (0.41 g, 87%), m.p. 132 °C. δ_H ($CDCl_3$): 0.19 (6H, s, $SiMe_2NH_2$), 0.25 (18H, s, $SiMe_2$), 1.00 (3H, s, SiMe) and 7.2–8.0 (10H, m, Ph). IR: 3480 w, 3410 w, 2980 s, 2960 s, 2940 s, 2900 s, 1540 m and 1430 s. m/z 429 (28%, $[M]^+$), 414 (93, $[M-Me]^+$), 397 (85), 352 (100), 325 (380), 247 (51), 197 (38) and 135 (56). Anal. Found: C, 61.4; H, 9.1; N, 3.2. $C_{22}H_{39}Si_4N$ Calc.: C, 61.5; H, 9.1; N, 3.3%.

3.5. Attempted reactions of $TsiSiMe_2NCS$

A mixture of $TsiSiMe_2NCS$ (0.5 g, 0.94 mmol), NaOH (1.6 g, 40 mmol), MeOH (10 cm^3) and CH_2Cl_2 (10 cm^3) was stirred at room temperature for 24 h. The usual work-up gave a solid, which was shown by its ^1H NMR spectrum to be unchanged starting material.

3.6. Hydrolysis of TsiSiMeHNCO

A solution of TsiSiMeHNCO (0.2 g, 0.63 mmol) in a mixture of MeCN (9 cm^3) and H_2O (1 cm^3) was refluxed for 24 h. The solvent was evaporated off, and the residue was dissolved in CCl_4. The solvent was dried ($MgSO_4$) and evaporated to give a solid, which was recrystallized from hexane to give TsiSiMeH(OH) (0.16 g, 87%), m.p. 286 °C (Lit. m.p. 286 °C [14]). δ_H 0.24 (27H, s, Tsi), 0.42 (3H, d, $J = 3$ Hz, SiMeH) and 4.2 (1H, q, Si, H). ν(OH) 3690, ν(SiH) 2120 cm^{-1}.

3.7. Methanolysis of $TsiSiMe_2NCO$

(a) A 1 M solution of NaOMe in MeOH (5 cm^3) was added to a solution of $TsiSiMe_2NCO$ (0.2 g, 0.6 mmol) in CH_2Cl_2 (5 cm^3). The mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum to leave a solid, which was dissolved in a mixture of hexane (20 cm^3) and H_2O (20 cm^3). The organic layer was separated, dried ($MgSO_4$), and evaporated under vacuum to give a solid, which was shown by ^1H NMR spectrum and GLC-MS to be a ca. 35:25:40 mixture of $TsiSiMe_2NCO$, $TsiSiMe_2NH_2$ and $TsiSiMe_2NHCOOMe$. For this last compound: δ 0.28 (27H, s, Tsi), 0.52 (6H, s, $SiMe_2N$) and 3.63 (3H, s, OMe). m/z 348 (100, $[M-Me]^+$), 316 (65), 275 (8), 217 (10), 201 (47), 132 (6), 73 (80) and 59 (33).

(b) A 1 M solution of NaOMe (5 cm^3) was added to a solution of $TsiSiMe_2NCO$ (0.2 g, 0.6 mmol). The mixture was stirred at room temperature for 24 h. The solvent was then removed under vacuum and hexane was added to the residue. Filtration and removal of solvent gave a solid, which was shown from its ^1H NMR spectrum to be a mixture of starting material (40%) and $TsiSiMe_2NHCOOMe$ (60%). TLC gave $TsiSiMe_2NHCO_2Me$ (0.07 g, 32%), m.p. 263 °C. Anal. Found: C, 46.26; H, 10.19; N, 3.85. $C_{14}Si_4H_{37}NO_2$ Calc.: C, 46.28; H, 10.19; N, 3.86%.

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