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SOME PROPERTIES OF THE STERICALLY-HINDERED AMINOSILANE $(Me_3Si)_3CSiMe_2NH_2$

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Summary

The amine $(Me_3Si)_3CSiMe_2NH_2$ has been made by treatment of $(Me_3Si)_3CSiMe_2OClO_3$ with liquid ammonia. It is recovered unchanged from its solutions in methanol containing acid or base or in trifluoroacetic acid, and is unaffected by various diazotizing agents.

The hydrochloride $(Me_3Si)_3CSiMe_2NH_3Cl$ has a pK_a of 4.1 in ca. 42/58 v/v H_2O/THF at 20°C.

Introduction

Compounds of the type $(Me_3Si)_3CSiMe_2X$, containing the very bulky tris(trimethylsilyl)methyl group (the "trisyl" group, denoted below by Tsi), are known to be very resistant to attack of nucleophiles at the silicon atom of the Si—X bond [1], and in consequence methanolysis takes place readily by an ionization mechanism when X is an exceptionally good leaving groups such as $OClO_3$ [2] or OSO_2CF_3 [3] *. Since the Si—N bond is relatively weak, and should be even weaker when the amine is protonated and the possibility of $(p \rightarrow d)_\pi$ bonding removed, it seemed possible that the protonated NH_3^+ group would also be a sufficiently good leaving group to give rise to ready S_N1 solvolysis. We shall show below, however, that this is not the case.

Since there was not ready cleavage of the Si—N bond, it was possible to determine the base strength of the amine as measured by the pK_a of the hydrochloride $TsiSiMe_2NH_3Cl$ in aqueous tetrahydrofuran, and compare the results with those for other sterically hindered aminosilanes previously studied, viz. Me_3AdNEt_2 (1-diethylamino-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane), t-Bu_3SiNH_2 and t-Bu_3SiNMe_2 [4].

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* The probability that the much slower methanolysis of the iodide $TsiSiMe_2I$ also involves an S_N1 process is under investigation.

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The possibility of diazotizing $TsiSiNH_2$, and hence of generating a cation by loss of N_2^+, was also examined.

Results and discussion

The amino derivative $TsiSiMe_2NMe_2$ was previously made by treating the perchlorate $TsiSiMe_2OClO_3$ with $LiNMe_2/Me_2NH$ [5]. We found that the perchlorate readily reacted with liquid ammonia to give $TsiSiMe_2NH_2$.

$TsiSiMe_2OClO_3 + 2\ NH_3 \rightarrow TsiSiMe_2NH_2 + NH_4ClO_4$

The amine $TsiSiMe_2NH_2$ was recovered unchanged when its solution in methanol, alone or containing 0.12 M NaOMe, was refluxed for 24 h. Treatment of the amine with hydrogen chloride in pentane give the salt $TsiSiNH_3Cl$, and the same salt was obtained by treating the amine with methanolic hydrogen chloride and subsequently evaporating off the solvent. When a solution of this salt in MeOH was kept for 1 h at room temperature and the solvent then removed, the salt was recovered unchanged, while treatment of a solution of the salt in MeOH with aqueous NaOH gave the free amine. Similarly when $TsiSiMe_2NH_2$ was dissolved in MeOH containing CF_3CO_2H and the solvent and excess of acid evaporated off, the residue was the trifluoroacetate salt $TsiSiMe_2$-$NH_3[O_2CCF_3]$, containing no detectable amount of the methoxide $TsiSiMe_2OMe$. The fluoroacetate salt was also the sole product when a solution of the amine in anhydrous CF_3CO_2H was boiled under reflux for 65 h and the acid then evaporated off. It is evident that in the $TsiSiMe_2X$ species. NH_3^+ is a much poorer leaving group than ClO_4 in methanolysis and a much poorer leaving group than I in trifluoroacetolysis. (The iodide undergoes about 30% of trifluoroacetolysis in 18 h [6].)

Attempts to diazotize the amine failed. Thus (a) treatment with pentylnitrite in refluxing benzene [cf. 7] gave back the amine, while similar treatment but with additions of CH_3CO_2H, gave a mixture of the amine and the acetate salt; (b) treatment with concentrated hydrochloric acid and sodium nitrite gave only the hydrochloride, $TsiSiMe_2NH_3Cl$; and (c) treatment of a solution in CF_3CO_2H with aqueous sodium nitrite and subsequent addition of water gave only the trifluoroacetate salt, $TsiSiMe_2NH_3[O_2CCF_3]$. (We confirmed that under the conditions used in attempt (c), aniline, a base of comparable strength was converted into phenol.) It is impossible to say whether the resistance to diazotization is a property of the Si—NH_2 bond or arises in this case from steric hindrance.

We determined the pK_a for the hydrochloride $TsiSiMe_2NH_3Cl$ by the method used by Sommer et al. for $(t\text{-}Bu)_3SiNH_3Cl$ [4], involving measurement of the pH of a half neutralized solution of the amine in ca. 40/60 v/v H_2O/THF at 20°C. (In our measurements the H_2O/THF ratio was, in fact, closer to 42/58 v/v, as indicated in the Experimental section). We obtained a pK_a value of 4.1 for $TsiSiMe_2NH_3Cl$, compared with values of 3.75, 4.05, and 10.5, for *m*-toluidine, *p*-toluidine, and t-butylamine, respectively, determined under similar conditions. Thus the base strength of $TsiSiMe_2NH_2$ ($pK_B = 9.9$) is rather similar to that of *p*-toluidine and falls within the range observed for other hindered silylamines, viz. $t\text{-}Bu_3SiNH_2$ ($pK_B = 8.2$), Me_3AdNEt_2 ($pK_B = 8.3$), $t\text{-}Bu_3SiNHMe$

($pK_B = 9.4$) and t-Bu_3SiNMe_2 ($pK_B = 10.8$) [4].

It is known from various other measures that organosilylamines are weak bases, and this is usually attributed to $(p \rightarrow d)_\pi$ bonding between the nitrogen and silicon atoms [8]. It is not clear, however, to what extent the presence of the bulky substituents in, for example, the primary amines $TsiSiMe_2NH_2$ and t-Bu_3SiNH_2 affects the pK_B, probably mainly by steric inhibition of solvation of the protonated species, and it is possible that a simpler silylamine such as Me_3SiNH_2 would be significantly more basic.

Experimental

Preparation of $TsiSiMe_2NH_2$

A solution of $TsiSiMe_2OClO_3$ (0.26 g) in CH_2Cl_2 (1 cm^3) was added to liquid ammonia (10 cm^3) under nitrogen, and the mixture was stirred under a flow of nitrogen until all the ammonia had evaporated (ca. 1 h). The residue was extracted with pentane, and the pentane solution was evaporated. The residue was sublimed at reduced pressure to give $TsiSiMe_2NH_2$ (0.15 g; 75%), m.p. (in sealed tube) 296°C; ^1H NMR spectrum, δ (in CCl_4) 0.23 (s, 27 H), 0.29 ppm (s, 6 H); IR (in CCl_4), 3680w, 3480w, 3405m, 2980s, 2960s, 2890s, 1540m cm^{-1} (Found: C, 47.2; H, 11.3; N, 4.2. Calcd. for $C_{12}H_{35}NSi_4$: C, 47.2; H, 11.5; N, 4.6%).

Formation of $TsiSiMe_2NH_3Cl$ *and regeneration of* $TsiSiMe_2NH_2$

(a) Hydrogen chloride was bubbled through a solution of $TsiSiMe_2NH_2$ (0.12 g) in pentane (10 cm^3). A white precipitate immediately formed, and was judged to be the expected hydrochloride; ^1H NMR spectrum, δ (ppm, in CCl_4), 0.34 (s, 27 H), 0.67 (s, 6 H).

(b) Hydrochloric acid (0.6 cm^3 of 1 *M* solution) was shaken with a solution of $TsiSiMe_2NH_2$ (0.02 g) in pentane. The white precipitate was taken up in methanol, and evaporation of the methanol left $TsiSiSiMe_2NH_3Cl$, identical with that described under (a).

(c) $TsiSiMe_2NH_2$ was dissolved in an excess of hydrogen chloride in MeOH (0.2 *M*). The methanol was evaporated off with warming to leave pure $TsiSiNH_3Cl$.

(d) A sample of $TsiSiMe_2NH_3Cl$ was shaken with hexane and an equivalent amount of aqueous NaOH. The solid disappeared, and the hexane solution was separated and evaporated to give $TsiSiMe_2NH_2$ in >90% yield.

Attempted solvolysis of $TsiSiMe_2NH_2$

(a) A solution of $TsiSiMe_2NH_2$ (0.1 g) in MeOH (5 cm^3) was refluxed for 24 h. The methanol was evaporated off, to leave unchanged $TsiSiMe_2NH_2$, as indicated by the ^1H NMR spectrum.

(b) A solution of $TsiSiMe_2NH_2$ (0.1 g) in 0.20 *M* NaOMe in MeOH (5 cm^3) was refluxed for 24 h. The solvent was evaporated off, and the residue was extracted with pentane. The pentane solution was evaporated to dryness to leave only unchanged $TsiSiMe_2NH_2$.

(c) A solution of $TsiSiMe_2NH_3Cl$ in MeOH was set aside at room temperature for 1 week. The methanol was then evaporated off with warming. The residue was unchanged $TsiSiMe_2NH_3Cl$.

(d) A solution of $TsiSiMe_2NH_2$ in MeOH containing an excess of CF_3CO_2H (0.1 *M*) was evaporated to dryness with warming. The residue was exclusively $TsiSiMe_2NH_3[O_2CCF_3]$, $\delta(CCl_4)$ 0.30, (s, 27 H), 0.63 (s, 6 H) ppm; IR ν(CO) 1765 cm^{-1}.

(e) A solution of $TsiSiMe_2NH_2$ (0.1 mmol) in CF_3CO_2H (4 cm^3) was boiled under reflux for 65 h. The excess of the acid was then evaporated off to leave a solid which was shown by its IR and ^1H NMR spectra to be essentially pure $TsiSiMe_2NH_3[O_2CCF_3]$. Treatment with NaOH/MeOH followed by extraction with pentane and evaporation of the solvent gave back the starting amine.

Attempted diazotization of $TsiSiMe_2NH_2$

(a) A solution of $TsiSiMe_2NH_2$ (0.20 g, 0.65 mmol) and pentyl nitrite (0.10 g, 0.85 mmol) in benzene (3 cm^3) was refluxed for 4 h. Volatile material was removed by rotary evaporation, and the residue was shown to be unchanged $TsiSiMe_2NH_2$.

(b) The same procedure as in (a) was followed, except that 2 molar equivalents of glacial acetic acid were added in portions at intervals during the refluxing. The product was a ca. 1/1 mixture of the original amine and the acetate salt, $TsiSiNH_3[O_2CCH_3]$: $\delta(CCl_4)$ 0.28 (s, 27 H), 0.37 (s, 6 H) and 1.94 ppm (s, 3 H, O_2CCH_3).

(c) A cold solution of $NaNO_2$ (0.048 g, 0.85 mmol) in water (0.2 cm^3) was added to a mixture of $TsiSiMe_2NH_2$ (0.20 g, 0.65 mmol) and hydrochloric acid (0.13 ml of 12 *M* acid) at 0—4°C. The mixture was stirred for 1 h and then added to boiling MeOH. The solution was filtered, and the solvent removed, to leave $TsiSiMe_2NH_3Cl$ as the only organic product.

(d) Trifluoroacetic acid (0.28 g, 2.5 mmol) was added to $TsiSiMe_2NH_2$ (0.33 g, 1.1 mmol). A cold solution of $NaNO_2$ (0.83 g, 1.2 mmol) in water (1.0 cm^3) was added dropwise with stirring. Volatile material was evaporated off. The residue was extracted with CCl_4, and the solution shown by its ^1H NMR spectrum to contain only $TsiSiMe_2NH_3[O_2CCF_3]$; $\delta(CCl_4)$ 0.30 (s, 27 H) and 0.63 ppm (s, 6 H).

When aniline was treated similarly, phenol was obtained.

Measurement of pK_a *of* $TsiSiMe_2NH_3Cl$ *(cf. ref. 4).*

A sample of $TsiSiMe_2NH_2$ ($3—5 \times 10^{-4}$ mol) was carefully weighed into a 50 cm^3 volumetric flask, and 0.10 *M* aqueous hydrochloric acid needed for half neutralization was added. Sufficient 40/60 v/v H_2O/THF was added to make the total volume 50 cm^3. The pH of the solution at 20°C was determined with a glass electrode; the mean value from several determinations was 4.10, giving a pK_a of 4.10 for $TsiSiMe_2NH_3Cl$.

Similar measurements gave values of 3.75, 4.05 and 10.50 for the hydrochlorides of *m*-toluidine, *p*-toluidine, and *t*-butylamine, respectively.

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