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Note

Structural and electronic effects on the reactivity of carbamoylsilanes towards acrylonitrile addition

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Abstract

The effect of substituents on Si and N on $t_{1/2}$ values in the addition of carbamoylsilanes to acrylonitrile was explored. After examination of steric and structural parameters, the best correlation was found to be that rates increased with a decrease in the ionization potential of the carbamoylsilane.

Keywords: Carbamoylsilane; X-ray parameters; Ionization potential; Acrylonitrile

1. Introduction

We have previously reported on the ability to thermally add carbamoylsilanes **1d** and **1e** to a variety of electrophilically substituted alkenes (for example, acrylonitrile) to regioselectively form the corresponding adducts **2** [1]. An intriguing finding was that the rate of alkene addition, as measured by $t_{1/2}$ values, was faster for **1d** than for **1e**. Since this observation was contrary to simple expectations based on steric grounds, preliminary explanations for the rate disparity were advanced which involved the effect of silyl group substituents on either the ionization potential (IP) or geometry of **1d** and **1e**. The latter spoke to the possibility that compressional forces (between the silyl and amido groups) within the more crowded carbamoylsilane accelerated its conversion, by silyl group migration from carbon to oxygen, to a reactive radical cation or carbene form. Alteration of the structure of **1** is presented here as a way to further evaluate these hypotheses. Since we had also determined that the facility of **1d** or **1e** to add to an alkenic co-reactant depended on the electronegativity of alkenic substituents, expansion of the scope of the reaction to less activated alkenes might be possible if heightened reactivity in **1** could be introduced structurally .

2. Results and discussion

2.1. Synthesis

In order to address these questions, an expanded series of carbamoylsilanes has been prepared (**1a**–**1h**) bearing varied substituents on both silicon and nitrogen (Table 1). The ''parent'' species **1e** and **1g** were obtained as previously described by low-temperature metalation-(trimethyl)silylation of the corresponding *N*,*N*-dialkylformamide [2]. Attempts to access the minimally more crowded **1** ($R^1_3 = Et_3$; $R^2 = Me$) using chlorotriethylsilane failed to provide this carbamoylsilane in synthetically useful yields and purity. Also, although the trimethylsilyl analogue **1g** was easily produced from *N*,*N*-diisopropylformamide and chlorotrimethylsilane, no product resulted when the more crowded *N*-formyl-2,2,6,6-tetramethylpiperidine was employed. The other carbamoylsilanes were prepared by silyl group exchange using the appropriate silyl chloride and **1e** or **1g** neat at 100–140 °C [3]. However, we were unable to convert **1e** into its triisopropylsilyl (TIPS) analogue by using TIPS chloride, or **1g** into its TIPS analogue

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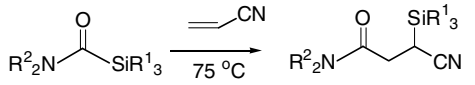
Table 1
Products **2** and half-lives of **1** in the reaction with acrylonitrile[a]



			$t_{1/2}$ (h)
1a	R^1_3 = Thexyl Me_2, R^2 = Me	**2a**	1.5
1b	R^1_3 = iBu$_3$, R^2 = Me	**2b**	2.2
1c	R^1_3 = Cumyl Me_2, R^2 = Me	**2c**	2.3
1d	R^1_3 = tBuMe$_2$, R^2 = Me	**2d**	3.6
1e	R^1_3 = Me_3, R^2 = Me	**2e**	5.5
1f	R^1_3 = PhMe$_2$, R^2 = Me	**2f**	7.3
1g	R^1_3 = Me_3, R^2 = iPr	**2g**	1.4
1h	R^1_3 = tBuMe$_2$, R^2 = iPr	**2h**	1.4

[a] In benzene-d_6 (0.2 M, 1:1.2 acrylonitrile:silane); toluene as internal standard; $t_{1/2}$ obtained by ^{1}H NMR measurements.

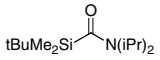
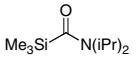
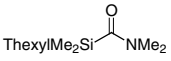
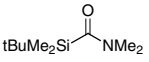
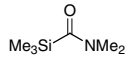
using either TIPS fluoride or TIPS trifluoromethanesulfonate. These experiments outline the steric borders of carbamoylsilane accessibility by these entry modes.

2.2. Results and discussion

An examination of the $t_{1/2}$ values (Table 1) exhibited by the series of *N*,*N*-dimethylcarbamoylsilanes (**1a**–**1f**) with a test alkene (acrylonitrile) at 75 °C indicates that the rate of addition generally increases with an increase in the steric requirements of the silyl group, as judged from a compilation of silyl group sizes [4]. The exception is **1f**, which may introduce new electrostatic effects due to the change to sp^2 hybridization of carbon at silicon. However, with this same entry aside, the expected stabilizing effects of a larger overall molecular structure on a radical cation would also be in concert with the data. This latter interpretation gains more credence when the rates of the *N*,*N*-diisopropyl carbamoylsilanes (**1g**, **1h**) are included in the comparison. While these faster rates (relative to that of **1e**) could also be consistent with an increased steric compression within **1g** and **1h** due to introduction of the isopropyl groups, the fact that $t_{1/2}$ values for both of these carbamoylsilanes are identical points to an explanation other than steric acceleration. X-ray crystallographic parameters (Table 2) determined for those carbamoylsilanes which were obtained as single crystals are also supportive of this conclusion. These indicate that changes in steric demands introduced by either the silyl group or the amido substituents have little, if any, effect on structural parameters and the concept of steric compression is seen not to correlate with differences in rates.

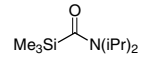
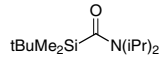
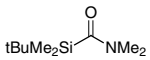
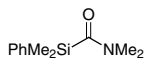
The first ionization potential (IP) of a carbamoylsilane would seem to be the most direct probe of its ability to transform into a radical cation. IP values for a selected series of carbamoylsilanes are presented in Table 3. The general trend in these values bolsters the supposition that

Table 3
Carbamoylsilane ionization potentials

Carbamoylsilane		$t_{1/2}$ (h)	IP (eV)[a]
1h		1.4	8.14
1g		1.4	8.25
1a		1.5	8.43
1d		3.6	8.47
1e		5.5	8.60

[a] ±0.02 eV.

Table 2
Crystallographic parameters for carbamoylsilanes[a]

Carbamoylsilane		$t_{1/2}$ (h)	Angle (°)			Bond length (Å)			Non-bonded distance (Å)		
			SiCN	SiCO	NCO	Si—C(O)	C=O	(O)C—N	SiN	SiO	ON
1g		1.4	124	115	122	1.94	1.24	1.35	2.91	2.70	2.27
1h		1.4	123	118	120	1.93	1.21	1.36	2.90	2.71	2.22
1d		3.6	126	114	120	1.93	1.24	1.35	2.94	2.69	2.25
1f		7.3	126	115	119	1.91	1.25	1.34	2.90	2.70	2.23

[a] The *s-cis* SiCNC dihedral angles are: **1h**, 1.5°; **1i**, 0.8°; **1d**, 1.3°; **1f**, 0.1°.

larger alkyl substitution in either the silyl or amido group leads to an increase in rate. It also supports the superiority of N-substitution over Si-substitution in this regard (**1g** vs. **1e**). However, the dependency of $t_{1/2}$ on IP is not exact between **1h** and **1g**, nor even approximate between **1a** and **1d**, and more subtle factors influencing reactivity must also be present. Nevertheless, these findings are in concert with a "collision-induced" SET process [5] in which collapse and reorganization of a transient radical cation–radical anion pair occurs within a solvent shell [1].

3. Experimental

3.1. General

Toluene and THF were distilled from sodium-benzophenone ketyl immediately before use. ^{1}H and ^{13}C NMR spectra were determined in C_6D_6 for **1** and in $CDCl_3$ for **2** at 11.75 T unless otherwise indicated. Deuterated NMR solvents were stored over 3 Å molecular sieves. IR spectra were determined on neat samples using an FT-IR spectrometer. Boiling points refer to distillation or kugelrohr oven temperatures, as indicated by procedures. All transfers of **1** were carried out by syringe and manipulations done under Ar.

α-Cumyldimethylchlorosilane was purchased from TCI America. **1d**, **1e**, **1g**, **2d**, and **2e** were prepared as previously described [1–3].

3.2. Preparations of *1*

A microdistillation apparatus equipped with a two-neck adapter bearing a flask and a Schlenk tube was flame dried under vacuum and refilled with Ar (3×). The pot was then charged with either **1e** or **1g** and the appropriate silyl chloride (1.2–1.5 molar excess) and heated at 100–150 °C (760 mm Hg) causing chlorotrimethylsilane to distill. When distillation ceased, the reaction was cooled to 25 °C and high vacuum established in the system. Distillation into the Schlenk tube afforded the exchanged carbamoylsilane.

3.2.1. N,N-Dimethylcarbamoyl(thexyl)dimethylsilane (*1a*)

A mixture of 1.9 g (13.1 mmol) of **1e** and 1.8 g (10.3 mmol) of (1,1,2-trimethylpropyl)(dimethyl)chlorosilane was stirred at 130 °C for 18 h to give 1.0 g (45%) of **1a**, bp 84 °C (0.1 mm Hg). IR: 1570 cm^{-1}. ^{1}H NMR: δ 2.77 (s, 3H), 2.64 (s, 3H), 1.84 (sept, $J = 7$ Hz, 1H), 1.08 (s, 6H), 0.98 (d, $J = 7$ Hz, 6H), 0.38 (s, 6H). ^{13}C NMR: δ 185.7, 36.5, 34.5, 32.4, 24.5, 21.3, 18.4, −1.6. Anal. Calcd. for $C_{11}H_{25}NOSi$: C, 61.33; H, 11.70; N, 6.50. Found: C, 61.23; H, 11.43; N, 6.75%.

3.2.2. N,N-Dimethylcarbamoyl(tri-isobutyl)silane (*1b*)

A mixture of 1.9 g (13.1 mmol) of **1e** and 2.0 g (18.5 mmol) of triisobutylchlorosilane was stirred at 100 °C for 72 h to give 1.4 g (62%) of **1b**, bp 98 °C (1 mm Hg). IR: 1576 cm^{-1}. ^{1}H NMR: δ 2.79 (s, 3H), 2.67 (s, 3H), 1.97 (m, 3H), 1.11 (d, $J = 7$ Hz, 18H), 1.01 (d, $J = 7$ Hz, 6H). ^{13}C NMR: δ 185.7, 36.5, 34.5, 32.4, 24.5, 21.3, 18.4, −1.6. Anal. Calcd. for $C_{15}H_{33}NOSi$: C, 66.35; H, 12.25; N, 5.16. Found: C, 66.35; H, 12.33; N, 5.07%.

3.2.3. N,N-Dimethylcarbamoyl(α-cumyl)dimethylsilane(*1c*)

A mixture of 1.5 g (10.0 mmol) of **1e** and 1.6 g (7.4 mmol) of (1-methyl-1-phenylethyl)(dimethyl)chlorosilane was stirred at 120 °C for 21 h to give 1.3 g (67%) of **1c**, bp 87 °C (0.05 mm Hg). IR: 1566 cm^{-1}. ^{1}H NMR: δ 7.1–7.3 (m, 5H), 2.71 (s, 3H), 2.00 (s, 3H), 1.55 (s, 6H), 0.30 (s, 6H). ^{13}C NMR(D_2CCl_2): δ 184.4, 148.0, 127.9, 126.2, 124.6, 36.2, 32.4, 27.2, 23.9, −3.8. Anal. Calcd. for $C_{14}H_{23}NOSi$: C, 67.42; H, 9.29; N, 5.62. Found: C, 67.16; H, 9.38; N, 5.59%.

3.2.4. N,N-Dimethylcarbamoyldimethyl(phenyl)silane (*1f*)

A mixture of 1.1 g (7.6 mmol) of **1e** and dimethyl(phenyl)chlorosilane (1.1 g, 6.3 mmol) was heated at 150 °C for 18 h to give 91 mg (69%) of **1f**, bp 82 °C (0.1 mm Hg). IR: 1567 cm^{-1}. ^{1}H NMR: δ 7.59 (m, 2 H), 7.27 (m, 3 H), 2.74 (s, 3 H), 2.44 (s, 3 H), 0.61 (s, 6 H). ^{13}C NMR: δ 184.0, 136.7, 133.8, 129.5, 128.2, 36.4, 32.2, −2.5. Anal. Calcd. for $C_{11}H_{17}NOSi$: C, 63.72; H, 8.26; N, 6.76. Found: C, 63.57; H, 8.21; N, 6.66%.

3.2.5. N,N-Diisopropylcarbamoyl(t-butyldimethyl)silane (*1h*)

A mixture of 1.2 g (5.8 mmol) of **1g** and *t*-butyldimethylchlorosilane (2.5 g, 16 mmol) was heated at 150 °C for 3 h to give 1.3 g of impure oil, bp 92 °C (0.5 mm Hg), which subsequently solidified. Recrystallization from dry pentane gave 0.98 g (69%) of **1h**, m.p. 73–75 °C. IR: 1565 cm^{-1}. ^{1}H NMR: δ 4.01 (sept, $J = 7$ Hz, 1 H), 3.09 (sept, $J = 7$ Hz, 1 H), 1.61 (d, $J = 7$ Hz, 6 H), 1.16 (s, 9 H), 1.00 (d, $J = 7$ Hz, 6 H), 0.34 (s, 6 H). ^{13}C NMR: δ 185.4, 48.6, 45.9, 27.0, 21.1, 20.9, 17.2, −4.0. Anal. Calcd. for $C_{13}H_{29}NOSi$: C, 64.13; H, 12.01; N, 5.75. Found: C, 64.13; H, 11.95; N, 6.03%.

3.3. Half-life experiments and formation of *2*

An NMR tube was treated with bis(trimethylsilyl)acetamide, washed with toluene and evacuated in the entry chamber of a dry box. In the dry box, the tube was charged with 0.12 mmol of the appropriate **1**, 0.5 mL of C_6D_6, 0.10 mmol of acrylonitrile and 0.10 mmol of toluene as internal standard. The reaction progress was monitored at 75 °C in the bore of an 11.75 T NMR spectrometer. The rate of disappearance of acrylonitrile was followed for $t_{1/2}$ determinations. In several instances, the rates of disappearance of **1** and the appearance of **2** were also followed and were seen to parallel the rate of acrylonitrile disappearance. After the reaction was complete, the addition product was isolated by kugelrohr distillation or chromatography on Florisil (hexane–EtOAc). When needed, larger amounts of **2** were obtained by conducting the reaction at 100 °C in a sealed one-piece reaction ampuole with Teflon screw

valve and side arm using toluene (2.5 mL), acrylonitrile (0.5 mmol), and 0.6 mmol of carbamoylsilane **1**.

*3.3.1. N,N-Dimethyl-3-cyano-3-(thexyldimethylsilyl)propanamide (**2a**)*

B.p. 202 °C (0.05 mm Hg). IR: 2224, 1651 cm^{-1}. ^1H NMR (4.7T): δ 3.06 (s, 3H), 3.03 (s, 3H), 2.71 (m, 2H), 2.46 (m, 1H), 1.75 (m, 1H), 1.03 (s, 3H), 0.99 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H), 0.31 (s, 3H), 0.17 (s, 3H). ^{13}C NMR: δ 169.5, 122.8, 37.1, 35.9, 34.5, 31.6, 24.4, 21.1, 20.8, 18.6, 18.3, 12.4, −4.7, −4.8. Anal. Calcd. for $C_{14}H_{28}N_2OSi$: C, 62.63; H, 10.51; N, 10.43. Found: C, 62.46; H, 10.60; N, 10.55%.

*3.3.2. N,N-Dimethyl-3-cyano-3-(triisobutylsilyl)propanamide (**2b**)*

B.p. 200 °C (0.5 mm Hg). IR: 2223, 1655 cm^{-1}. ^1H NMR: δ 3.06 (s, 3H), 3.02 (s, 3H), 2.74 (dd, $J = 16$ Hz, 11 Hz, 1H), 2.63 (dd, $J = 11$ Hz, 4 Hz, 1H), 2.35 (dd, $J = 16$ Hz, 4 Hz, 1 H), 1.89 (m, 3H), 1.01 (m, 18H), 0.79 (d, $J = 7$ Hz, 6H). ^{13}C NMR: δ 169.6, 122.5, 37.1, 35.9, 30.8, 26.6, 24.5, 23.0, 13.3. Anal. Calcd. for $C_{18}H_{36}N_2OSi$: C, 66.61; H, 11.18; N, 8.63. Found: C, 66.37; H, 11.13; N, 8.47%.

*3.3.3. N,N-Dimethyl-3-cyano-3-(cumyldimethylsilyl)-propanamide (**2c**)*

B.p. 225 °C (0.05 mm Hg). IR: 2224, 1655 cm^{-1}. ^1H NMR: δ 7.2–7.4 (m, 5H), 2.92 (s, 3H), 2.75 (s, 3H), 2.49 (dd, $J = 10$ Hz, 3 Hz, 1H), 2.16 (dd, $J = 17$ Hz, 10 Hz, 1H), 1.69 (dd, $J = 17$ Hz, 3 Hz, 1H), 1.54 (s, 3H), 1.49 (s, 3H), 0.27 (s, 3 H), 0.17 (s, 3H). ^{13}C NMR: δ 169.3, 147.2, 128.4, 126.2, 125.2, 122.4, 36.7, 35.8, 30.8, 27.5, 24.5, 24.3, 11.7, −6.2, −6.4. Anal. Calcd. for $C_{17}H_{26}N_2OSi$: C, 67.50; H, 8.66; N, 9.26. Found: C, 67.43; H, 8.67; N, 9.34%.

*3.3.4. N,N-Dimethyl-3-cyano-3-(phenyldimethylsilyl)-propanamide (**2f**)*

B.p. 230 °C (0.05 mm Hg). IR: 2224, 1649 cm^{-1}. ^1H NMR (4.7T): δ 7.60 (m, 2H), 7.46 (m, 3H), 2.95 (s, 3H), 2.91 (s, 3H), 2.76 (dd, $J = 9$ Hz, 4 Hz, 1H), 2.61 (dd, $J = 19$ Hz, 9 Hz, 1H), 2.32 (dd, $J = 19$ Hz, 4 Hz, 1H), 0.58 (s, 3H), 0.56 (s, 3H). ^{13}C NMR (4.7T): δ 169.2, 133.9, 133.6, 130.3, 128.2, 122.0, 36.9, 35.8, 30.9, 14.4, −4.3, −4.8. Anal. Calcd. for $C_{14}H_{20}N_2OSi$: C, 64.57; H, 7.74; N, 10.76. Found: C, 64.36; H, 7.44; N, 10.80%.

*3.3.5. N,N-Diisopropyl-3-cyano-3-(trimethylsilyl)-propanamide (**2g**)*

B.p. 142 °C (12 mm Hg). IR: 2222, 1640 cm^{-1}. ^1H NMR (C_6D_6): δ 3.41 (m, 1H), 3.14 (m, 1H), 2.74 (t, $J = 7$ Hz, 1H), 2.41 (dd, $J = 16$ Hz, 6 Hz, 1H), 2.21 (dd, $J = 16$ Hz, 7 Hz, 1H), 1.49 (d, $J = 6$ Hz, 3H), 1.45 (d, $J = 6$ Hz, 3H), 0.83 (d, $J = 6$ Hz, 3H), 0.80 (d, $J = 6$ Hz, 3H), 0.15 (s, 9H). ^{13}C NMR (C_6D_6): δ 167.0, 121.9, 47.8, 45.8, 32.5, 20.4, 13.9, −3.0. Anal. Calcd. for $C_{13}H_{26}N_2OSi$: C, 61.36; H, 10.30; N, 11.01. Found: C, 61.39; H, 10.45; N, 10.68%.

*3.3.6. N,N-Diisopropyl-3-cyano-3-(t-butyldimethylsilyl)-propanamide (**2h**)*

B.p. 141 °C (3 mm Hg). IR: 2224, 1649 cm^{-1}. ^1H NMR(C_6D_6): δ 3.47 (m, 1H), 3.17 (m, 1H), 3.00 (t, $J = 6$ Hz, 1H), 2.49 (dd, $J = 16$ Hz, 6 Hz, 1H), 2.31 (dd, $J = 16$ Hz, 6 Hz, 1H), 1.50 (d, $J = 6$ Hz, 3H), 1.46 (d, $J = 6$ Hz, 3H), 1.04 (s, 9H), 0.86 (d, $J = 6$ Hz, 3H), 0.83 (d, $J = 6$ Hz, 3 H), 0.29 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (C_6D_6): δ 167.2, 122.5, 47.8, 45.8, 33.0, 26.5, 20.4, 17.3, 10.6, −7.17, −7.15. Anal. Calcd. for $C_{16}H_{32}N_2OSi$: C, 64.81; H, 10.88; N, 9.45. Found: C, 64.76; H, 10.93; N, 9.63%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 295972 (**1d**), 295973 (**1f**), 295974 (**1g**), and 295975 (**1h**). Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, or by e-mail: deposit@ccdc.ac.uk or at http://www.ccdc.ac.uk.

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References

[1] R.F. Cunico, A.R. Motta, Org. Lett. 7 (2005) 771–774.
[2] R.F. Cunico, J. Chen, Synth. Commun. 33 (2003) 1963–1968.
[3] R.F. Cunico, Tetrahedron Lett. 42 (2001) 1423–1425, We have determined that the use of CsF in these exchanges is superfluous.
[4] J.R. Hwu, S. Tsay, B. Cheng, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organosilicon Compounds, vol. 2, Wiley, Chichester, 1998 (Pt 1, Chapter 8).
[5] For a discussion, see: R. Rathore, J.K. Kochi, Adv. Phys. Org. Chem. 35 (2000) 193–318.