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STRUCTURE AND DYNAMICS OF t-BUTYLDIMETHYLSILYL AMIDES

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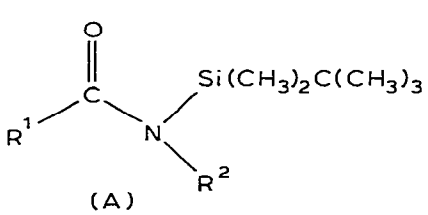
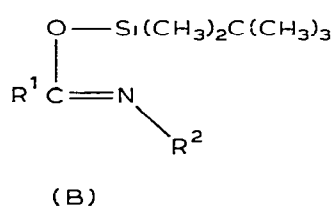
Summary

A series of *N*-alkyl- and *N*-aryl-t-butyldimethylsilyl amides have been prepared by amination and their structures determined by IR and NMR spectroscopy. Like their trimethylsilyl counterparts, the *N*-alkyl derivatives exist as amides while the *N*-aryl derivates exist as amide/imidate mixtures. The percentage of imidate and the free energies of activation for the imidate/amide exchange in the aryl derivatives are greater than those in the trimethylsilyl derivatives. The barriers to rotation in the amide form of the aryl derivatives are similar to those of the trimethylsilyl derivatives. The barrier for rotation in t-butyldimethylsilyl-*N*-methyl formamide, however, is lower than that of the trimethylsilyl derivative. Isomer ratios and free energies of activation are rationalized in terms of the steric effect of the t-butyl group.

The effects of substituents at the carbonyl carbon and nitrogen on the structure and dynamics of trimethylsilyl amides have been systematically explored [1—5]. Until recently, when a series of bis(trialkylsilyl) and bis(alkylarylsilyl) amides were prepared and studied [6], the substituents on the silicon atom had been limited to the methyl group. Attempts to prepare amides with halomethyl groups on silicon resulted in substitution at the halomethyl group [7]. The present investigation explores the effect of the large, non-reactive t-butyl substituent on the structure and dynamics of t-butyldimethylsilyl amides. Like their trimethylsilyl analogs, these compounds can exist in either the amide (A) or imidate (B) forms or as mixtures of both forms.



(A)



(B)

TABLE 1

ACTIVATION PARAMETERS FOR EXCHANGE AND ROTATION OF $R^1CONR^2Si(CH_3)_2X$]

R^1	R^2	X = $C(CH_3)_3$					X = CH_3		
		T_c(K) [b]	$\Delta\nu$(Hz) [c]	P_a [a]	$\Delta G^{\neq}_{a\rightarrow b}$ (kcal/mol)	$\Delta G^{\neq}_{b\rightarrow a}$	P_a	$\Delta G^{\neq}_{a\rightarrow b}$	$\Delta G^{\neq}_{b\rightarrow a}$
Exchange									
H	C_6H_5	353	19.4	0.81	19.8	18.7	0.47	19.3	19.4
H	C_6H_4Cl	362	18.1	0.84	19.7	18.6	0.63	19.3	18.9
H	$C_6H_4OCH_3$	367	17.7	0.65	19.4	19.0	0.23	18.8	19.6
CH_3	C_6H_5	313	27.6	0.88	17.0	15.8	0.48	15.8	15.8
Rotation									
H	CH_3	323	8.5	0.93	17.1	18.7	0.87	18.5	19.8
H	C_6H_5	313	15.2	0.78	16.2	17.0	0.81	15.8	16.6
H	C_6H_4Cl	323	15.2	0.85	16.9	18.0	0.71	15.8	16.3
H	$C_6H_4OCH_3$	315	16.9	0.78	16.2	17.0	0.74	16.1	16.8

[a] For exchange P_a is population of imidate form; for rotation P_a represents population of major rotamer. [b] Coalescence temperature. [c] $\Delta\nu$ extrapolated from low temperature values (by least squares) to T_c.

Experimental

All reagents and glassware were dried and reactions were carried out in a nitrogen atmosphere. The compounds were prepared by amination of t-butyldimethylchlorosilane with the appropriate amide in the presence of triethylamine in equal molar ratios. Solvents used in the preparation and reflux times following addition are given in parentheses. $R^1CONR^2[Si(CH_3)_2C(CH_3)_3]$: I, R^1 = H, R^2 = CH_3(C_6H_6, 2 h), b.p. 80—85°C/9 mmHg, m.p. 54—56°C, 67% yield (Found: C, 54.89; H, 10.64. $C_{18}H_{19}NOSi$ calcd.: C, 55.42; H, 11.07%). II, R^1 = H, R^2 = C_6H_5 (C_6H_6, 18 h), b.p. 142°C/17 mmHg, 83% yield (Found: C, 66.19; H, 8.87. $C_{13}H_{21}NOSi$ calcd.: C, 66.31; H, 9.01%). III, R^1 = H, R^2 = C_6H_4Cl (C_6H_6, 18 h), b.p. 172°C/19 mmHg, 15% yield (Found: C, 57.82; H, 7.42. $C_{13}H_{20}NOSiCl$ calcd.: C, 57.86, H, 7.48%). IV, R^1 = H, R^2 = $C_6H_4OCH_3$ (THF, 6 h) b.p. 175°C/18 mmHg, 75% yield (Found: C, 63.58; H, 9.02. $C_{14}H_{23}NO_2Si$ calcd.: C, 63,34; H, 8.75%). V, R^1 = CH_3, R^2 = H (dioxane, 24 h), b.p. 105—110°C/14 mmHg, m.p. 57—60°C, yield 44% (Found: C, 55.76; H, 11.15. $C_8H_{19}NOSi$ calcd.: C, 55.42; H, 11.07%). VI, R^1 = CH_3, R^2 = C_6H_5 (C_6H_6, 8 h) b.p. 132°C/12 mmHg, 65% yield (Found: C, 67,76; H, 9,39. $C_{14}H_{23}NOSi$ calcd.: C, 67.40; H, 9.31%).

Infrared spectra were run on a Perkin—Elmer 621 spectrophotometer. NMR spectra were obtained on a 90 MHz Perkin—Elmer R-32 spectrometer. Isomer ratios and free energies of activation were determined by the method described previously [1].

Results and discussion

Both *N*-alkyl- and *N*-aryl-t-butyldimethylsilyl amides were prepared by amination in moderate to good yields. Several attempts to prepare bis(t-butyldimethylsilyl)acetamide using dioxane and triethylamine as solvents with reflux times up to 48 h produced only the mono derivative V.

The NMR spectrum of t-butyldimethylsilyl-*N*-methylformamide (I) at 20°C in ClC_6H_5 contains a doublet (*J* 0.7 Hz) at 2.4 ppm and a much less intense, broad singlet at 2.5 ppm in the *N*-methyl region. In the t-butyl region, a singlet appears at 0.6 ppm with a smaller singlet at 0.8 ppm while in the $Si(CH_3)_2$ region singlets appear at 0.01 and 0.1 ppm. At ca. 50°C the two peaks in each region coalesce to a single peak. The number of peaks in each region and their temperature dependent behavior is similar to that of trimethylsilyl-*N*-methyl formamide which exists in the amide form [5]. The free energies of activation for the coalescence as calculated by the method of Shanan-Atidi and Bar-Eli [8] were about 1 kcal/mol lower than those determined previously for the trimethylsilyl analog [5]. Because an increase in size of the nitrogen substituent on *N*-methyl formamides generally results in a decrease in the rotational barrier [9], both the NMR pattern and the free energies of activation are consistent with the existence of rotational isomers in the amide form of I. The infrared spectrum of I, which contains peaks at 1650 and 984 cm^{-1} (both with shoulders) attributable to C=O and Si—N vibrations respectively, also supports the amide structure.

The conformations of the rotamers for I can be assigned on the basis of the generally larger *trans* proton—proton coupling [9]. Thus, the major isomer

which displays the larger HC(O)NCH coupling ($N—CH_3$ doublet) has the formyl proton and *N*-methyl group in the *trans* orientation and the t-butyldimethylsilyl group is therefore *cis* to the carbonyl. The same conformation has been assigned to the major rotamer of trimethylsilyl-*N*-methylformamide [5].

The NMR spectra of the formanilides (II—IV) contain three peaks in the t-butyl and $Si(CH_3)_2$ regions at low temperatures (<10° C). As the temperature is increased the small upfield peak in the t-butyl region coalesces with the lowest field singlet and in the dimethylsilyl region the small upfield peak coalesces with the middle peak. When the temperature is raised to over 95° C, the two peaks in each region coalesce to single t-butyl and $Si(CH_3)_2$ peaks. Hence, there are two coalescences that almost certainly correspond to rotational averaging (at low temperatures) and exchange of the t-butyldimethylsilyl group between amide and imidate forms at higher temperatures. Since the highest and lowest field peaks in the t-butyl region are due to rotamers the middle peak corresponds to the imidate form. In the $Si(CH_3)_2$ region the lowest field peak can be assigned to the imidate form. The populations (Table 1) of the amide and imidate forms and the rotamers show the same dependence on substituent observed previously for the trimethylsilyl formanilides [1]. On the basis of the differential shifts [9] of the rotamer peaks in chlorobenzene the higher field rotamer peak was attributed to the rotamer with the t-butyldimethylsilyl group *trans* to the carbonyl. The major rotamer therefore has the organometallic group *cis* to the carbonyl, consistent with the conformational assignments for the trimethylsilyl derivatives [1].

The NMR spectral behavior of t-butyldimethylsilyl acetanilide and acetamide also parallel the behavior of the trimethylsilyl analogs. The acetanilide exhibits two peaks in the t-butyl and $Si(CH_3)_2$ regions below 40° C due to the amide and imidate forms. No further splitting is observed down to —30° C presumably because of the 100% population of the *cis* rotamer. The NMR spectrum of the acetamide shows no temperature dependent behavior down to —30° C which is probably a result of the existence on only the *cis* rotamer as observed also for the trimethylsilyl derivative [5].

The activation parameters for the t-butyldimethylsilyl dervatives are compared with those of the trimethylsilyl derivatives in Table 1. Of interest there is the greater abundance of the imidate form in the t-butyl derivatives. Space-filling models indicate considerably greater repulsions in the amide form of the t-butyl derivatives and this spatial effect probably accounts for the greater population of imidate form in these derivatives. If the transition state for the intramolecular exchange [1] of silyl groups from imidate to amide is assumed to involve bonding of the silicon to both nitrogen and oxygen (and to have therefore some amide character) the same steric repulsions in the transition state would account for the slightly higher $\Delta G^{\ddagger}_{a\rightarrow b}$ values for the t-butyl derivatives.

For rotation, on the other hand, the populations and free energies for the t-butyldimethylsilyl- and trimethylsilyl-formanilide analogs are similar. The insensitivity of the rotational barrier to size of substituent has been previously documented for *N*-alkyl-*N*-methylformanilides [10]. For the *N*-methylformamide derivatives, however, the t-butyl derivative definitely has the lower barrier to rotation. A similar size effect is found in *N*-alkyl-*N*-methyl formamides [9].

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