Journal of Organometallic Chemistry 492 (1995) 129-133

A multinuclear NMR study of *N*-(chlorodimethylsilylmethyl) amides

Claude H. Yoder [a,*], Wendy D. Smith [a], Beth L. Buckwalter [a], Charles D. Schaeffer, Jr. [b,*], Kelly J. Sullivan [b], Monica F. Lehman [b]

[a] *Department of Chemistry, Franklin and Marshall College, Lancaster, PA 17604, USA*
[b] *Department of Chemistry, Elizabethtown College, Elizabethtown, PA 17022, USA*

Received 10 June 1994; in revised form 26 October 1994

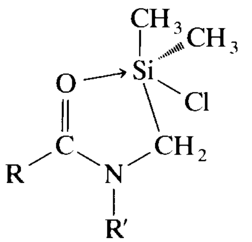
Abstract

A series of *N*-(chlorodimethylsilylmethyl) amides of the type RCONR'($CH_2Si(CH_3)_2Cl$), where R = H, R' = CH_3; R = CH_3, R' = CH_3; R = H, R' = C_6H_5; and R = CH_3, R' = *p*-XC_6H_4 (X = H, OCH_3, Cl, Br, CF_3, NO_2) were prepared by amination or transsilylation. The ^1H, ^{13}C, ^{14}N, ^{17}O, and ^{29}Si NMR spectra were obtained and used to determine the structure of the compounds. The ^{14}N and ^{17}O shifts are indicative of the amide structure reported previously. The ^{17}O and ^{29}Si shifts can be related to the extent of dative interaction between the carbonyl oxygen and the silicon and correlate with the carbonyl stretching frequencies. The ^1H spectra of most of the acetanilides in $CDCl_3$ contain a broad peak for the $Si(CH_3)_2$ protons. At lower temperatures this peak separates into two sharp peaks of unequal intensities. The two peaks can be attributed to rotamers, with the large peak at higher frequencies being due to the rotamer with the $CH_2Si(CH_3)_2Cl$ group *cis* to the carbonyl oxygen. In toluene, CH_2Cl_2 and THF, the $Si(CH_3)_2$ protons appear as a sharp peak which does not broaden upon heating to the boiling point of the solvent. The free energies of activation for rotation about the carbon–nitrogen bond were determined by the approximate method of Shanan-Atidi and Bar-Eli and show a rough correlation with the sigma constant of the substituent.

Keywords: Silicon; NMR; Group 14; Amide; Carbon-13; Rotamers

1. Introduction

Amides containing the $CH_2Si(CH_3)_2Cl$ group were first reported by Kowalski and Lasocki [1] and the structure of the bisacetamide was determined by Onan et al. [2]. Later work on formamides, acetamides, formanilides, and acetanilides used similarities in infrared carbonyl stretching frequencies and proton NMR chemical shifts to assign the amide structure to these compounds [3,4]. The compounds are solids, as opposed to the aliphatic *N*-trimethylsilyl derivatives which are generally liquids, and have considerable dative bonding between the carbonyl oxygen and silicon, thereby making the silicon hypervalent.



Recent review articles [5–7] summarize extensive studies of similar derivatives.

We have previously found that the ^{14}N and ^{17}O shifts can be used to easily distinguish between the amide and imidate form of trimethylsilyl "amides". We have now examined the proton, ^{13}C, ^{14}N, ^{17}O, and ^{29}Si spectra of a series of aliphatic and aromatic derivatives containing the $CH_2Si(CH_3)_2Cl$ group in an attempt to further define the bonding and structure of these derivatives.

---

[*] Corresponding authors.

SSDI 0022-328X(94)05297-2

2. Experimental section

2.1. Compounds

All synthetic manipulations were conducted under an atmosphere of argon or nitrogen in glassware that was oven-dried at 110 °C for at least one hour. Filtrations were performed in a glove bag. n-Butyllithium (2.5 M) solution in hexanes, chloromethyldimethylchlorosilane (CMDS), and starting organic amides were purchased commercially and were used without further purification. Solvents were dried by storage over sodium wire and were degassed prior to use. Tetrahydrofuran (THF) was distilled from calcium hydride under an argon atmosphere and stored over molecular sieves prior to use. Vacuum distillations were performed on either a 6-inch jacketed vigreux column or a straight column packed with glass beads or helices and surmounted with an Ace Mini-Lab® distillation head. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Carbon and hydrogen combustion analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Purity of all compounds probably exceeded 95% as indicated by the absence of spurious signals in all NMR spectra.

Amination reactions were carried out in essentially quantitative yields by adding CMDS dropwise and with magnetic stirring to a mixture of the appropriate amide and triethylamine (equimolar ratios) in *n*-hexane or THF according to published procedures [2–4]. The exothermic addition was followed by several hours of stirring at room temperature, filtration of the precipitated triethylamine hydrochloride, and solvent removal at atmospheric pressure. Crude solid products were dissolved in warm toluene and were filtered to remove any remaining undissolved material. Several milliliters of *n*-hexane were added until the filtrate became cloudy, and this solution was refrigerated at 0 °C. White crystals normally formed within three days, and these were dried under high vacuum. Substituted acetanilides were obtained according to this procedure.

N-(Chlorodimethylsilylmethyl)acetanilides: *p*-H, m.p. 98–100 °C (lit. [3] m.p. 97–99 °C); *p*-OCH_3, m.p. 97–99 °C. (Anal. Found: C, 52.79; H, 6.72. $C_{12}H_{18}ClNO_2Si$ calc.: C, 53.02; H, 6.68%.); *p*-Cl, m.p. 126.5–129 °C. (Anal. Found: C, 49.17; H, 5.47. $C_{11}H_{15}Cl_2NOSi$ calc.: C, 47.83; H, 5.47%.); *p*-Br, m.p. 141–144 °C. (Anal. Found: C, 41.57; H, 4.91. $C_{11}H_{15}BrClNOSi$ calc.: C, 41.20; H, 4.72%.); *p*-CF_3, m.p. 95–97 °C. (Anal. Found: C, 46.95; H, 5.04. $C_{12}H_{15}ClF_3NOSi$ calc.: C, 46.53; H, 4.88%.); *p*-NO_2, m.p. 152.5–154 °C. (Anal. Found: C, 47.01; H, 5.50. $C_{11}H_{15}ClN_2O_3Si$ Calc.: C, 46.07; H, 5.27%).

N-(Chlorodimethylsilylmethyl)-*N*-methylformamide was prepared by amination of *N*-methylformamide in the presence of triethylamine using a procedure similar to that employed for the acetanilides. This product was purified by vacuum distillation of the solid remaining after solvent removal: b.p. 63–65 °C/0.05 Torr (lit. [3] b.p. 76–78 °C/0.16 Torr). *N*-(Chlorodimethylsilylmethyl)formanilide was secured in a similar fashion from formanilide: b.p. 82–85 °C/0.01 Torr (lit. [3] b.p. 110 °C/0.05 Torr). Equimolar amounts of CMDS and *N*-trimethylsilyl-*N*-methylacetamide (from United Chemical Technologies; formerly, Hüls of America Inc.) reacted in *n*-hexane to form the white transsilylation product *N*-(chlorodimethylsilylmethyl)-*N*-methylacetamide [3], which was purified by washing with *n*-hexane. Physical properties for these latter derivatives are in close agreement with literature values.

2.2. NMR measurements

Proton spectra for routine identification were recorded on a Varian EM-360A spectrometer operat-

Table 1
Proton and carbon-13 NMR chemical shifts for $RCONR'(CH_2Si(CH_3)_2Cl$ [a]

Compound		$\delta(^1H)$				$\delta(^{13}C)$				
R	R′	CH_2	$SiCH_3$	R	R′	CO	CH_2	CH_3	$SiCH_3$	R′ [b]
H	CH_3	2.53	0.48	7.75	2.99	163.5	40.0		6.1	36.7
H	C_6H_5	3.15	0.73	8.33	7.22–7.47	162.7	39.8		5.8	140.1, 121.6, 129.6, 127.3
CH_3	CH_3	2.65	0.37	2.01	2.99	173.2	43.9	16.9	6.5	37.0
CH_3	C_6H_5	3.05	0.68	1.87	7.05–7.42	173.8	45.9	18.2	6.7	140.3, 125.4, 129.9, 128.7
CH_3	$C_6H_4OCH_3$	3.07	0.64	1.92	6.90–7.09 [c]	173.6	46.0	18.0	6.9	132.8, 126.5, 114.8, 159.2 [d]
CH_3	C_6H_4Cl	3.07	0.65	1.95	7.12–7.44	173.3	45.8	18.4	6.8	139.0, 127.0, 130.1, 134.5
CH_3	C_6H_4Br	3.06	0.65	1.93	7.05–7.56	173.2	45.7	18.4	6.7	139.5, 127.3, 133.1, 122.4
CH_3	$C_6H_4CF_3$	3.11	0.66	1.98	7.24–7.75	173.2	45.7	18.7	6.8	143.9, 126.4, 127.2, 130.9 [e]
CH_3	$C_6H_4NO_2$	3.12	0.67	2.01	7.24–8.35	173.0	45.6	19.1	6.6	146.4, 127.0 125.5, 147.3

[a] Chemical shifts are in ppm relative to external TMS in $CDCl_3$ (±0.05 ppm for proton; ±0.1 ppm for carbon-13).

[b] Aryl carbon shifts are listed in the order: C(1), C(2,6), C(3,5), and (C4). C(1) is the carbon atom attached to nitrogen.

[c] $\delta(^1H)$ OCH_3, 3.80 ppm.

[d] $\delta(^{13}C)$ OCH_3, 55.2 ppm.

[e] $\delta(^{13}C)$ CF_3, 123.3 ppm; $|^1J(^{19}F-^{13}C)|$, 272.2 Hz; $|^2J(^{19}F-^{13}C)|$, 33.0 Hz.

Table 2
Nitrogen-14, oxygen-17 and silicon-29 NMR chemical shifts for $RCONR'(CH_2Si(CH_3)_2Cl)$ [a]

Compound		$\delta(^{14}N)$	$\delta(^{17}O)$	$\delta(^{29}Si)$
R	R'			
H	CH_3	−255	274	−19.8
H	C_6H_5	−236	305	−9.5
CH_3	CH_3	−252	258	−37.6
CH_3	C_6H_5	−235	– [b]	−34.1
CH_3	$C_6H_4OCH_3$	−234	340 [c]	−34.0
CH_3	C_6H_4Cl	−245	340	−30.7
CH_3	C_6H_4Br	−240	– [b]	−31.1
CH_3	$C_6H_4CF_3$	−250	340	−29.0
CH_3	$C_6H_4NO_2$	−250 (vb) [d]	340 [e]	−26.9

[a] Chemical shifts in $CDCl_3$ are in ppm relative to NO_3^- for ^{14}N, D_2O for ^{17}O, and TMS for ^{29}Si (all external). ^{14}N and ^{17}O, ±1 ppm; ^{29}Si, ±0.5 ppm. Vb, very broad.

[b] Not observed or determined.

[c] $\delta(^{17}O)$ OCH_3, not determined.

[d] $\delta(^{14}N)$ NO_2, −12 ppm.

[e] $\delta(^{17}O)$ NO_2, 537 ppm.

ing at 60 MHz. All other NMR spectra were obtained on a Varian UNITY 300 MHz instrument. Gated decoupling with no nuclear Overhauser effect was used for all nuclei. Spectra were obtained with a coaxial inner tube containing the appropriate reference compound. Chemical shift reference compounds (all external) were tetramethylsilane (TMS) for proton, ^{13}C and ^{29}Si spectra; aqueous ammonium nitrate (NO_3^-) for ^{14}N; and deuterium oxide for ^{17}O. Spectra were normally recorded as saturated solutions in deuterochloroform, which also served as the spectrometer lock material. Variable-temperature ^{13}C spectra were recorded on the Varian UNITY 300 instrument. Variables used to determine the free energies of activation are averages of at least three different temperatures. The procedure for approximating $\Delta G^{\neq}$ [8,9] at the coalescence temperature using the method of Shanan-Atidi and Bar-Eli [10] for unsymmetric doublets has been described previously [11]. Populations were determined by electronic integration or by tracing, cutting and weighing peaks on good grade paper. Free energies of activation were obtained for saturated solutions in deuterochloroform.

3. Results

Table 1 contains proton and ^{13}C chemical shifts for the compounds. Assignments of aromatic carbon resonances are based on (1) additivity relationships among the ring carbon shifts, (2) the number of directly attached protons, obtained from coupled carbon-13 spectra, and (3) relative magnitudes of $|J(^{19}F-^{13}C)|$ spin-spin coupling constants in the *para*-CF_3 compound. Carbon-13 chemical shifts recorded for aromatic carbons of the acetanilides, when expressed relative to internal benzene, are in good qualitative agreement with those estimated from additivity (±1–3 ppm differences between calculated and observed shifts, at worst). Proton, ^{14}N, ^{17}O, and ^{29}Si chemical shifts are gathered in Table 2. Activation parameters for rotation about the C–N bond in the substituted acetanilides are presented in Table 3. Because of the difficulty in estimating the coalescence temperature in two site systems with widely different population, free energies of activation are believed to be accurate to about ±0.6 kcal mol^{-1}.

4. Discussion

Proton data for the simple aliphatic and aromatic compounds in chlorobenzene were reported previously [3]. A comparison of these data for the *N*-methylacetamide derivative, for example, shows that there is a definite solvent effect, particularly in the $COCH_3$ (1.52 ppm (ClC_6H_5), 2.01 ppm ($CDCl_3$)) and N-CH_3 (2.40 ppm (ClC_6H_5), 2.99 ppm ($CDCl_3$)) resonances. We have repeated this work in toluene and find an even

Table 3
Activation parameters for rotation in substituted acetanilides $(CH_3)CON(XC_6H_4)(CH_2Si(CH_3)_2Cl)$

X	T_c (K) [a]	$\Delta\nu_c$ (Hz) [b]	P_b [c]	$\Delta G_a^{\neq}$ (kcal mol^{-1}) [d,e]	$\Delta G_b^{\neq}$ (kcal mol^{-1}) [e]
H	285	166.3	0.11	13.3	14.5
p-OCH_3	248	181.5	0.005	11.4	14.0
p-Cl	243	169.0	0.02	11.2	13.1
p-Br	248	170.2	0.0225	11.5	13.3
p-CF_3	298	150.3	0.014	14.0	16.5
p-NO_2 [f]	360	188.0	0.08	16.9	18.6

[a] Temperature at which $Si(CH_3)_2$ peaks coalesce.

[b] Chemical shift difference for the isomers at T_c.

[c] Population of the low-frequency *trans* rotamer.

[d] Free energy of activation for the conversion minor → major rotomer.

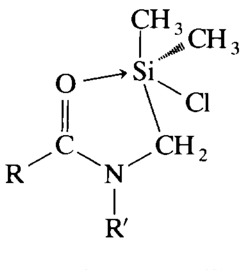
[e] $\Delta G^{\neq}$ ±0.6 kcal mol^{-1}.

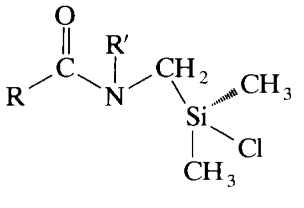
[f] Assume coalescence at 360 K. Population and frequencies estimated.

greater difference in these two resonances (1.20, 2.04 ppm). We attribute the differences between the resonances in the two aromatic solvents and $CDCl_3$ to both the anisotropy effect of the aromatic ring [12] and hydrogen-bonding of the $CDCl_3$ to the oxygen (vide infra). A particularly interesting difference in the proton spectra taken in toluene as compared to $CDCl_3$ is the relative intensity of the $Si(CH_3)_2$ peaks in the *N*-methylformamide and -acetanilide derivatives. For both compounds the $Si(CH_3)_2$ peaks are broader and less intense in $CDCl_3$. We have also examined the proton spectra in THF and CH_2Cl_2 and find that the relative intensities are similar to those in toluene.

When the proton spectrum of the acetanilide derivative in $CDCl_3$ is obtained at lower temperatures the $Si(CH_3)_2$ peak sharpens and increases in intensity. At these lower temperatures a small broad peak is observed about 0.5 ppm upfield from the main $Si(CH_3)_2$ peak. As the temperature is increased this small peak moves downfield as the larger peak sharpens. The same phenomenon was observed for the other acetanilide derivatives.

We attribute this temperature dependent behavior to hindered rotation about the amide C–N bond. The major isomer (that is, the most populated rotamer) has the $ClSi(CH_3)_2CH_2$ group *cis* to the carbonyl as determined previously [3]. We have examined the spectrum of the acetanilide in toluene and mesitylene between −60 and 100, and −100 and 140 °C, respectively, and have observed no change in intensity of the $Si(CH_3)_2$ peak. Thus, in these solvents there is either a 100% population of the major isomer or the free energy of activation is considerably higher. Because no other peak was observed in the $Si(CH_3)_2$ region we assume that only one rotamer exists in appreciable quantities in most solvents. In $CDCl_3$ the solvent competes as a Lewis acid (through hydrogen-bonding) with the silicon, thereby reducing the amount of rotamer with dative bonding to silicon. The two rotamers are shown below.





In the acetanilide derivatives the free energy of activation increases as the electron-withdrawing effect of the substituent increases (Table 3). On the other hand, there seems to be no discernible relationship between substituent effect and populations. The free energy of activation dependence is contrary to that observed for the barriers to rotation in substituted formanilides [11], where electron-withdrawing substitutents decrease the barrier, presumably because of their destabilization of the resonance structure with a formal positive charge on nitrogen. We propose that hydrogen-bonding to the carbonyl oxygen in the transition state, where the carbonyl is less sterically hindered, lowers the energy of the transition state and consequently lowers the barrier to rotation. We attribute the increase in barrier with increase in electron-withdrawal to the concommitant decrease in basicity of the carbonyl nitrogen and smaller amount of hydrogen-bonding between the chloroform and the carbonyl group in the transition state.

Table 2 contains the ^{14}N, ^{17}O, and ^{29}Si resonances for the compounds in $CDCl_3$. It is instructive to compare these to the values obtained previously for *N*,*O*-bis(trimethylsilyl)acetimidate (^{14}N, −120 ppm; ^{17}O, 170 ppm; and ^{29}Si, −5.5, 16.6 ppm) and for *N*, *N*-bis(trimethylsilyl)formamide (^{14}N, −245 ppm; ^{17}O, 403 ppm; and ^{29}Si, 8.2 ppm). We have also obtained the values for *N*-methyl-*N*-trimethylsilylacetamide: ^{14}N, −265 ppm; ^{17}O, 359 ppm; and ^{29}Si, 9.3 ppm (lit. [13] 8.8 ppm). Thus, the compounds that exist as amides have ^{14}N resonances in the −240 to −260 ppm region, ^{17}O resonances in the 390 to 410 ppm region, and ^{29}Si resonances in the −5 to 20 ppm region [14]. The imidate structure, with its lower pi-bond character in the carbon–oxygen bond and greater pi-character in the carbon–nitrogen bond, has a distinctly smaller ^{17}O chemical shift and a greater ^{14}N chemical shift.

The $Cl(CH_3)_2SiCH_2$ derivatives have ^{14}N resonances in the −230 to −260 ppm range, clearly indicative of the amide rather than the imidate structure. The range for the ^{17}O resonance in the aliphatic compounds is in the 260 to 280 ppm range while the aromatic derivatives show peaks in the 300 to 350 ppm region. These resonances are clearly outside of the imidate region but are generally not as high as those observed for the trimethylsilyl analogs. We attribute this decrease in the ^{17}O resonance to donation of electron density from the oxygen to the silicon with its concommitant decrease in the pi-character at the oxygen. It is significant that the lowest frequency ^{14}N shifts, which occur in the aromatic derivatives, are produced by the same derivatives that have the highest frequency ^{17}O shifts. This behavior suggests that interpretations of these shifts in terms of the contribution of the pi-character to the paramagnetic term is reasonable. As the pi-character in the carbon–nitrogen bond increases, the pi-character at the oxygen decreases.

This same phenomenon is observed in the ^{29}Si shifts: the $Cl(CH_3)_2SiCH_2$ derivatives have ^{29}Si shifts in the −10 to −38 ppm region, indicative of an increase in electron density at the silicon. The formyl derivatives have the highest frequency shifts, indicative of the smallest amount of electron density at the silicon in these derivatives. The previously reported carbonyl stretching frequencies [3] also show greater dative interactions in the acetyl derivatives. The increase in the frequency of the shift in the acetanilides as the electron-withdrawing ability of the substituent increases is consistent with electron withdrawal from the silicon by the aromatic group. It is also consistent with destabilization of the positive charge on nitrogen in the charge-separated amide resonance form and the consequent stabilization of the amide resonance form which should be less amenable to electron donation to silicon. The lack of a correlation between the ^{17}O (and ^{14}N) shifts and the ^{29}Si shifts suggests that at least two factors influence either (or both) the ^{17}O and ^{29}Si shifts. The ^{29}Si shift appears to be the better probe of dative interaction between oxygen and silicon.

Acknowledgments

We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Merck & Company Inc., for partial support of this research. We also thank the Franklin and Marshall College Hackman program and the Elizabethtown College Faculty Grants Committee for summer stipends. Preliminary results of this work were presented at the 207th National Meeting of the American Chemical Society in San Diego, CA. We thank the ACS Division of Chemical Education/Society Committee on Education for supporting student attendance at the meeting (M.F.L. and K.J.S.). We thank the National Science Foundation, Armstrong World Industries, and Franklin and Marshall College for assistance in acquiring a Varian UNITY 300-MHz NMR spectrometer and support facilities.

References

[1] J. Kowalski and Z. Lasocki, *J. Organomet. Chem., 116* (1976) 75.
[2] K.D. Onan, A.T. McPhail, C.H. Yoder and R.W. Hillyard, Jr., *J. Chem. Soc., Chem. Commun.*, (1978) 209.
[3] R.W. Hillyard, Jr., C.M. Ryan and C.H. Yoder, *J. Organomet. Chem., 153* (1978) 369.
[4] C.H. Yoder, C.M. Ryan, G.F. Martin and P.S. Ho, *J. Organomet. Chem., 190* (1980) 1.
[5] M.G. Voronkov, V.A. Pestunovich and Yu. I. Baukov, *Metalloorg. Khim., 4* (1991) 1210.
[6] V.E. Shklover, Y.T. Struchkov and M.G. Voronkov, *Main Group Met. Chem., 11* (1988) 109.
[7] C. Chuit, R.J.P. Corriu, C. Reye and J.C. Young, *Chem. Rev., 93* (1993) 1371.
[8] D. Kost, E.H. Carlson and M. Raban, *Chem. Commun.*, (1971) 656.
[9] A. Allerhand, H.S. Gutowsky, J. Jonas and R.A. Meinzer, *J. Am. Chem. Soc., 88* (1966) 3185.
[10] H. Shanan-Atidi and K.H. Bar-Eli, *J. Phys. Chem., 74* (1970) 961.
[11] C.H. Yoder, J.A. Sandberg and W.S. Moore, *J. Am. Chem. Soc., 96* (1974) 2260.
[12] W.E. Stewart and T.H. Siddall III, *Chem. Rev., 70* (1970) 517.
[13] I.D. Kalikhman, A.I. Albanov, O.B. Bannikova, L.I. Belousova, M.G. Voronkov, V.A. Pestunovich, A.G. Shipov, E.P. Kramarova and Yu. I. Baukov, *J. Organomet. Chem., 361* (1989) 147.
[14] M.S. Samples, C.H. Yoder and C.D. Schaeffer, Jr., *J. Chem. Educ., 64* (1987) 177.