Journal of Organometallic Chemistry, 114 (1976) 251—256

HINDERED ROTATION AND EXCHANGE IN TRIMETHYLSILYLANILIDES

CLAUDE H. YODER * and ARTHUR D. BELBER

Department of Chemistry, Franklin and Marshall College, Lancaster, PA 17604 (U.S.A.)

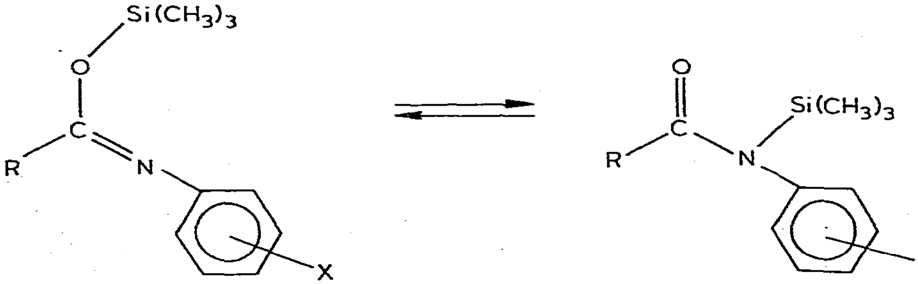
(Received January 30th, 1976)

Summary

A series of trimethylsilylanilides were prepared and characterized as amide—imidate mixtures. Low temperature NMR spectra reveal both hindered rotation and exchange processes for the formanilides and benzanilides and exchange for the acetanilides. Isomer ratios and free energies of activation are reported and used to postulate a mechanism for the exchange process.

The structures of a variety of trimethylsilylamides are known: mono-substituted amides exist in the amide form [1], bis(trimethylsilyl)amides (except bis(trimethylsilyl)formamide) exist as imidates [2], and trimethylsilylacetanilides exist as mixtures of both amide and imidate [3]. When the tautomeric form is the amide, hindered rotation about the carbonyl—nitrogen bond has been observed [1,2], whereas in the imidate form exchange of the trimethylsilyl group occurs from oxygen to nitrogen [2]. The trimethylsilylanilides are particularly interesting because they comprise a system where both hindered rotation and exchange are possible. Moreover, the 1,3-migration of the trimethylsilyl group from oxygen to nitrogen is analogous to the Chapman rearrangement of imidates to amides [4].

Hence, the objectives of this study were to: *(a)* determine the effects of substitution at the nitrogen and carbonyl carbon of trimethylsilylanilides on the barriers to rotation and exchange and *(b)* determine how closely analogous the mechanism of the exchange process is to that of the aryl Chapman rearrangement. Accordingly, three series of compounds were prepared and studied by



NMR spectroscopy: trimethylsilylformanilides ($R = H$), trimethylsilylacetanilides ($R = CH_3$), and trimethylsilylbenzanilides ($R = XC_6H_4$).

Experimental

Compounds

All operations were performed under a nitrogen atmosphere using oven-dried glassware and dry reagents. The trimethylsilyl-formanilides and -acetanilides were prepared by the reaction of trimethylchlorosilane with the substituted formanilide (or acetanilide) in the presence of triethylamine using THF as solvent. The precipitated triethylamine hydrochloride was removed by filtration and the filtrate subjected to fractional distillation.

Trimethylsilylacetanilides: p-OCH_3, b.p. 85°C/0.1 mmHg (Lit [5] b.p. 75—76°C/0.2 mmHg). p-CH_3, b.p. 90°C/2 mmHg (Lit. [5] b.p. 50—53°C/0.2 mmHg. p-H, b.p. 90°C/2 mmHg (Lit. [6] b.p. 45°C/0.1 mmHg). p-Cl, b.p. 75°C/2 mmHg (Lit. [5] b.p. 61—63°C/0.2 mmHg).

Trimethylsilylformanilides: p-OCH_3, b.p. 100°C/2 mmHg. (Found: C, 59.82; H, 7.87. $C_{11}H_{17}NO_2Si$ calcd.: C, 59.15; H, 7.67.) p-H, b.p. 85°C/3 mmHg. (Found: C, 62.45; H, 8.10. $C_{10}H_{15}NOSi$ calcd.: C, 62.13; H, 7.82.) p-Cl, b.p. 89°C/3 mmHg. (Found: C, 52.90; H, 6.40. $C_{10}H_{14}ClNOSi$ calcd.: C, 52.70; H, 6.20.)

The *trimethylsilylbenzanilides* were prepared by reaction of trimethylchlorosilane with the lithium salt (from butyllithium) of the appropriate substituted benzanilides. p-OCH_3, b.p. 163°C/2 mmHg. (Found: C, 69.19; H, 7.06. $C_{17}H_{21}NO_2Si$ calcd.: C, 68.18; H. 7.07.) p-CH_3, b.p. 130°C/1 mmHg. (Found: C, 71.19; H, 7.88. $C_{17}H_{21}NOSi$ calcd.: C, 72.03; H, 4.47.) p-H, b.p. 133°C/1 mmHg (Lit. [6] b.p. 106°C/0.15 mmHg).

NMR measurements

NMR spectra were obtained on a Varian A-60D spectrometer equipped with variable-temperature accessory V-4341/V-6057. Temperatures were measured with methanol and ethylene glycol samples and the equations of Van Geet [7]. Variables used in the determination of free energies of activation are averages of at least four scans at the appropriate temperatures. The procedure used for obtaining $\Delta G^{\neq}$ by the method of Shanan-Atidi and Bar-Eli [8] has been described previously [9]. This method has been shown to give $\Delta G^{\neq}$ values in good agreement with those obtained from total line shape analysis if $\Delta\nu$ is greater than 4 Hz [10]. Populations were determined by tracing, cutting, and weighing peaks on good grade paper and are averages of at least four scans.

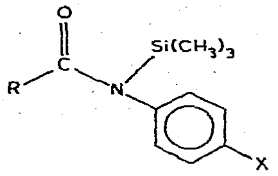
Free energies of activation were determined for 30% solutions in dry chlorobenzene containing a small amount of CH_2Cl_2 as a resolution standard.

Results and discussion

The trimethylsilyl region of the NMR spectra of the formanilides contains two peaks at room temperature. The relative intensities of the peaks are sensitive to the nature of the substituent on the benzene ring but for all substituents the two peaks coalesce to a single peak as the temperature is increased. As the tem-

TABLE 1

ACTIVATION PARAMETERS FOR EXCHANGE IN COMPOUNDS:



R	X	T_c (K) [a]	$\Delta\nu_c$ (Hz) [b]	P_I [c]	$\Delta G^{\neq}_{I\rightarrow A}$ [d,e]	$\Delta G^{\neq}_{A\rightarrow I}$ [e]
H	OCH_3	352.0	7.47	0.23	18.8	19.6
H	H	358.4	5.78	0.47	19.3	19.4
H	Cl	354.6	8.13	0.63	19.3	18.9
CH_3	OCH_3	286.8	9.38	0.08	15.0	16.4
CH_3	CH_3	289.7	8.63	0.31	15.3	15.7
CH_3	H	299.7	8.90	0.48	15.8	15.8
CH_3	Cl	296.6	10.1	0.75	16.2	15.5
$C_6H_4OCH_3$	H	293.2	29.4	0.66	15.1	14.8
$C_6H_4CH_3$	H	295.6	27.9	0.63	15.2	14.9
C_6H_5	H	293.3	28.4	0.67	15.2	14.8

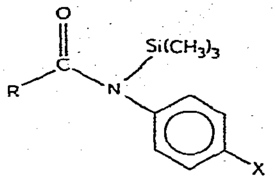
[a] Temperature at which $Si(CH_3)_3$ peaks coalesce. [b] Chemical shift difference for the isomers at T_c. [c] Population of the imidate form. [d] Free energy of activation for the conversion of imidate to amide. [e] $\Delta G^{\neq} \pm 0.3$ kcal mol^{-1}.

perature is decreased the higher field peak broadens and splits into two. Thus, at low temperature there are three peaks in the trimethylsilyl region of the NMR spectra of each of the substituted formanilides. For the parent trimethylsilylformanilide at 0°C these peaks occur at 0.29, 0.18, and 0.06 ppm. The relative intensities of the two higher field peaks vary only slightly as the substituent is changed.

The two dynamic processes leading to these two coalescences are almost certainly rotation about the carbonyl—nitrogen bond and exchange of trimethylsilyl groups. The process resulting in coalescence at the lower temperature can be assigned to rotation on the basis of three observations: *(a)* Variation of substituents has little effect on the population of the rotamers of *N*-methylformanilides [9]. The populations of the low field peaks (which coalesce at higher temperature) of the trimethylsilylformanilides (Table 1), however, are obviously heavily dependent upon the nature of the substituent. The populations of the higher field peaks are given in Table 2 and are relatively insensitive to the nature of the substituent. *(b)* Electron-releasing substituents increase the free energies of activation for rotation in *N*-methylformanilides [9]. The same relationship is apparent for the free energies of activation obtained for the higher field peaks of the trimethylsilylformanilides. The free energies of activation for the lower field peaks, on the other hand, seem to be consistent with the opposite trend: the electron-releasing methoxy group gives rise to a lower $\Delta G^{\neq}$ (but $\Delta G^{\neq}$ for the other two derivatives are experimentally indistinguishable). *(c)* The free energy of activation for rotation is lower for amides with *N*-trimethylsilyl groups than for *N*-t-butylamides [1,2]. The free energy of activation for conversion of the major rotamer to the minor rotamer of *N*-t-butylformanilide is

TABLE 2

ACTIVATION PARAMETERS FOR ROTATION OF COMPOUNDS:



R	X	T_c (K)	$\Delta\nu_c$ (Hz)	P_a	$\Delta G^{\neq}_{a\rightarrow b}$ [a]	$\Delta G^{\neq}_{b\rightarrow a}$ [a]
H	OCH_3	304.3	7.47	0.74	16.8	16.1
H	H	297.8	7.57	0.81	16.6	15.8
H	Cl	293.4	5.35	0.71	16.3	15.8
$C_6H_4OCH_3$	H	254.8	6.67	0.78	14.1	13.5
$C_6H_5CH_3$	H	259.3	8.61	0.77	14.2	13.6
C_6H_5	H	275.1	7.44	0.83	15.4	14.5

[a] $\Delta G^{\neq}$ ±0.3 kcal mol^{-1}.

18.4 kcal mol^{-1} [9] and only the free energies of activation for the coalescence of the higher field peaks of the trimethylsilylformanilides are lower than this value. Therefore, the higher field peaks are due to the rotamers of the amide form while the low field peak is due to the imidate form. It should be noted that there seems to be no evidence for *syn,anti* isomerism of the imidate form.

The structure of the rotamers responsible for the upfield peaks can be assigned by observing the shift of the peaks upon dilution with benzene [11]. Since the smaller of the two upfield peaks shifted upfield more than the larger peak upon dilution, this peak is presumably associated with the rotamer containing the trimethylsilyl group *trans* to the carbonyl oxygen. The major rotamer therefore has the trimethylsilyl group *cis* to the carbonyl oxygen as shown in the structural formula in Table 2. This same conformation is favored for *N*-alkylformanilides [9] and *N*-trimethylgermylformanilides [12].

The NMR spectra of the trimethylsilylacetanilides exhibit only two peaks in the trimethylsilyl region at low temperatures. As the temperature is increased these peaks coalesce to a single peak. The populations of the lower field peaks and the free energies of activation for the process resulting in coalescence are given in Table 1. These parameters show the same variation with substituent as those for the coalescence of the lower field peaks of the formanilides. These peaks can therefore also be attributed to the imidate and amide tautomer. Since the low field peak in the trimethylsilyl region of the formanilides has been assigned to the imidate form it seems likely that the low field peaks in the acetanilides is also attributable to the imidate form. Moreover, a study of ^{15}N-*N,O*-bis(trimethylsilyl)acetamide has shown that the lower field trimethylsilyl resonance is associated with the trimethylsilyl group attached to oxygen [13].

The absence of a second amide peak in the NMR spectra of the acetanilide even at temperatures down to −60°C could be a result of *(a)* rapid rotation even at −60°C, *(b)* the predominance of one rotamer, or *(c)* coincidental equivalence of the rotamer chemical shifts. The same behavior has been observed for t-butyl- [11], trimethylsilyl- [1], and trimethylgermyl- [12] -acetamides and for trimethylgermylacetanilides [12] and is almost certainly due to virtually 100% abundance of the *cis* rotamer. The greater abundance of the *cis* rotamer of acetamides relative to formamides has been discussed by La Planche and Rogers [14].

The free energies of activation recorded in Table 1 for the acetanilides are therefore associated with exchange of trimethylsilyl groups from imidate to amide ($\Delta G^{\neq}{}_{\mathrm{I}\to\mathrm{A}}$) and vice versa. A plot of $\Delta G^{\neq}{}_{\mathrm{I}\to\mathrm{A}}$ against the Hammett σ constants of the substituents gives a correlation coefficient of 0.991 and a slope of 2.4. The positive slope is indicative of acceleration of the exchange by electron-releasing substituents.

The NMR spectra of the trimethylsilylbenzanilides, like the formanilides, contain three peaks in the trimethylsilyl region at low temperatures. In this case, however, the low field peaks coalesce at a lower temperature than that at which the higher field peaks coalesce. The lower temperature coalescence can be attributed, nevertheless, to the rotation process because of the increase in free energy of activation as the substituent becomes more electron-attracting. The effect of substituents at the carbonyl carbon on the free energy of activation for rotation is contrary to the effect of substituents at the nitrogen and has been documented for substituted dimethylbenzamides [15]. Moreover, the trimethylsilyl protons of the amide form of *N*-methyltrimethylsilylbenzamide also absorb at a lower field than those of the imidate form [6]. The change in relative positions of the amide and imidate peaks resulting from a change from formanilides or acetanilides to benzanilides is probably due in part to the anisotropy of the benzene ring attached to the carbonyl carbon.

The activation parameters for the higher temperature coalescence of the benzanilides are given in Table 1. The free energies of activation for the exchange process are clearly only very slightly affected by substituents on the carbonyl and phenyl groups. The coalescence temperatures for other trimethylsilylanilides bearing electronegative substituents closer to the carbonyl indicate that electron-withdrawing groups increase the free energy of activation but the effect is not great [6].

The effect of substituents at both nitrogen and carbonyl carbon on the rate of exchange of the trimethylsilyl group parallels closely the effect of substituents on the migration of the phenyl group in the Chapman rearrangement of aryl benzimidates. Chapman found that electron-releasing substituents increase the rate of migration at both nitrogen and carbon, although the effect at the carbon is apparently not as great [16]. Wiberg and Rowland concluded that the intramolecular [17,18] migration involves nucleophilic displacement at the migrating aryl group by the lone pair of electrons at nitrogen and proceeds through a 4-membered cyclic transition state [17]. If the concentration-independent exchange of trimethylsilyl group is assumed to be intramolecular, the same mechanism can be postulated; that is, a nucleophilic displacement at silicon via a cyclic transition state.

Although the mechanisms of the two reactions are probably similar the rearrangement of aryl benzimidates and trimethylsilyl benzimidates differ in two important respects. First, the rearrangement of the trimethylsilyl derivatives is reversible, due presumably to the greater similarity of the free energies of the amide and imidate forms brought about by the high Si—O bond energy. And second, the rearrangement of the trimethylsilyl derivatives is considerably faster, perhaps a result of the lowering of the energy of the transition state by the Lewis interaction of the nitrogen lone pair with the *d*-orbitals of silicon.

Acknowledgements

The authors are indebted to the Camille and Henry Dreyfus Foundation for partial support of this work.

References

1 A. Komoriya and C.H. Yoder, J. Amer. Chem. Soc., 94 (1972) 5285.
2 C.H. Yoder, W.C. Copenhafer and B. DuBeshter, J. Amer. Chem. Soc., 96 (1974) 4283.
3 J. Klebe, Acc. Chem. Res., 3 (1970) 299.
4 J.W. Schulenberg and S. Archer, Org. React., 14 (1965) 1.
5 J.F. Klebe, H. Finkbeiner and D.M. White, J. Amer. Chem. Soc., 88 (1966) 3390.
6 M. Fukui, K. Itoh and Y. Ishii, J. Chem. Soc. Perkin II, (1972) 1043.
7 A.L. van Geet, Anal. Chem., 42 (1970) 679.
8 H. Shanan-Atidi and K.H. Bar-Eli, J. Phys. Chem., 74 (1970) 961.
9 C.H. Yoder, J.A. Sandberg and W.S. Moore, J. Amer. Chem. Soc., 96 (1974) 2260.
10 D. Kost, E.H. Carlson and M. Raban, Chem. Commun., (1971) 656.
11 W.E. Stewart and T.H. Siddall III, Chem. Rev., 70 (1970) 517.
12 C.H. Yoder, W.S. Moore, W.C. Copenhafer and J. Sigel, J. Organometal. Chem., 82 (1974) 353.
13 C.H. Yoder and D. Bonelli, Inorg. Nucl. Chem. Lett., 8 (1972) 1027.
14 L.A. La Planche and M.T. Rogers, J. Amer. Chem. Soc., 86 (1964) 337.
15 L.M. Jackman, T.E. Kavanagh and R.C. Haddon, Org. Magn. Reson., 1 (1969) 109.
16 A.W. Chapman, J. Chem. Soc., (1927) 1743.
17 K.B. Wiberg and B.I. Rowland, J. Amer. Chem. Soc., 77 (1955) 2205.
18 O.H. Wheeler, F. Roman and O. Rosado, J. Org. Chem., 34 (1969) 966.