Migration of the Trimethylsilyl Group in Silylated Acylamides

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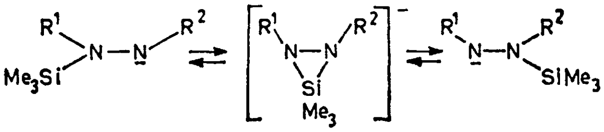
Variable temperature n.m.r. studies were made for several *N*-trimethylsilylacylamides $R^1CO{\cdot}N(SiMe_3)R^2$ (R^1 = alkyl or aryl. R^2 = Ph or Me). Based on the careful determination of the values of $J_{^{29}Si-H}$ for the CH_3–N proton signals in the case of $PhCO{\cdot}NMe(SiMe_3)$ the non-equivalence of the trimethylsilyl ^1H resonances was explained in terms of 1,3-migration of the trimethylsilyl group between the nitrogen and oxygen atoms. A study of the variation of the coalescence temperatures and the activation energies for eight *N*-phenyl-*N*-trimethylsilylacylamides $RCO{\cdot}NPh(SiMe_3)$, showed that the basicity of the amide largely determined the rate of 1,3-migration of the trimethylsilyl group.

THE migration of the trimethylsilyl group has been investigated for the anionic 1,2-migration of silylhydrazines[1] [equation (1)] and for 1,3-migrations in silyl-imidates,[2,3] -amides,[4,5] or -amidines[6] [equation (2)].



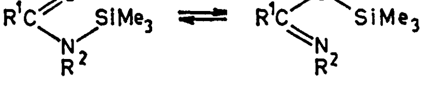
(1)

N.m.r. spectroscopy is the most convenient method for studying such 'silicotropies' since trimethylsilyl protons are observable as singlets with considerable intensities and their rates of migration are frequently within the n.m.r. time scale. In particular, variable temperature n.m.r. measurements often give considerable information about this kind of rearrangement. The concept of 1,3-migration of the trimethylsilyl groups rationalized the varied reaction behaviours of heterocumulenes with bis(trimethylsilyl) derivatives of amines,[7-10] phosphines,[11] or sulphides.[12]

(2)

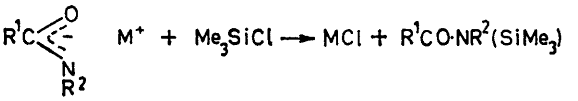
$X = N{\cdot}SiMe_3$, $Y = O$
$X = O$, $Y = NMe$
$X = Y = NMe$

We describe herein some evidence for a 1,3-migration of the trimethylsilyl group in the equilibria (3) between silylacylamides (A) and the corresponding imidates (B) by means of variable temperature n.m.r. spectroscopy. The effect of substituents R^1 on the migration were also studied.



(A) (B) (3)

Ten trimethylsilylacylamides were prepared by the treatment of the relevant sodium or lithium acylamides with trimethylchlorosilane [equation (4)]. N.m.r.



$$R^1C(O)(NR^2)^-\ M^+ + Me_3SiCl \rightarrow MCl + R^1CO{\cdot}NR^2(SiMe_3) \quad (4)$$

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[1] R. West, 'Organosilicon Chemistry,' Butterworths, London, 1969, vol. 19, nos. 3—4, p. 291.

[2] K. Itoh, M. Katsuda, and Y. Ishii, *J. Chem. Soc.* (*B*), 1970, 302.

[3] J. Pump and E. G. Rochow, *Chem. Ber.*, 1964, **97**, 623.

[4] J. F. Klebe, 'International Symposium on Organosilicon Chemistry,' Prague, 1965.

[5] J. F. Klebe, *J. Amer. Chem. Soc.*, 1968, **90**, 5246.

[6] O. J. Scherer, *Chem. Ber.*, 1968, **101**, 2533.

[7] K. Itoh, I. K. Lee, I. Matsuda, S. Sakai, and Y. Ishii, *Tetrahedron Letters*, 1967, 2667.

[8] I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc.* (*C*), 1969, 701.

[9] K. Itoh, N. Kato, and Y. Ishii, *J. Chem. Soc.* (*C*), 1969, 2005.

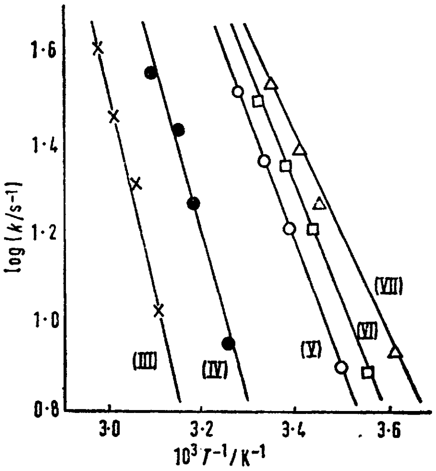
[10] I. Matsuda, K. Itoh, and Y. Ishii, *J. Organometallic Chem.*, 1969, **19**, 339.

[11] K. Itoh, M. Fukui, and Y. Ishii, *J. Chem. Soc.* (*C*), 1968, 2002.

[12] K. Itoh, K. Matsuzaki, and Y. Ishii, *J. Chem. Soc.* (*C*), 1968, 2709.

measurements were performed with 20% solutions (v/v) in trichloroethylene over the temperature range −86 to +80 °C. Rate constants were determined by the usual method using the half-line width and the chemical shift differences when the coalescence of two trimethylsilyl proton signals was observed within the measured temperatures.

Arrhenius plots for five *N*-phenyl-*N*-trimethylsilylacylamides (III)—(VII), are shown in the Figure and activation energies as well as coalescence temperatures of various acylamides are summarized in Table 1.



Arrhenius plot of compounds (III)—(VII)

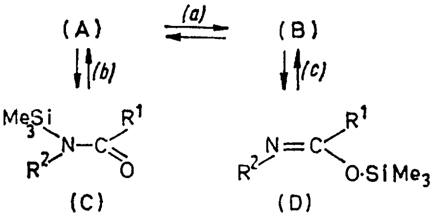
TABLE 1

Coalescence temperatures and activation energies of substituted trimethylsilylamides $R^1CO\cdot NR^2(SiMe_3)$

	Compounds		Coalescence temp.	
	R^1	R^2	(°C)	E_a/kcal mol^{-1}
(I)	CF_3	Ph	*a*	*c*
(II)	CCl_3	Ph	*a*	*c*
(III)	$CHCl_2$	Ph	58·0	19·2
(IV)	CH_2Cl	Ph	43·0	17·5
(V)	Me	Ph	26·0	11·2
(VI)	Et	Ph	23·0	11·6
(VII)	Pr^i	Ph	21·0	9·5
(VIII)	Bu^t	Ph	*a*	*c*
(IX)	Ph	Ph	22·0	*d*
(X)	Ph	Me	*b*	*c*

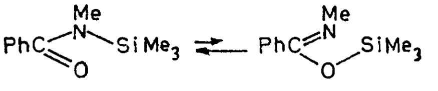
[a] Coalescence temperature was not observed within the range −86 to +80 °C. [b] Two asymmetric sharp signals were observed at τ 9·80 and 9·82 in the ratio 3 : 1. [c] Activation energy could not be calculated from the Arrhenius plot. [d] Activation energy could not be calculated because of the complexity of the trimethylsilyl proton signal.

Prior to discussion of the results in Table 1, it is necessary to establish which of the two trimethylsilyl proton signals may be ascribed to $Me_3Si–O$ linkage and which arises from the imino-ether structure (B). The n.m.r. spectrum of *N*-methyl-*N*-trimethylsilylbenzamide (X) suggested the presence of the two isomers in the ratio 3 : 1. Only one $CH_3–N$ proton signal at τ 7·26 showed satellite bands due to ^{29}Si (natural abundance 4·7%) with $J_{^{29}Si–H}$ 2·9 Hz; the other signal at τ 6·98 with lower intensity did not show any satellite bands. Based on these observations, it would be reasonable to suggest that the higher intensity peak should be due to the isomer (Xa) and the other to (Xb). Therefore, the trimethylsilyl protons at higher field (τ 9·82) should be ascribed to the $Me_3Si–O$ linkage in (Xb). Some values of the long range coupling constants $J_{^{29}Si–H}$ are summarized in Table 2.



SCHEME The three possibilities of trimethylsilyl proton non-equivalence

The non-equivalence of the trimethylsilyl proton signals may be caused by any of three possibilities; (*a*) 1,3-migration of the trimethylsilyl group to give a mixture of two isomers, the acylamide form (A) and imino-ether form (B), (*b*) fixed rotation around C–N bonds of the two amide forms (A) and (C), and (*c*) an inversion at the sp^2 nitrogen atom between the imino-ether forms (B) and (D) (Scheme).



(5)

(Xa) (Xb)

Xa : Xb = 3 : 1

TABLE 2

Long range coupling constants $J_{^{29}Si–H}$

Compound	τ(CH_3–N)	$J_{^{29}Si–H}$/Hz
(Xa)	7·26	2·9
(Xb)	6·98	0
$Me_3Si\cdot NMe_2$	7·68	3·7
$(Me_3Si)_2\cdot NMe$	7·62	4·7

Only possibility (*a*) is consistent with the observation of $J_{^{29}Si–H}$ satellites for only one CH_3–N proton signal in the case of compound (X). Thus, if the observed non-equivalence comes from the fixed rotation of the acylamides (*b*), which is well established for *NN*-dialkylacylamides, both CH_3–N proton signals at τ 7·26 and 6·98 should show satellite bands due to ^{29}Si with approximately the same coupling constants. Moreover, the activation energy differences in typical fixed rotations with variation of the substituents on the acyl group were reported to be only 1·4 kcal mol^{-1} [13] (Table 3) although the coalescence temperature varied from 14·1 to 94·9 °C. Conversely, the results in Table 1 suggest a considerable difference (*ca.* 10 kcal mol^{-1}) and no coalescence was observed for the strongly electronegative trichloro- or trifluoro-methyl substituents.

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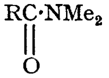
[13] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, 1962, **66**, 540.

Therefore, possibility (*b*), the fixed rotation around C–N bonds, (A) $\rightleftharpoons$ (C), may be discarded.

Secondly, if the observed non-equivalence is ascribed to the inversion process at the *sp*^{2} nitrogen atom, (B) $\rightleftharpoons$ (D) (*c*), both the trimethylsilyl groups in (B) and (D) would be situated on oxygen atoms. Consequently, neither of the CH_3–N proton signals should show satellites due to ^{29}Si because the methyl groups on the nitrogen atom would be located too far away to couple with the silicon atom. Furthermore, it has been reported that bulkier substituents decrease the activation energies for inversion of *sp*^{2} nitrogen atoms.[14] This trend is the complete reverse of that for activation energies for (II)—(VII) (Table 2). Consequently, possibility (*c*) may also be rejected.

TABLE 3

Coalescence temperatures and activation energies of *NN*-dimethylacylamides [13]

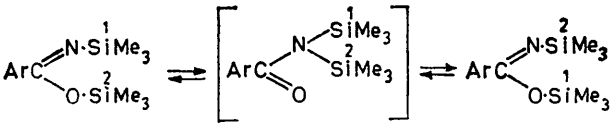


$RC(=O)\cdot NMe_2$

R	Coalescence temp. (°C)	E_a/kcal mol^{-1}
Me	87·3	10·6 ± 0·4
Pr^i	61·4	9·2 ± 0·7
CF_3	94·9	9·3 ± 0·6
CCl_3	14·1	9·9 ± 0·3

We therefore conclude that the observed non-equivalence of trimethylsilyl proton signals may be explained only by a 1,3-migration of the trimethylsilyl group and that the silylacylamides exist as an equilibrium mixture of the acylamide (A) and the imino-ether form (B).

Both coalescence temperatures and activation energies for the *N*-phenyltrimethylsilylacylamides (I)—(VIII) suggested that the 1,3-migration of the trimethylsilyl group occurs in the order $CF_3 \sim CCl_3 \ll CHCl_2 < CH_2Cl < Me \lesssim Et < Pr^i \ll Bu^t$ (Table 1). Consequently the 1,3-migration is accelerated by electron-releasing substituents on the carbonyl group to which the trimethylsilyl group migrates. This conclusion is consistent with our previous results [2] for the exchange of trimethylsilyl groups in bistrimethylsilylbenzimidates [equation (6)] where electron-donating substituents accelerated the rate of exchange (Hammett ρ —1·05).



(6)

EXPERIMENTAL

N.m.r. measurements were performed with JNM-C-60HL and JNM-C-60 spectrometers for 20% solutions (v/v) of purified trichloroethylene. Coupling constants were measured by the internal lock method (to a proton of trichloroethylene) with the conditions of 10 min sweep time and one fifth expansion. Precision of resolution was within ±0·3 Hz.

Materials.—Two typical preparations are presented. (a) N-*Phenyl*-N-*trimethylsilylacetamide* (V). A mixture of acetanilide (0·1 mol) and sodium (0·1 mol) was stirred in benzene or toluene overnight, and then trimethylchlorosilane (0·1 mol) was added dropwise. The mixture was refluxed for 3 h and the precipitated sodium chloride was centrifuged off. After evaporation of the filtrate, *N*-phenyl-*N*-trimethylsilylacetamide (63%) was isolated by distillation, b.p. 45 °C at 1 mmHg.

(b) N-*Phenyl*-N-*trimethylsilyltrifluoroacetamide* (I). Trimethylchlorosilane (0·016 mol) was added dropwise to lithium trifluoroacetanilide {prepared from BuLi (0·016 mol) [1·05N in light petroleum (b.p. 39—40 °C)] and trifluoroacetanilide (0·016 mol) in light petroleum (30 ml) (b.p. 39—40 °C)}. The mixture was refluxed for 3 h. After lithium chloride was centrifuged off, solvent was removed by distillation. Successive distillations under reduced pressure gave *N*-phenyl-*N*-trimethylsilyltrifluoroacetamide (77%), b.p. 90 °C at 20 mmHg.

TABLE 4

Substituted trimethylsilylacylamides $R^1CO\cdot NR^2(SiMe_3)$

Compound	Yield (%)	Method	B.p. (°C/mmHg)	Analysis Found (%) C	H	Calc. (%) C	H
(I)	77	(b)	90/20	50·75	5·5	50·45	5·4
(II)	52	(b)	62/0·2	43·8	4·75	42·55	4·55
(III)	25	(b)	69/0·25	47·3	5·65	47·85	5·45
(IV)	20	(b)	76/0·25	55·3	6·85	54·65	6·65
(V)	63	(a)	45/0·1	63·55	8·4	63·7	8·25
(VI)	48	(b)	72/0·6	65·3	8·8	65·1	8·65
(VII)	47	(a)	53/0·3	66·13	9·1	66·35	9·0
(VIII)	58	(b)	73/0·4	67·6	9·4	67·4	9·3
(IX)	68	(b)	106/0·15	71·45	7·25	71·35	7·1
(X)	47	(b)	67/0·2	63·65	8·3	63·75	8·25

Other trimethylsilylacylamides were prepared by similar procedures (Table 4).

[1/1150 *Received, 5th July*, 1971]

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[14] M. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219.