Catalytic silylotropy in *N*-trimethylsilylpyrazole derivatives

V. A. Lopyrev, L. I. Larina, A. I. Albanov, M. S. Sorokin, and G. V. Dolgushin*

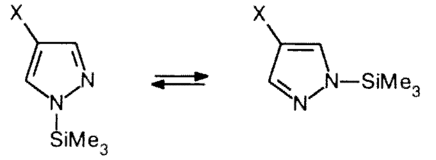
Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: 007 (395 2) 35 6046. E-mail: root@irioch.irkutsk.su

Silylotropy in 4-substituted *N*-trimethylsilylpyrazoles is studied by dynamic ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The catalytic 1,2-migration of a trimethylsilyl group in 4-halo-*N*-trimethylsilylpyrazoles was detected. Silylotropy in *N*-trimethylsilylpyrazoles in the presence of halogens or trimethylhalosilanes is believed to proceed through formation of *N,N'*-bis(trimethylsilyl)pyrazolium salts, the barrier of silylotropy in pyrazoles being markedly reduced.

Key words: silylotropy, dynamic ^{1}H, ^{13}C, and ^{29}Si NMR; *N*-trimethylsilylpyrazoles, halogens, trimethylhalosilanes.

It is known that annular prototropic tautomerism in azoles, including pyrazoles, can be described by a general equation of acid-base catalysis.[1,2] However, catalysis of elementotropy in azoles has not hitherto been observed. Nevertheless, irreversible migration of alkyl and phenacyl groups in 1,2,4-triazoles under the action of catalytic amounts of alkyl and phenacyl halides is documented.[3]

In the study of silylotropy in 4-halo-1-trimethylsilylpyrazoles by dynamic ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, we paid attention to the difference in behavior of 4-chloro- (**1**) and 4-bromo-1-trimethylsilylpyrazole (**2**), on the one hand, and of 4-ododerivative (**3**), on the other hand. These compounds were obtained by silylating the corresponding 4-halopyrazoles with hexamethyldisilazane (HMDS) according to a procedure similar to that applied for silylation of pyrazole.[4–6] The increased activity of 4-halopyrazoles in silylation with hexamethyldisilazane made it possible to reduce the reaction time from 10 h (in the case of silylation of pyrazole) to 2—2.5 h and to carry out this reaction in the absence of $(NH_4)_2SO_4$, a common silylation catalyst, at an equimolar ratio of 4-halopyrazole and HMDS.



(1)

1—3

X = Cl (**1**), Br (**2**), I (**3**)

Coalescence of the signals of the protons at positions 3 and 5 of the pyrazole ring is observed in the ^{1}H NMR spectra of silylpyrazoles **1** and **2** at 165 and 159 °C, respectively (Table 1). Decreasing temperature to ~20 °C transforms the spectra into their original appearance. Thus, we deal with a reversible process. Coalescence of the resonance signals of the ring protons (δ_H (H-3, H-5) = 7.65) also occurs on heating silylpyrazole **3** (up to ~140—160 °C). However, as the temperature decreases, the coalescence of the signals is detected only at

Table 1. Parameters of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of *N*-trimethylsilylpyrazoles **1**—**4** (neat liquids without solvents) and *N,N'*-bis(trimethylsilyl)pyrazolium bromide **5**

Compound	δ ^{1}H			δ ^{13}C				δ ^{29}Si	$\Delta G_c^{\neq}$ /kcal mol^{-1}	$\Delta\nu$/Hz	T_c/K
	H-3	H-5	$Si(CH_3)_3$	C-3	C-4	C-5	$Si(CH_3)_3$				
1	7.59	7.54	0.38	141.77	110.88	131.69	−1.1	17.1	24.0	4.1	438
2	7.60	7.56	0.39	143.60	94.1	133.80	−1.1	17.0	23.8	3.5	432
3	7.68	7.63	0.40	147.36	57.68	137.86	−1.2	17.0			
4[a]	7.65 7.73[c]	7.55 7.56[c]	0.37	143.00 142.85[c] 143.5[d]	106.30 105.71[c] 106.3[d]	133.64 133.29[c] 134.0[d]	−0.85 −1.2[c]	14.2 14.6[c]	23.1[b]	11.6[b]	438[b]
5[e]	7.84	7.84	0.59	136.76	106.59	136.76	2.34	24.3			

[a] δ_H (H-4): 6.22 (neat liquid) or 6.28 (a solution in $CDCl_3$). [b] See Ref. 4. [c] In solution in $CDCl_3$. [d] See Ref. 7. [e] δ_H (H-4): 6.48 ($CDCl_3$).

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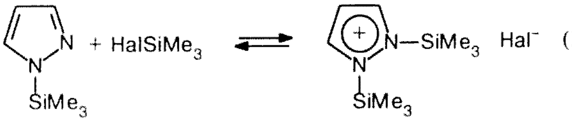
-45 °C, and complete separation of the signals occurs in the range of -70 to -90 °C ($\Delta G_c^{\neq} = 12.2$ kcal mol^{-1}, $\Delta\nu = 4$ Hz, CD_2Cl_2).

We assumed that heating silylpyrazole **3** results in its partial decomposition, and the decomposition products catalyze silylotropy. The most likely decomposition process of compound **3** can be thermolysis of the C—I bond. To verify this assumption, we studied the influence of halogens on the migration of the trimethylsilyl group in 1-trimethylsilylpyrazole (**4**). Indeed, the addition of traces of iodine to compound **4** accelerates silylotropy. This followed from the coalescence of the signals of H-3 and H-5 in the ^{1}H NMR spectra, which was observed even at room temperature. Bromine is less active, and it was necessary to heat the sample to attain a similar effect.

The mechanism of the effect of halogens on the trimethylsilyl group migration consists probably in the formation of intermediate trimethylhalosilane followed by its reaction with the substrate. Indeed, the addition of a small amount of trimethylhalosilane (except for $ClSiMe_3$) to compound **4** leads to the coalescence of the signals of the ring protons, which is due likely to the rapid degenerate exchange between the initial *N*-trimethylsilylpyrazole **4** and *N*,*N'*-bis(trimethylsilyl)pyrazolium halide (**5**) formed.



(2)

4 **5**

Hal = Br, I

Indeed, the formation of *N*,*N'*-bis(trimethylsilyl)imidazolium salts and their participation in exchange processes were reported earlier.[8,9]

As in the case of imidazole derivatives,[8] the equilibrium (2) is significantly shifted towards salt formation. Mixing of equimolar amounts of $BrSiMe_3$ and *N*-trimethylsilylpyrazole led to deposition of a white precipitate of *N*,*N'*-bis(trimethylsilyl)pyrazolium bromide. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of its solutions in $CDCl_3$ confirm completely the assumed structure (see Table 1).

It is known that the migration of the trimethylsilyl group in silylated pyrazoles occurs owing to the intramolecular exchange.[4,10] A similar migration of the trimethylsilyl group in the presence of triorganylhalosilanes occurs through the formation of *N*,*N'*-bis(triorganylsilyl)pyrazolium salts. The barrier to silylotropic exchange is thereby significantly decreased (from ~23—24 kcal mol^{-1} without catalysts to 12.2 kcal mol^{-1}, see Table 1).

Experimental

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL FX 90 Q spectrometer. The chemical shifts were measured with respect to Me_4Si as the internal standard. The samples were studied as neat liquids (without solvents) because of extremely high hydrolyzability of the compounds. The coalescence temperatures were measured with the accuracy of 0.5 °C, and $\Delta\nu$ were measured with the accuracy of 0.1 Hz. $\Delta G_c^{\neq}$ values were calculated using the known formula.[11]

Table 2. Physicochemical characteristics of 4-halo-1-trimethylsilylpyrazoles **1—3**

Compound	Yield (%)	M.p./°C (*p*/Torr)	n_D^{25}
1	85	59—61 (5)	1.4750
2	90	48—49 (1)	1.4965
3	95	78—79 (1)	[a]

[a] The index of refraction was not determined because of rapid hydrolysis of the substance in the air.

The physicochemical characteristics of 4-halo-1-trimethylsilylpyrazoles are given in Table 2. All the compounds are colorless oily liquids, which are easily hydrolyzed in the air.

General procedure of silylation. A mixture of equimolar amounts of the corresponding pyrazole and HMDS was refluxed (calcium chloride tube). The reaction mixture was then distilled *in vacuo* in an atmosphere of dry argon.

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