Journal of Organometallic Chemistry, 70 (1974) 347—352

SILICON MIGRATION IN *N*-(TRIMETHYLSILYL)-3,5-DIMETHYLAZOLES

V.N. TOROCHESHNIKOV, N.M. SERGEYEV, N.A. VIKTOROV, G.S. GOLDIN, V.G. PODDUBNY and A.N. KOLTSOVA
NMR Laboratory, Chemical Department, M.V. Lomonosov State University, Moscow (U.S.S.R.)
(Received October 10th, 1973)

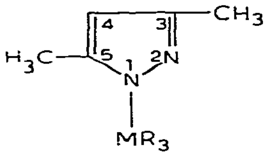
Summary

The ^1H and ^{13}C NMR spectra of the following six compounds have been examined over a wide range of temperatures: four derivatives of 3,5-dimethylpyrazole substituted at the nitrogen atom by organometallic groups such as $Si(CH_3)_3$ (I), $Si(C_2H_5)_3$ (II), $Si(OC_2H_5)_3$ (III), $Ge(CH_3)_3$ (IV), 3,5-dimethyl-1-trimethylsilyl-1,2,4-triazole (V) and 1-trimethylsilylimidazole (VI). Activation energies of the metal migration have been found for the compounds (I—V) by the total NMR line-shape analysis. Proton and carbon spectra of the compound (VI) show equivalence of the positions 4 and 5 in the imidazole ring. No temperature-dependent changes in the spectra were observed at —80 to +80°. These facts may be interpreted by assuming that the organometallic group undergoes an intermolecular exchange.

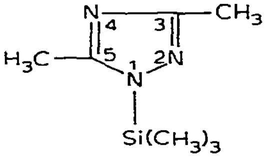
In 1971 O'Brien and Chang-Po-Hrung [1] established the fluxional behaviour of 1-trimethylsilylpyrazole while studying temperature-dependent PMR spectra. The silicon-containing group $Si(CH_3)_3$ migrated from one nitrogen atom to the other and thus the process should be regarded as degenerate. Similar behaviour has been found by Kravtsov et al. [2] for mercurated pyrazoles. More recently Cotton and Ciappenelli [3] on the basis of their dynamic NMR studies concluded that metal migration also occurred in a germyl derivative of pyrazole. Special attention has been drawn in these papers [1—3] to the evidence of intramolecularity of the migration. Experiments with various solvents and with various concentrations led the authors to conclude that silicon, mercury and germanium migrations were indeed purely intramolecular.

Another problem is the determination of the energy parameters for the metal migration. By using temperature-dependent NMR spectra O'Brien and Chang-Po-Hrung determined the activation parameters in trimethylsilylpyrazole, 3,5-dimethyl-1-trimethylsilylpyrazole and 3,4,5-trimethyl-1-trimethylsilylpyrazole, but their accuracy seems rather too low to achieve any quantitative comparison. Cotton and Ciappenelli determined the energy of activation for germyl migration in 1-trimethylgermylpyrazole and 3,5-dimethyl-1-trimethylgermylpyrazole with standard accuracy.

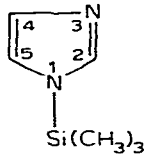
While searching for some comparative parameters specific to a metallotropic rearrangement in fluxional organometallic molecules we studied three pyrazoles (I—III) substituted by silicon-containing groups: 3,5-dimethyl-1-trimethylgermylpyrazole (IV), 3,5-dimethyl-1-trimethylsilyl-1,2,4-triazole (V) and 1-trimethylsilylimidazole (VI).



[(I) M = Si, R = CH_3;
(II) M = Si, R = C_2H_5;
(III) M = Si, R = OC_2H_5;
(IV) M = Ge, R = CH_3]



(V)

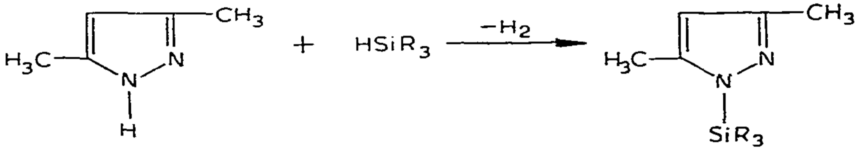


(VI)

Experimental

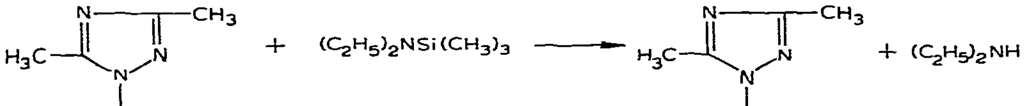
Synthesis

Compounds (I, IV and VI) were synthesized according to known methods [1, 4, 5]. Compounds (II and III) were synthesized by catalytic dehydrocondensation (eqn. 1). A more detailed description of the synthesis may be found elsewhere [6].



(1)

Compound (V) was obtained by reaction 2 [7].



(2)

NMR measurements

A Varian XL-100-15 NMR spectrometer equipped with a variable temperature probe was used for both ^1H and ^{13}C NMR spectra. Internal proton lock [$Si(CH_3)_3$ signal was used to provide the lock signal] and internal deuterium lock (DMSO-d_6) were used for proton and carbon spectra respectively. Chemical shifts are reported in ppm downfield from internal tetramethylsilane. Fourier transform techniques and proton band width noise decoupling were used to ob-

TABLE 1

PROTON CHEMICAL SHIFTS FOR THE COMPOUNDS (I—VI) [a]

Compound	Chemical shifts (δ-scale)				
	$3\text{-}CH_3$	$5\text{-}CH_3$	H2	H4	H4,5
(I)	2.12	2.18		5.71	
(II)	2.13	2.22		5.73	
(III)	2.20	2.33		5.75	
(IV)	2.17	2.17		5.72	
(IV) [b]	2.13	2.21		5.65	
(V)	2.20	2.34			
(VI)			7.65		7.11

[a] Chemical shifts were measured for neat liquids at ambient temperature and are reported in ppm downfield from internal TMS. [b] 10% molar solution in CCl_4.

tain ^{13}C NMR spectra. Temperature was measured using an ethylene glycol sample, the accuracy being ± 1°C.

Activation energy determinations

The values of the rate constant, $k = 1/2\,\tau$, were calculated by total line shape analysis based on the equations derived by Gutowsky and Holm [8] for the two-site exchange. The program was written for a Varian 620/F (16K) computer. Signals of the methyl carbons were used throughout, the C3 and C5 signals not being analyzed because these tertiary substituted nuclei have relatively large spin-lattice relaxation times T_1, hence the time which is necessary for the accumulation is significantly larger than that for the methyl carbons [9].

Results

Proton chemical shifts of the compounds (I—VI) are collected in Table 1.

We have found that the peak separation of the 3,5 methyl groups depends not only on the solvent and concentration [1] but also on the temperature; for the neat liquid, it increases with temperature. This phenomenon might be explained by self-association of the *N*-substituted azoles.

The signals of the ring methyls are slightly broadened because of the spin-coupling with proton H4. One of the peaks is a broadened singlet (an unresolved multiplet), the other is a doublet with small coupling (0.7 Hz). The doublet peak at lower field is assigned to the 5-methyl group since the C4—C5 bond is assumed to have a higher bond order compared with the C4—C3 bond. For the assignment in the case of 3,5-dimethyl-1-trimethylsilyl-1,2,4-triazole (V) we used the analogy with the assignment in *N*-substituted pyrazoles; the upfield resonance was assigned to the 3-methyl group. The absence of any noticeable spin-coupling constants from the ^1H NMR spectrum of the compound makes it impossible to assign the signals in any other way than by using the analogy with the pyrazole spectra. For the neat liquid of (IV) the 3,5-resonances were superimposed and we observed only one signal in the ^1H NMR spectrum. When the compound was dissolved in carbon tetrachloride or benzene the methyl groups became magnetically non-equivalent and two signals appeared in the spectrum.

TABLE 2

CARBON CHEMICAL SHIFTS FOR THE COMPOUNDS (I—VI) [a]

Compound	Chemical shifts (δ-scale)					
	C2	C3	C4	C4,5	C5	3-CH_3	5-CH_3
(I)		150.93	107.86		145.28	13.29	13.02
(II)		151.18	107.53		146.24	13.77	12.47
(III)		152.00	107.13		146.54	13.66	12.66
(IV)		149.97	106.56		144.60	14.10	12.82
(V)		163.10			150.17	15.42	15.26
(VI)	140.62			128.65			

[a] Chemical shifts were measured on neat liquids at ambient temperature and are reported in ppm downfield from internal TMS.

The ^{13}C NMR spectra of the compounds under study do not show any noticeable dependence of the carbon chemical shifts on temperature for the neat liquids, except for compound (V). As has been found recently CMR spectroscopy is a more convenient method for the study of dynamic processes than is PMR spectroscopy [10]. This is due to the absence of spin-multiplicity from the proton noise-decoupled ^{13}C NMR spectra and to a higher range of the carbon resonance frequencies. Another reason for application of carbon NMR spectroscopy is the independence of the carbon chemical shifts from temperature.

Carbon chemical shifts are presented in Table 2.

The signals of the following three groups of carbon nuclei can be assigned through the off-resonance decoupling: (1). The tertiary carbons C3 and C5. (2). The carbon C4 of the type =CH—. (3). The methyl carbons 3-CH_3 and 5-CH_3. A more detailed assignment of the signals of the C3 and C5 carbons and methyl carbons in the 3,5 positions may be accomplished with the help of the selective decoupling $^{13}C—\{^1H\}$, since the assignment of the signals in the ^1H NMR spectra is already known [1,4]. The assignment for the ^{13}C NMR spectrum of the compound (V) was performed in the same manner as for the PMR spectrum, i.e. by analogy with carbon spectra of *N*-substituted pyrazoles. The selective decoupling is hardly applicable in this case since the difference between the methyl carbon chemical shifts is relatively small (4 Hz).

In order to prove the intramolecularity of the metal migration in pyrazoles and the triazole we studied the influence of the solvent on the magnitude of the rate constant and found that the rate of migration of metal does not depend upon the solvent (carbon tetrachloride, nitrobenzene and anisole). For this reason, the process of metal migration in azoles shoud be considered intramolecular.

Both carbon and proton dynamic NMR spectra were used for the activation energy determination. Thermodynamic parameters of the silicon and germanium migration in azoles calculated for neat liquids are summarized in Table 3.

Our value of the activation energy for the compound (I) differs from that derived by O'Brien and Chang-Po-Hrung (E_a 28 kcal/mole). The value cited in Table 3 should be considered the more exact one because we used data of the two methods (^1H and ^{13}C) in a wide temperature range; also the rate constant calculations were performed by total line-shape analysis whereas the other authors used approximate formulae.

TABLE 3

THERMODYNAMIC PARAMETERS OF THE METAL MIGRATION IN THE 3,5-DIMETHYLAZOLES [a]

Compound	E_a (kcal·mol^{-1})	S (cal·mol^{-1}·K^{-1}
(I)	22.9 ± 0.8	6 ± 2
(II)	23.0 ± 0.8	7 ± 2
(III)	25.3 ± 0.8	13 ± 3
(IV)	20.0 ± 0.8	−2 ± 2
(V)	27.1 ± 0.9	16 ± 3

[a] The values of the rate constant were calculated at 40 to 140°. The Arrhenius ln k vs. $1/T$ plot was treated by the least squares method.

Activation energy of the silicon migration in the compound (III) is ca. 2.5 kcal/mole higher than in the other two silicon derivatives. A similar increase of the activation energy was found for the silicon migration in cyclopentadienyl compounds when the methyl groups attached to the silicon were replaced by chlorine atoms [11].

In the ^{1}H NMR spectrum of 1-trimethylsilylimidazole (VI) at room temperature an averaged signal of the protons H4 and H5 is observed. When the sample is cooled down to −80° no observable changes occur in the spectrum. The ^{13}C NMR spectrum also exhibits equivalence of the C4 and C5 carbons at room temperature; in addition, this averaged signal is slightly broadened; at as high as 100° the signal is still broadened*.

Cotton and Ciappenelli also noted equivalence of the resonance positions 4 and 5 in 3,5-dimethyl-1-trimethylgermyl- and 1-trimethylgermyl-imidazole over a wide temperature range (40 to 190°). They concluded that no intramolecular migration via a 1,2 shift took place in the compound although at the same time no reliable explanation was given for the equivalence of the positions 4 and 5. An explanation may be provided by a rearrangement of the trimethylsilyl group between two nitrogen atoms, which occurs even at −80°. One may assume that in this case we deal with a fast intermolecular exchange of the trimethylsilyl groups, similar to the proton intermolecular exchange in the unsubstituted pyrazole and imidazole [13, 14].

It is worthwhile to note that in the pyrazole compounds germanium migrates faster than silicon (see Table 3), as in the cyclopentadienyl and indenyl series [15]. These facts may be interpreted on the basis of a migratory aptitude concept previously proposed [15].

References

1 D.H. O'Brien and Chang-Po-Hrung, J. Organometal. Chem., 27 (1971) 185.
2 D.N. Kravtsov, L.A. Fedorov, A.S. Peregudov and A.N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 196 (1971) 110.
3 F.A. Cotton and D.J. Ciappenelli, Synth. in Inorg. Metal-org. Chem., 2 (1972) 197.
4 J. Elguero, M. Riviere-Beudet and J. Satge, C.R. Acad. Sci. Ser. C, 266 (1968) 44.
5 L. Birkofer, P. Richter and A. Ritter, Chem. Ber., 12 (1960) 2804.
6 N.A. Victorov, submitted for publication.
7 G.S. Goldin, M.V. Maksakova, V.G. Poddubny, A.N. Koltsova, A.V. Kisin, V.N. Torocheshnikov and A.A. Simonova, Zh. Obshch. Khim., 44 (1974) 115.
8 H.S. Gutowsky and C.H. Holm, J. Chem. Phys., 25 (1956) 1228.

---

* See Note added in proof.

9 T.C. Farrar and E.D. Becker, Pulse and Fourier Transform NMR, Academic Press, New York, 1971.
10 Yu.K. Grishin, N.M. Sergeyev, O.A. Subbotin and Yu.A. Ustynyuk, Mol. Phys., 25 (1973) 297.
11 N.M. Sergeyev, G.I. Avramenko, A.V. Kisin, V.A. Korenevsky and Yu.A. Ustynyuk, J. Organometal. Chem., 34 (1972) 93.
12 F.J. Weigert and J.D. Roberts, J. Amer. Chem. Soc., 90 (1968) 3543.
13 H. Zimmerman, Angew. Chem., Int. Ed. Engl., 3 (1964) 157.
14 M.L. Roumestant, P. Viallefont, J. Elguero and R. Jacquier, Tetrahedron Lett., (1969) 495.
15 Yu.N. Luzikov, N.M. Sergeyev, and Yu.A. Ustynyuk, J. Organometal. Chem., 65 (1974) 303.

Note added in proof

Our recent experiments indicate that this broadening may or may not be attributed to the nitrogen contribution in the carbon nuclei relaxation (similar to the relaxation in pyrrole [12]); however, our recent experiments using ^{14}N decoupling do not agree with this assumption, hence an alternative is that rather complicated intermolecular exchange processes affect the spectra of (VI).