MAGNETIC RESONANCE IN CHEMISTRY, VOL. 36, 110–115 (1998)

NMR Study of *C*- and *N*-Trimethylsilylazole Derivatives

Lyudmila I. Larina,* Mikhail S. Sorokin, Aleksandr I. Albanov, Valentina N. Elokhina, Nadezhda I. Protsuk and Valentin A. Lopyrev

Irkutsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, 1 Favorsky St., 664033 Irkutsk, Russia

Received 11 June 1997; revised 21 August 1997; accepted 22 August 1997

ABSTRACT: *C*- and *N*-trimethylsilylazole derivatives were studied by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. Degenerated prototropic tautomerism of 4-trimethylsilylpyrazole in methanol and the silylotropy of 1-trimethylsilyl-4-methylpyrazole in a neat liquid were investigated for the first time. 3- and 5-tautomers of 3(5)-methylpyrazole in a ratio of 54:46 were found in methanol by use ^{13}C NMR spectroscopy ($T_c = 230$ K, $\Delta G_c^{\neq} = 10$ kcal mol^{-1}). © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; ^{29}Si NMR; trimethylsilylazoles; tautomerism; silylotropy

INTRODUCTION

Recently we have carried out a dynamic NMR investigation of the silylotropy of some *N*-trimethylsilyl pyrazole derivatives and found the phenomenon of the catalyzed 1,2-migration of the trimethylsilyl group in 4-substituted 1-trimethylsilylpyrazoles.[1,2] At present there are few published data on the ^{1}H NMR spectra of *C*-trimethylsilyl derivatives of azoles such as 3(5)-trimethylsilylpyrazoles, 4-trimethylsilylpyrazoles,[3] 3(5),4-bis(trimethylsilyl)pyrazoles[4] and 4-nitro-5-trimethylsilylpyrazoles and 4-nitro-5-trimethylsilyl-1,2,3-triazoles.[5] In the case of *N*-trimethylsilylpyrazoles, the silylotropic rearrangement (1,2-exchange) of the trimethylsilyl group in 1-trimethylsilylpyrazole[6] and its 3,5-dimethyl-[6,7] and 3,4,5-trimethyl derivatives[6] has been studied. Syntheses of some *C*- and *N*-trimethylsilylazole derivatives have been described.[8–10]

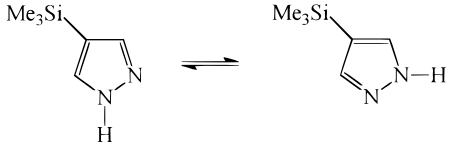
RESULTS AND DISCUSSION

Continuing our research on silylated azoles, in this work we synthesized and examined by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy some *C*- and *N*-trimethylsilylpyrazole derivatives (**1–9**), model analogs (**10** and **11**) (Table 1) and *N*-trimethylsilyl-1,2,3-triazoles (**12** and **13**) (Table 2).

As can be seen from Table 1 in *C*- and *N*-trimethylsilylated pyrazoles and their bis- and tris(trimethylsilyl) analogs the resonance of the *C*-trimethylsilyl group protons varies in the range 0.21–0.39 ppm whereas that of the *N*-trimethylsilyl group protons varies from 0.43 to 0.46 ppm. On introduction of the Me_3Si group into the pyrazole ring, the chemical shift of ring protons does not change much and is almost independent of the position of the Me_3Si group in the ring. The $\delta^{29}Si$ value for *C*-trimethylsilyl groups is observed in the range −9.3 to −11.0 ppm, whereas that of *N*-trimethylsilyl group occurs in the range 14–15 ppm. It should be noted that the ^{29}Si chemical shift of the trimethylsilyl group in the pyrazole ring position 3(5) of compound **2** does not differ much from that in the Me_3Si group in position 4 (compound **1**). At the same time, in compounds **3**, **4** and **5** the ^{29}Si chemical shifts of trimethylsilyl groups in positions 3 and 4 are 1 ppm different (see Table 1).

Pyrazole provides a convenient system for studying annular tautomerism and, therefore, the phenomenon of proton 1,2-migration in pyrazoles has been studied, in particular, by NMR spectroscopy.[11–16] Prototropic exchange processes in azoles are too fast on the NMR time-scale, so the technical difficulties encountered can be overcome by using solvents which allow prototropy to be followed at moderately low temperatures (e.g. methanol)[15] or even at room temperature (HMPA[16]). Taking into account the solvation properties of the latter, we did not use it in our research and chose methanol. We could observe degenerated prototropic tautomerism [Eqn (1)] of 4-trimethylsilylpyrazole (**1**), not investigated previously.

At room temperature there is only one resonance signal (7.57 ppm, CD_3OD) for the two protons in positions 3 and 5 of the pyrazole ring in **1** in the proton spectrum because of the fast proton migration between two nitrogen atoms (Table 1). On cooling the signal is progressively broadened and at −90 °C two well resolved signals are observed (7.70 and 7.56 ppm with regard to the nuclei H-3 and H-5, respectively). These signals coalesce at −44 °C. Then, at room temperature, there is



1 (1)

* *Correspondence to*: L. I. Larina, Irkutsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, 1 Favorsky St., 664033 Irkutsk, Russia.
E-mail: larina@irioch.irk.ru

CCC 0749–1581/98/020110–06 $17.50

Table 1. ^{1}H, ^{13}C and ^{29}Si NMR chemical shifts of C- and N-trimethylsilyl derivatives of pyrazole and some model analogs

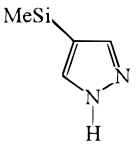
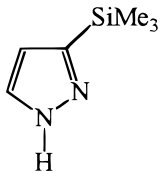
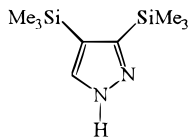
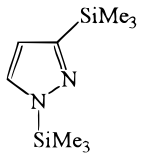
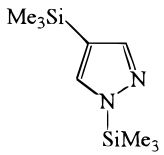
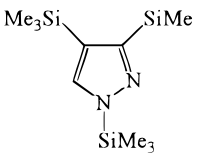
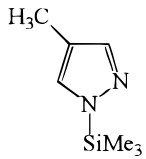
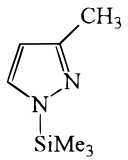
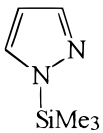
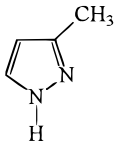
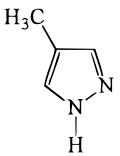
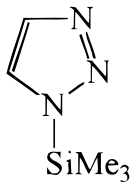
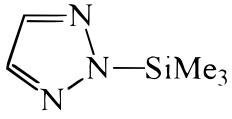
		$\delta^{1}H$ (ppm)					$\delta^{13}C$ (ppm)					
No.	Compound	H-3	H-4	H-5	$Si(CH_3)_3$	NH	C-3	C-4	C-5	$Si(CH_3)_3$	$\delta^{29}Si$ (ppm)	Solvent
1[a]		7.58 7.57 7.70 7.50[b]		7.58 7.57 7.56 7.50[b]	0.21 0.21 0.21 0.22[b]	12.97 14.78[b]	138.23	113.58	138.23	−0.22	−10.35	$CDCl_3$ CD_3OD CD_3OD (−90 °C)
2			6.40, 6.37[b]	7.64 7.62[b]	0.28 0.30[b]	12.99 13.78[b]	142.39	112.09	138.49	−1.06	−10.1	$CDCl_3$
3				7.66 7.60[c]	0.27, 0.39 0.30[c], 0.35[c]	10.88 12.60[c]	146.39	120.09	145.38	0.95, −0.15	−9.3, −10.3	$CDCl_3$
4			6.40	7.58	0.26, 0.44 C-Si, N-Si		156.76	112.22	133.55	−0.48, −0.80 C-Si, N-Si	−9.3, 13.92 C-Si, N-Si	$CDCl_3$
5		7.73 7.63		7.55 7.60	0.21, 0.46 0.17, 0.37 C-Si, N-Si		147.59 148.01	114.88 115.04	138.55 139.04	−0.28, −0.87 −0.06, 0.72 C-Si, N-Si	−10.7, 14.5 −11.1, 13.4 C-Si, N-Si	$CDCl_3$ Neat liquid
6				7.56	0.25, 0.31, 0.43		160.60	120.80	140.44	1.08, 0.30, −0.35	−11.0, 13.6 −8.2, C-Si, N-Si	$CDCl_3$

Table 1. *Continued*

No.	Compound	δ^1H (ppm) H-3	H-4	H-5	$Si(CH_3)_3$	NH	δ^{13}C (ppm) C-3	C-4	C-5	$Si(CH_3)_3$	δ^{29}Si (ppm)	Solvent
7[d]		7.53		7.39	0.40		144.82	116.86	132.86	−0.26	13.1	Neat liquid
8[e]			6.00	7.40	0.33		151.78	106.32	134.29	−0.85	12.9	Neat liquid
9[f]		7.73	6.28	7.56	0.44		142.85	106.71	133.29	−1.19	14.6	Neat liquid
10[g]			6.00	7.41			144.90	105.49	135.86			CD_3OD
11[h]		7.32 7.37		7.32 7.37		11.53	133.09 134.09	114.95 116.34	133.09 134.09			$CDCl_3$ CD_3OD

[a] $\Delta G_c^{\neq} = 11.9$ kcal mol^{-1} (1 kcal = 4.184 kJ) ($T_c = 229$ K, $\Delta\nu = 8.5$ Hz, CD_3OD).
[b] In CCl_4.[3]
[c] In CCl_4.[4]
[d] $\Delta G_c^{\neq} = 22.8$ kcal mol^{-1} ($T_c = 433$ K, $\Delta\nu = 12.5$ Hz), $\delta^1H(CH_3) = 2.08$ ppm.
[e] $\delta^1H(CH_3) = 2.21$ ppm;
[f] In $CDCl_3$.
[g] $\delta^1H(CH_3) = 2.23$ ppm, $\delta^{13}C(CH_3) = 12.17$ ppm.
[h] In $CDCl_3$, $\delta^1H(CH_3) = 2.04$ ppm, $\delta^{13}C(CH_3) = 8.50$ ppm in CD_3OD, $\delta^1H(CH_3) = 2.04$ ppm, $\delta^{13}C(CH_3) = 8.65$ ppm.

Table 2. ^{1}H, ^{13}C and ^{29}Si NMR chemical shifts of N-trimethylsilyl-1,2-3-triazoles

No.	Compound	$\delta^{1}H$ (ppm) H-4	H-5	$Si(CH_3)_3$	$\delta^{13}C$ (ppm) C-4	C-5	$Si(CH_3)_3$	$\delta^{29}Si$ (ppm)
12		7.92 7.07	7.92 6.98	0.58 0.25	132.70	126.59	−1.10	20.2
13		7.82 7.40	7.82 7.40	0.58 0.21	135.65	135.62	−1.32	22.0

one signal again. Hence, this temperature transformation is indicative of the dynamic exchange process of the N-H proton between the two nitrogen atoms in **1**. The exchange process barrier ($\Delta G_c^{\neq}$) of the N-H proton in 4-trimethylsilylpyrazole (0.2 mol l^{-1}, CD_3OD) is 11.9 kcal mol (Table 1). Previously[15] the $\Delta G_c^{\neq}$ values for 4-chloro- and 4-nitro-3,5-dimethylpyrazole were determined as 12.8 and 12.1 kcal mol^{-1} (CD_3OD), respectively. However, the concentrations at which $\Delta G_c^{\neq}$ values were determined were not reported.[15] We found $\Delta G_c^{\neq}$ to be greatly dependent on the pyrazole concentration (with increasing concentration $\Delta G_c^{\neq}$ diminishes and only in the 0.1–0.2 mol l^{-1} range is it nearly constant). An analogous $\Delta G_c^{\neq}$ dependence on azole concentration has also been observed earlier.[17] Moreover, the influence of concentration to the kinetic parameters of proton exchange in azoles has been studied.[18,19]

Removal of the tautomeric process degeneration in symmetrical pyrazoles by introducing a methyl group, for example, into the pyrazole ring at position 3(5) makes it possible to fix two tautomeric forms, those of 3- and 5-methylpyrazole, in the NMR spectra. The well understood 3(5)-methylpyrazole tautomerism [Eqn (2)][11,16,20] nevertheless attracts much attention.

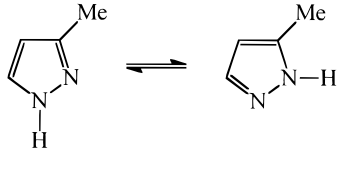
We found 3- and 5-tautomers of 3(5)-methylpyrazole in the ratio 54:46 by using ^{13}C NMR in methanol (−43 °C). The quantitative tautomer ratio was determined from ^{1}H and ^{13}C NMR spectra by the NNE technique (with proton decoupling and without Overhauser effect) (Table 1). Nearly the same tautomer ratio was observed in HMPA (at −17 °C).[16] The tautomeric process barrier for **10** determined from the coalescence of both ^{13}C signals of the CH_3 groups and C-3 and C-5 carbons (of both tautomers) is 10 kcal mol^{-1}, which is 4 kcal mol^{-1} lower than in HMPA [14 kcal mol^{-1} (Ref. 16)]. Slowing of the exchange process in HMPA seems to be due to the strong solvation properties of the latter.

As far as 3(5)-trimethylsilylpyrazole (**2**) is concerned [Eqn (3)], a decrease in the temperature of its solution in CD_3OD to −90 °C did not lead to NMR spectral changes. This seems to be indicative either of a very low prototropic exchange barrier in **2** or of the presence of only one tautomeric form, that of 3-trimethylsilylpyrazole. Quantum chemical calculations (AM1, MNDO) of the heats of formation of **2a** and **2b** show the 3-tautomer to be predominant in the gas phase (Table 3).

Analogous results were obtained for compounds **8** and **4**. For comparison, the results of same calculation on **10** are presented in Table 3, the ratio of 3-tautomer to the 5-tautomer being approximately equal. Nevertheless it is known that both 3(5)-nitropyrazole[11,21,22] and 3(5)-aminopyrazole[23] exist mainly as the 3-tautomer.

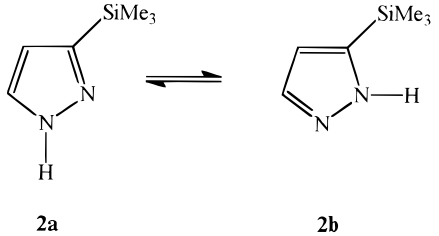
With increasing temperature, the Me_3Si group in *N*-trimethylsilylpyrazole derivatives is prone to reversible 1,2-migration.[1,2,6,7] In this study we found silylotropy of 1-trimethylsilyl-4-methylpyrazole (**7**) in the neat liquid. The silylotropy barrier (22.8 kcal mol^{-1}) in equilibrium (**4**) is comparable to that for the 1-trimethylsilylpyrazole[6] and 1-trimethylsilyl-3,5-dimethylpyrazole[6,7] studied earlier under similar conditions.

A study of 1,4-bis(trimethylsilyl)pyrazole (**5**) [Eqn (5)] under the same conditions did not lead to the expected



10a **10b**

(2)



2a **2b**

(3)

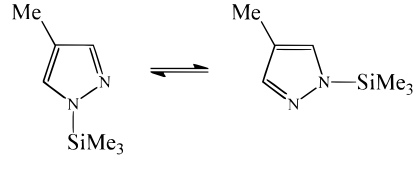
Table 3. Calculated heats of formation (ΔH) of 3- and 5-tautomers of some pyrazoles

Compound	Method	ΔH (kcal mol^{-1}) 3-Tautomer	5-Tautomer
2	AM1	17.207	18.990
	PM3	2.692	0.072
	MNDO	−13.459	−11.718
10	AM1	57.971	57.021
	PM3	39.564	38.572
	MNDO	34.023	34.019
8	AM1	0.221	0.847
	PM3	−22.840	−23.180
	MNDO	−35.881	−32.801
4	AM1	−40.237	−36.841
	PM3	−59.417	−60.683
	MNDO	−83.012	−72.119

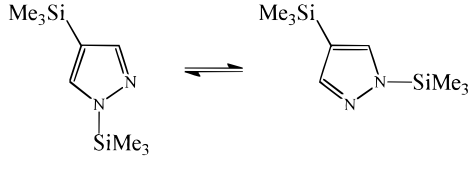
result, as we could not attain coalescence of the H-3 and H-5 proton signals ($T_c > 458$ K). A situation of this kind could be facilitated by the use of catalysts which diminish the silylotropy barrier as shown previously.[2] However, this problem is outside the scope of this work.

Opinions on *N*-trimethylsilyl-1,2,3-triazole reported in the literature are contradictory. Thus, for example, Birkofer and Wegner[24] suggested that the trimethylsilyl group in *N*-trimethylsilyl-1,2,3-triazole exchanges quickly between the N-1 and N-2 atoms. According to other data,[25] *N*-trimethylsilyl-1,2,3-triazole exists as 2-trimethylsilyl-1,2,3-triazole (2-tautomer). We performed the silylation of 1,2,3-triazole with hexamethyldisilazane [Eqn (6)] and found the *N*-silylated 1,2,3-triazole to exist as two isomers: 1-trimethylsilyl- (**12**) and 2-trimethylsilyl-1,2,3-triazole (**13**) in a 1:5 ratio, both in $CDCl_3$ solution and as the neat liquid (Table 2).

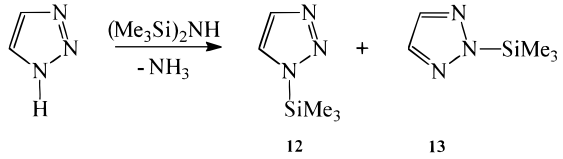
The tautomer ratio was determined from ^{13}C NMR spectra by means of the NNE technique. The data on ^{1}H, ^{13}C and ^{29}Si NMR spectra are presented in Table 2. These results are in agreement with *ab initio* calculations indicating that the 2H-tautomer of 1,2,3-triazole is preferred.[20]



(4)



(5)



(6)

EXPERIMENTAL

Spectra

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL FX 90 Q spectrometer at 89.55, 22.49 and 17.85 MHz, respectively. Chemical shifts (ppm) were measured relative to tetramethylsilane as an internal standard. The accuracy of chemical shift measurements was 0.01 ppm for ^{1}H, 0.02 ppm for ^{13}C, and 0.1 ppm for ^{29}Si. Samples were analyzed as neat liquids or in CD_3OD or $CDCl_3$ solution. Coupled ^{13}C NMR spectra were obtained by the gated decoupling method (NNE). The pulse sequence INEPT with refocusing pulses was utilized to obtain ^{29}Si spectra. Temperatures were measured to within 0.5 °C. $\Delta G_c^{\neq}$ values were calculated from an equation[26] using T_c (coalescence temperature) and $\Delta\nu$ (the difference in chemical shifts of two sites at T_c) with an accuracy of 0.5 kcal mol^{-1}. Quantum chemical calculations on azoles were carried out by AM1, MNDO and PM3 methods with full optimization of geometry.[27]

Compounds

Previously unknown *N*-trimethylsilyl-substituted pyrazoles (4–8) were prepared by silylation of the corresponding pyrazole derivatives with hexamethyldisilazane. With slight excess of the latter and in the presence of catalyst (saccharin) the reaction was completed within 0.5–1 h to give the target *N*-silylated pyrazoles (**4–8**) in virtually quantitative yields. The silylation of *C*-trimethylsilylpyrazoles with hexamethyldisilazane occurs as smoothly in the absence of any catalyst, but the reaction time is longer (3–4 h). All the *N*-trimethylsilylpyrazole derivatives are colorless oily liquids readily hydrolyzable in air to form the corresponding pyrazole derivatives and hexamethyldisiloxane. Unlike compounds **4** and **5**, compound **6** crystallizes when allowed to stand or on rapid cooling to 10–12 °C. In the air compound **6** crystallizes considerably more slowly.

4-Trimethylsilylpyrazole (1), 3(5)-trimethylsilylpyrazole (2) and 3(5),4-bis(trimethylsilyl)pyrazole (3). Compounds **1–3** were prepared by a described technique.[3,4]

1,3-Bis(trimethylsilyl)pyrazole (4). (a) A mixture of 6.5 g (0.046 mol) of 3(5)-trimethylsilylpyrazole (**2**), 4.5 g (0.028 mol) of hexamethyldisilazane and 0.01 g of saccharin was refluxed for 1 h. After vacuum distillation of the reaction mixture, 9.2 g of a colorless oily liquid was isolated in 96% yield.

(b) A mixture of 1.4 g (0.01 mol) of 3(5)-trimethylsilylpyrazole (**2**) and 1.6 g (0.01 mol) of hexamethyldisilazane was refluxed for 4 h.

Table 4. Analytical characteristics of C- and N-trimethylsilylpyrazole derivatives

Compound	Yield (%)	B.p. (°C/mmHg)	n_D^{25}	Found (%)				Calculated (%)			
				C	H	N	Si	C	H	N	Si
4	96.2	47–48/1.5	1.4592	51.21	10.01	13.14	26.58	51.29	9.48	18.18	26.43
5	98.5	64–65/1.5	1.4640	51.20	9.70	13.35	25.99	51.29	9.48	18.18	26.43
6	95.7	80–81/1.0	1.4710	50.81	10.16	10.15	29.21	50.63	9.91	9.84	29.60
7	66.7	50–51/5.0	1.4635	54.37	9.01	17.95	18.16	54.49	9.15	18.16	18.32
8	85.5	37–38/1.5	1.4620	54.28	8.94	18.01	18.21	54.49	9.15	18.16	18.32

After vacuum distillation of the reaction mixture, 2.1 g of 1,3-bis(trimethylsilyl)pyrazole was obtained (Table 4).

1,4-Bis(trimethylsilyl)pyrazole (5) and 1,3,4-tris(trimethylsilyl)pyrazole (6). Compounds **5** and **6** were prepared in an analogous manner, i.e. by silylation of 4-trimethylsilylpyrazole and 3(5),4-bis(trimethylsilyl)pyrazole, respectively (see Table 4).

3(5)-Methyl-1-trimethylsilylpyrazole (8). (a) A mixture of 9.5 g of 3-methylpyrazole and 10 g of hexamethyldisilazane was refluxed in an apparatus connected with a calcium chloride tube for 8 h. Distillation of the reaction mixture gave 15 g (*ca.* 84%) of the target product, a colorless oily liquid readily hydrolyzable with air moisture.

(b) Into a mixture of 10.4 g (0.1 mol) of the anhydrous sodium salt of 3-methylpyrazole (from 0.8 g of 3-methylpyrazole and 12.1 g of 33% aqueous NaOH solution) in 50 ml of anhydrous CH_3CN, 11.0 g of Me_3SiCl were dropped with stirring and cooling and the mixture was refluxed for 1 h. After separation of the NaCl residue the solvent and excess Me_3SiCl were distilled from the solution. After distillation of the residue under vacuum 13.2 g (85.5%) of 3(5)-methyl-1-trimethylsilylpyrazole (**8**) were isolated as a colorless oily liquid (Table 4).

1-Trimethylsilylpyrazole (9). This was synthesized by a published procedure.[6,8]

4-Methyl-1-trimethylsilylpyrazole (7). Compound **7** was prepared analogously to compound **9** (see Table 4).

3(5)-Methylpyrazole (10). This is a commercial product.

4-Methylpyrazole (11). Compound **11** was prepared by a published method.[28]

***N*-Trimethylsilyl-1,2,3-triazole (12) and (13).** A mixture of 6.9 g (0.1 mol) of 1,2,3-triazole and 10 g (0.06 mol) of hexamethyldisilazane was refluxed for 6 h. After vacuum distillation of the reaction mixture, 11.5 g (81.4%) of a fraction of b.p. 33–35 °C/12 mmHg (n_D^{25} 1.4520) was obtained as a colorless oily liquid containing 1- and 2-trimethylsilyl-1,2,3-triazoles in a 1 : 5 ratio.

REFERENCES

1. L. I. Larina, M. S. Sorokin, A. I. Albanov and V. A. Lopyrev, *XI International Symposium on Organosilicon Chemistry, Montpellier, France, September 1–6*, Abstract PC 25 (1996).
2. V. A. Lopyrev, L. I. Larina, A. I. Albanov, M. S. Sorokin and G. V. Dolgushin, *Izv. Akad. Nauk, Ser. Khim.* 3011 (1996).
3. L. Birkofer and M. Franz, *Chem. Ber.* **105**, 1759 (1972).
4. L. Birkofer and M. Franz, *Chem. Ber.* **100**, 2681 (1967).
5. J. C. Bottaro, R. J. Schmitt, C. D. Bedford, R. Gilardi and C. George, *J. Org. Chem.* **55**, 1916 (1990).
6. D. H. O'Brien and C. P. Hrung, *J. Organomet. Chem.* **27**, 185 (1971).
7. V. N. Torocheshnikov, N. M. Sergeyev, N. A. Victorov, G. S. Goldin, V. G. Poddubny and A. N. Koltsova, *J. Organomet. Chem.* **70**, 347 (1974).
8. M. Begtrup and P. Larsen, *Acta Chem. Scand.* **44**, 1050 (1990).
9. F. Effenberger and A. Krebs, *J. Org. Chem.* **49**, 4687 (1984).
10. D. Spinelli and P. Zanirato, *J. Chem. Soc. Perkin Trans. 2* 1129 (1993).
11. J. Elguero, C. Marzin, A. R. Katritzky and P. Linda, *The Tautomerism of Heterocycles*. Academic Press, New York (1976).
12. M. Begtrup, G. Boyer, P. Cabildo, C. Cativiela, R. M. Claramunt, J. Elguero, J. I. Garcia, C. Toiron and P. Vedso, *Magn. Reson. Chem.* **31**, 107 (1993).
13. C. Lopez, R. M. Claramunt, S. Trofimenko and J. Elguero, *Can. J. Chem.* **71**, 678 (1993).
14. J. Elguero, F. H. Cano, C. Foces-Foces, A. L. Llamas-Saiz, H.-H. Limbach, F. Aguilar-Parrilla, R. M. Claramunt and C. Lopez, *J. Heterocycl. Chem.* **31**, 695 (1994).
15. M. Perrin, A. Thozet, P. Cabildo, R. M. Claramunt, E. Valenti and J. Elguero, *Can. J. Chem.* **71**, 1443 (1993).
16. M. T. Chenon, C. Coupry, D. M. Grant and R. J. Pugmire, *J. Org. Chem.* **42**, 659 (1977).
17. I. D. Kalikhman, V. A. Lopyrev, E. F. Shibanova, V. A. Pestunovich and M. G. Voronkov, *Izv. Akad. Nauk, Ser. Khim.* 2390 (1977).
18. A. N. Nesmeyanov, E. B. Zavelovich, V. N. Babin, N. S. Kochetkova and E. I. Fedin, *Tetrahedron* **31**, 1463 (1975).
19. R. M. Claramunt, J. Elguero, C. Marzin and J. Seite, *An. Quim.* **75**, 701 (1979).
20. J. Catalan, M. Sanchez-Cabezudo, J. L. G. de Paz, J. Elguero, R. W. Taft and F. Anvia, *J. Comput. Chem.* **10**, 426 (1989).
21. A. I. Vokin, T. N. Komarova, L. I. Larina and V. A. Lopyrev, *Izv. Akad. Nauk. Ser. Khim.* 310 (1997).
22. A. Fruchier, V. Pellergrin, R. M. Claramunt and J. Elguero, *Org. Magn. Reson.* **22**, 473 (1984).
23. H. Dorn, *J. Prakt. Chem.* **315**, 382 (1973).
24. L. Birkofer and P. Wegner, *Chem. Ber.* **99**, 2512 (1966).
25. W. Peterson, B. Arkles and S. Washburne, *J. Organomet. Chem.* **121**, 2851 (1976).
26. M. Oki, *Application of Dynamic NMR Spectroscopy to Organic Chemistry*, p. 5. VCH, Deefield Beach, FL (1985).
27. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
28. V. T. Klimenko, T. V. Protopopova and A. P. Skoldinov, *Zh. Obshch. Khim.* **31**, 170 (1961).