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Study of the Addition of Diazoles to Vinylsilanes

V. D. Sheludyakov[a], N. E. Kuz'mina[b], A. M. Abramkin[a], D. A. Cheshkov[a], and P. A. Storozhenko[a]

[a] *State Research Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 38, Moscow, 105118 Russia*
e-mail: vdsh2004@yandex.ru

[b] *Research Center of Expert Assessment of Means for Medical Application, Moscow, Russia*

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Abstract—The reaction of trimethoxy(vinyl)silane with diazoles in the presence of metal lithium was studied. The structure of the reaction products was assigned by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si, COSY, NOESY, HMBC, and HSQC). An explanation for the different reactivities of reagents (aliphatic amines, diazoles, allylalkylsilanes, vinylalkylsilanes, and vinylalkoxysilanes) was provided.

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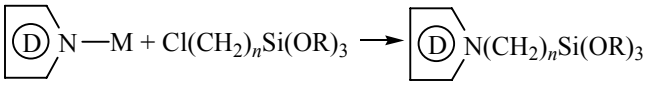
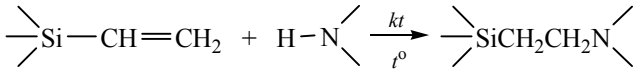
Carbofunctional organosilicon compounds with nitrogen-containing substituents occupy a respectable place among auxiliary substances in the chemistry and chemical engineering of silicon materials (curing catalysts, finishing agents for glass fiber, modifiers for silica, ceramics, glass, mica, paper, elastomers, etc.). Diazoles and their numerous derivatives, in their turn, present interest for medicine and agricultural chemistry due to their antioxidant, bactericide, fungicide, sedative, antitumor, psychopharmacological, and other biological activity. Therefore, synthesis of mixed compounds containing a silyl (R_3Si) and diazole (DN) components in a single molecule of the general formula $R_3Si(CH_2)_nND$, where $n \geq 1$, is quite interesting from the scientific viewpoint and hold promise from the applied viewpoint. Mutual effects of such different functions are the stronger the smaller n value. In the present work we studied the *N*-[β-(trimethoxysilyl)ethyl derivatives of imidazole and pyrazole which belong specifically to such series of compounds (n = 2). The so-called α- and γ-analogs are known since they are readily prepared by a classical scheme.



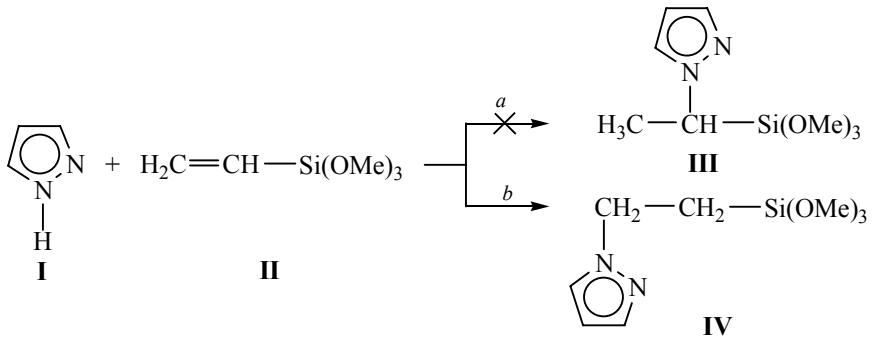
M = Na, Li; R = Me, Et; n = 1, 3.

β-Chloroethylsilanes are impossible to synthesize by this scheme in view of their susceptibility for β-elimination under the action of temperature and various reagents. At the same time, we could in principle approach this problem by synthesizing certain representatives of this series of compounds N-alkylation of diazoles with vinylalkoxysilanes [1].

As known, nucleophilic addition of nitrogen-containing compounds (primary, secondary, linear, and cyclic amines, including aziridine and diazoles) to vinylsilanes and vinylalkozysilanes forms β-(trialkylsilyl)ethyl and β-(trialkoxysilyl)ethyl derivatives of corresponding nitrogen-containing compounds [1–9]. The reaction occurs by the following scheme.



Reactivity studies showed that aliphatic amines exhibit a higher nucleophilic activity in this reactions than diazoles, the reaction with pyrazoles is more facile than with imidazoles, and the electrophilic activity of organosilanes decrease in the order $VinSi(OR)_3$ > $VinSiR_3$ > $AllSiR_3$. For example, there is a facile reaction between aliphatic amines (including azirine) and vinylsilanes $VinSiMe_3$ and $VinSiEt_3$, whereas diazoles fail to add to trimethyl(vinyl)silane in standard conditions. When the vinyl groups is replaced by allyl, the nucleophilic addition of aliphatic amines to organosilanes occurs poorer and at lower yields.



It was established that this reactions gives rise exclusively to β-adducts, even though formally two reaction routes are possible as illustrated below by the reaction of pyrazole **I** with trimethoxy(vinyl)silane (**II**).

Theoretical calculations of the thermodynamic parameters of reactions *a* and *b* showed that both routes are thermodynamically allowed.

The aim of the present work was to explain the different reactivity of reagents (aliphatic amines, diazoles, allylalkylsilanes, vinylalkylsilanes, and vinylalkoxysilanes), theoretically substantiate the reasons for the exclusive formation of β-adducts, and assess the preparative potential of the nucleophic addition of diazoles to vinylalkoxysilanes.

To estimate the nucleophilic and electrophilic hardness and softness of reagents, we calculated the energies of frontier orbitals: HOMO and LUMO. It is commonly accepted that HOMO energies directly correlate with ionization potentials and characterize the sensitivity of a molecule to electrophilic attack. The energies of LUMO correlate with electron affinities and characterize the sensitivity of a molecule to nucleophilic attack [10]. These energies play quite an important role for understanding routes of chemical reactions [11].

To identify reaction centers in reagent molecules and qualitatively estimate their reactivity, we performed quantum-chemical calculations of indices of frontier electron density, which characterize contributions of atomic orbitals into the HOMO and LUMO. On this basis we could reveal electrophilic and nucleophilic centers and estimate their activities inside a single molecule [12].

$$F^{H} C^{i} = \sum(C^{i}_{HOMO})^2 \times 100\%,$$

$$F^{L} C^{i} = \sum(C^{i}_{LUMO})^2 \times 100\%.$$

Here C^{i}_{HOMO} and C^{i}_{LUMO} are the contribution of an *i*th atomic orbital into the HOMO and LUMO, respectively.

To compare the frontier electron density indices in different molecules, these values are normalized to the energy of the corresponding frontier orbital [12].

$$F^{H}_{n} C^{i} = F^{H} C^{i}/|E_{HOMO}|,$$

$$F^{L}_{n} C^{i} = F^{L} C^{i}/|E_{LUMO}|.$$

Here E_{HOMO} and E_{LUMO} are the energies of the frontier orbitals.

We compared the electrophilic properties of trimethyl(vinyl)silane, allyltrimethylsilane, trimethoxy(vinyl)silane, and allyltrimethoxysilane. The LUMO energies and normalized contributions of the vinyl C^{α} and C^{β} atoms into the LUMO are shown in Table 1.

The calculations showed that the softest electrophile is $VinSi(OMe)_3$ and the hardest is $AllSiMe_3$, which correlates very well with experimental data. The LUMO energies of all the electrophilic reagents under consideration are mostly contributed by the p_z-AOs of vinyl carbon atoms. The largest contribution is from C^{β}, i.e. this atom is the most active electrophilic center, and it is preferentially attacked by a nucleophilic reagent. The electrophilic activity of C^{β} decreases in the order: $VinSi(OMe)_3 > VinSiMe_3 > AllSi(OMe)_3 > AllSiMe_3$. Thus, our analysis of the relative reactivities of the electrophilic centers in vinyl-containing alkyl- and alkoxysilanes provide a good rationalization of the exclusive formation of β-adducts.

As the nucleophilic reagents we used aziridine, pyrazole, and imidazole. In practice the addition of aliphatic amines and diazoles to $VinSiR_3$ and $VinSi(OR)_3$ is performed in the presence of a catalytic amount of lithium [1], which is suggested to induce formation of lithium salts of the corresponding nitrogen-

Table 1. Electrophilic properties of vinylsilanes (PM3 calculation)

Electrophile	E_{LUMO}, eV	$F^L C^\alpha$, %	$F_n^L C^\alpha$	$F^L C^\beta$, %	$F_n^L C^\beta$
$VinSiMe_3$	1.063	30.38	28.58	41.45	38.99
$AllSiMe_3$	1.155	24.25	20.99	31.13	26.95
$VinSi(OMe)_3$	0.869	19.47	22.41	34.18	39.33
$AllSi(OMe)_3$	0.944	27.70	29.34	33.19	35.16

Table 2. Nucleophilic properties of anions (PM3 calculation)

Nucleophile	E_{HOMO}, eV	$F^H N^1$, %	$F_n^H N^1$	$F^H N^2$,[a] %	$F_n^H N^2$
Aziridinate anion	–1.131	82.88	73.28	–	–
Pyrazolate anion	–3.420	15.07	4.41	15.20	4.44
Imidazolate anion	–3.104	3.23	1.04	3.24	1.04

[a] For the imidazole, N^2 relates to N^3.

containing compounds. With this in mind, we calculated the nucleophilic activities of anions rather than of the corresponding neutral molecules. The HOMO energies and normalized contributions of nitrogen AOs of nitrogen-containing anions into the HOMOs are listed in Table 2.

According to the calculations, the anions all are soft nucleophiles. This is evidenced by their high HOMO energies. For comparison, the HOMOs of neutral aziridine, pyrazole, and imidazole molecules are –10.326, –9.679, and –9.270 eV. The azidirinate anion is the most sensitive to reaction of electrophiles and the imidazolate ions is the least sensitive.

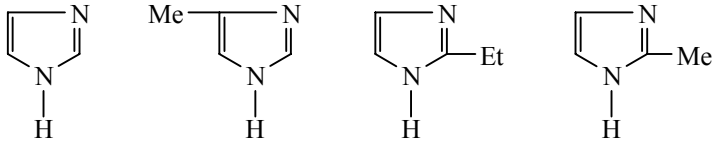
Analysis of the contributions of AOs into the HOMOs revealed a radical difference of the aliphatic amine from diazole. The HOMO of the aziridinate anion is formed primarily of the p_z-AO of the nitrogen atoma (its contribution is above 80%). The HOMOs of the diazole anions are mostly contributed of the p_z-AOs of the carbon atoms of the diazole ring. Thus, the total contribution of the p_z-AOs of the C^3 and C^5 atoms in the pyrazolate anion is 69.6%. Therewith, C^4 contributes nothing into the HOMO. The total contribution of all ring carbon p_z-AOs into the HOMO of the imidazolate anion is 93.6%. The p_z-AOs of the diazole nitrogens contribute less than the p_z-AO of the aliphatic nitrogen atom, and, therewith, this contribution the smallest in the imidazolate anion. It should be noted that the contributions of the two nitrogen atoms into the HOMO of the unsubstituted diazolate anion are almost equal to each other, and, therefore, these atoms are equivalent nucleophilic centers.

Thus, our estimates of the nucleophilic properties of nitrogen-containing anions, the nucleophilic activity of the nitrogen atoms in the diazolate anions is much lower compared to carbons, and therefore, the electrophilic attack by the N atoms can only take place if effective electrophiles like $VinSi(OR)_3$ are involved and reaction conditions are sufficiently rigid. By contrast, the nucleophilic activity of the nitrogen atom in the aliphatic amine anion is high, and it is a single nucleophilic center; therefore, successful electrophilic addition may take place with weaker electrophiles ($VinSiR_3$, $AllSiR_3$) and under milder conditions, and provide good yields.

Proceeding with research on the synthesis of novel derivatives of *N*-[β-(trimethoxysilyl)ethyl]diazoles by the nucleophilic addition reaction we have studied the reactions of trimethoxy(vinyl)silane with a wider range of substituted diazoles.

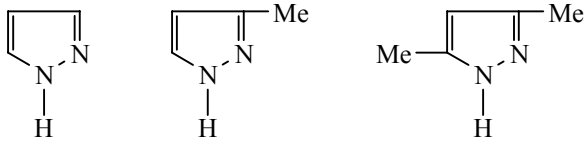
The general reaction scheme can be presented as follows. The reaction was performed by heating the reagent mixture to boiling. The catalyst was a finely dispersed stabilized metal lithium. The reaction progress was followed by the increase of the reaction

Imidazole and its derivatives



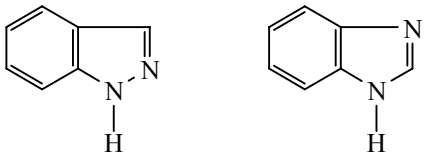
V **VI** **VII** **VIII**

Pyrazole and its derivatives



I **IX** **X**

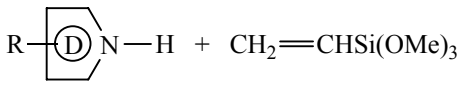
Benzodiazoles



XI **XII**

temperature. Completion of the reaction was established when the temperature no longer increased. The product was isolated by vacuum fractionation. The resulting data are listed in Table 3. The product yields varied from 45 to 86%. The yields of pyrazole derivatives were higher compared to imidazole analogs.

The structure of the synthesized silanes **XIII–XXI** was confirmed by elemental analysis and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra of isomer mixtures were assigned by means of homonucleus (^{1}H, ^{1}H-COSY, ^{1}H, ^{1}H-NOESY) and heteronucleus (^{1}H, ^{3}C-HSQC, ^{1}H, ^{13}C-HMBC) two-dimensional NMR spectroscopy (Figs. 1–6).



I, V–XII **II**

XIII–XXI

The reactions all resulted in exclusive formation of β-adducts. At the same time, unsymmetrically substituted diazoles gave isomeric mixtures of β-adducts. The formation of isomers is explained by prototropic transformations of the starting diazoles, which predetermine attack on the corresponding nitrogen atoms and lead to products **XIV** and **X**V which are readily differentiated by NMR spectroscopy. For example, the isomer ratios for 4- and 3-methylimidazoles are 2:1 and 1:1, respectively.

With condensed analogs of imidazole **V** and pyrazole **I**, specifically benzimidazole **XII** and indazole **XI**, respectively, too, β-adducts were obtained. Therewith, the indazole is alkylated by two nitrogen atoms to form a mixture of isomers: 1- and 2-[β-(trimethoxysilyl)ethyl]indazoles (**XIXa** and **XIXb**) in a 3:1 ratio.

Analysis of spectral characteristics of the synthesized positional isomers and their unsubstituted analogs gives insight into the interactions between the silyl and nitrogen-containing functional groups under the action of substituents of different nature in the pyrazole or imidazole rings.

The ^{1}H NMR spectra of $(MeO)_3SiCH_2CH_2ND$ reveal the following trends:

(a) varying substituents only slightly affects the $\delta(OC\underline{H}_3)$ value in the imidazole series **XIII, XVII**, and **XVIa**;

(b) the $SiC\underline{H}_2$ and $NC\underline{H}_2$ substituents in the ethylene bridge between the silyl and diazolyl substitutes show a different behavior in going from one diazole to another: The imidazole and pyrazole substituents deshield the $SiC\underline{H}_2$ group to the same

Table 3. Reaction conditions and properties of the resulting *N*-[β-(trimethoxysilyl)ethyl]diazoles

Comp. no.	Temperature, °C		Reaction time, h	Yield, %	bp, °C (mm Hg)	n_D^{20}
	initial	final				
XIII	123	195	20	54	133–135 (4)	1.4647
XIV	138	203	7	86	142–145 (23)	1.4585
XVa[a]	113	189	34	61	110–112 (3–4)	1.4576
XVb						
XVIa[b]	116	159	35	55	128–130 (3)	1.4660
XVIb						
XVII	120	171	33	49	111–112 (2)	1.4665
XVIII	124	180	16	56	110–112 (3)	1.4539
XIXa[c]	127	188	20	61	150–161 (3)	1.5170
XIXb						
XX	106	159	41	45	105–152 (2)	1.5446
XXI	120	176	16	47	118–119 (3)	1.4574

[a] A mixture of the 3- and 5-methyl derivatives. [b] A mixture of the 4- and 5-methyl derivatives. [c] A mixture of 1*H*-[2-(trimethoxysilyl)-ethyl]-1*H*-indazole and 2*H*-[2-(trimethoxysilyl)ethyl]-2*H*-indazole.

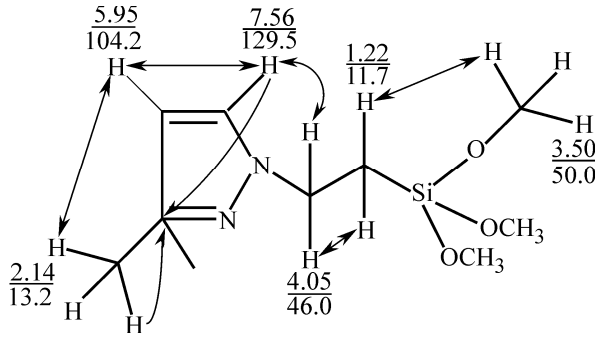


Fig. 1. HMBC, NOESY, and COSY correlations and assignment of signals (ppm) in the ^{1}H and ^{13}C NMR spectra of compound **XVa**.

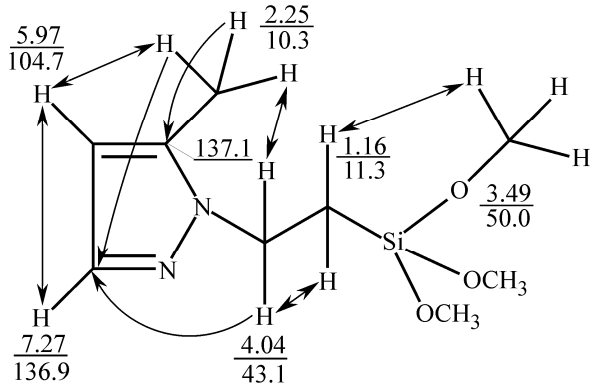


Fig. 2. HMBC, NOESY, and COSY correlations and assignment of signals (ppm) in the ^{1}H and ^{13}C NMR spectra of compound **XVb**.

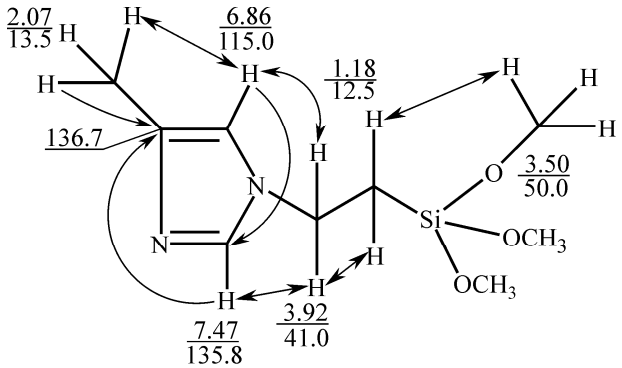


Fig. 3. HMBC, NOESY, and COSY correlations and assignment of signals (ppm) in the ^{1}H and ^{13}C NMR spectra of compound **XVIa**.

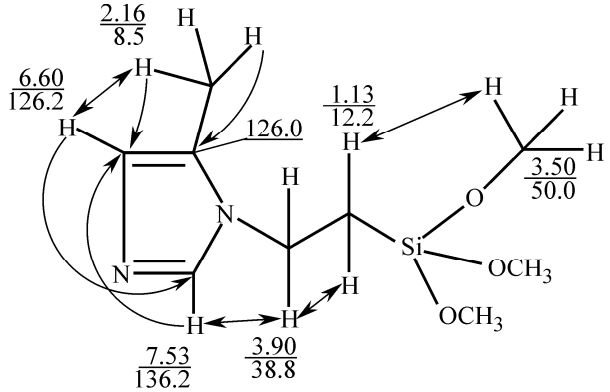


Fig. 4. HMBC, NOESY, and COSY correlations and assignment of signals (ppm) in the ^{1}H and ^{13}C NMR spectra of compound **XVIb**.

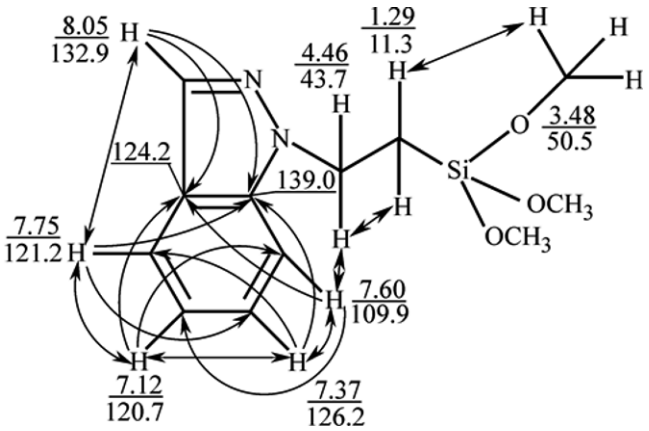


Fig. 5. HMBC, NOESY, and COSY correlations and assignment of signals (ppm) in the ^{1}H and ^{13}C NMR spectra of compound **XIXa**.

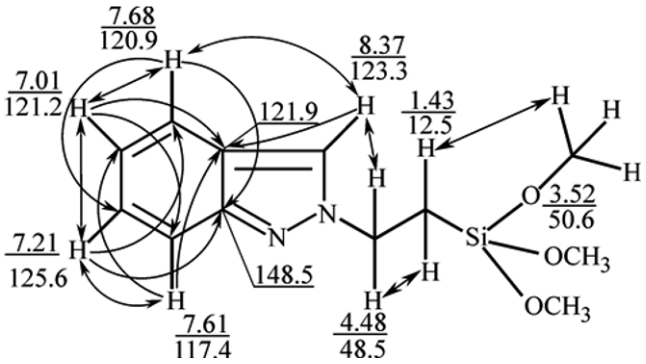
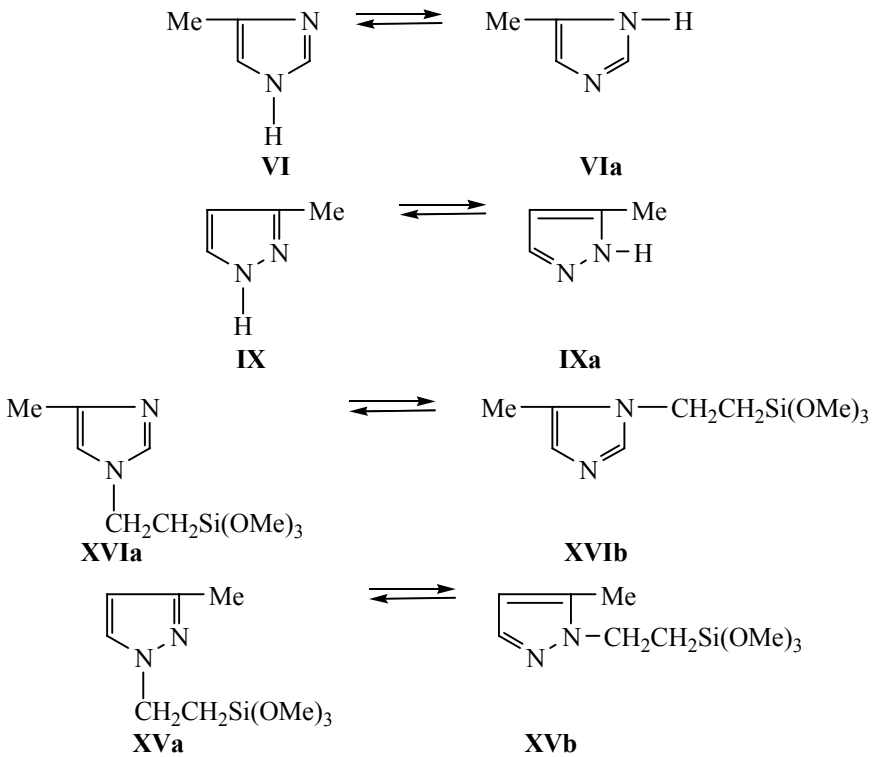
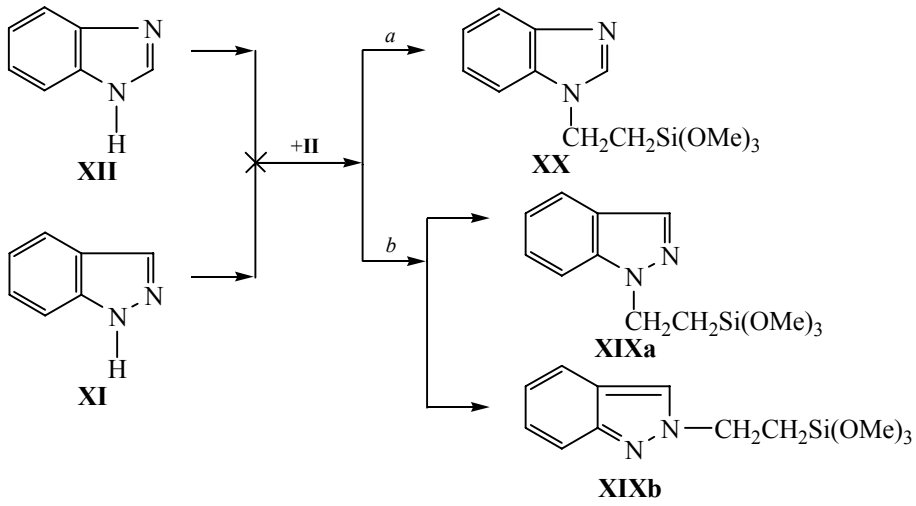


Fig. 6. HMBC, NOESY, and COSY correlations and assignment of signals (ppm) in the ^{1}H and ^{13}C NMR spectra of compound **XIXb**.

extent, whereas when the pyrazol group contains one or two methyl substituents, the δ(SiC$\underline{H}_2$) value remains almost unchanged.

Quite a different picture is observed in the series **XIII, XVII**, and **XVIa**: C-alkylation attenuates the deshielding effect on the SiC$\underline{H}_2$ hydrogens (1.17, 1.07, and 1.18 ppm, respectively). The NC$\underline{H}_2$ proton chemical shifts in the в imidazole series **XIII, XVII**, and **XVIa** (4.01, 3.86, and 3.92 ppm, respectively) reveal a slightly enhancing shielding effect due to the Me and Et substituents. In the pyrazole series **XVIII, XVa, XIV**, and **XVb** this effect is expressed to a lesser extent. Replacement of the imidazole ring by benzimidazole or of the pyrazole ring by indazole has almost no effect on δ(OC$\underline{H}_3$). At the same time, the deshielding of the NCH_2 protons is much enhanced: by 0.17 ppm in the first case and by 0.38 ppm in the second; as a result, the SiC$\underline{H}_2$ protons are also deshielded (by 0.04, 0.10, and 0.24 ppm).





It can be concluded that the diazole substituent in compounds of the general formula $(MeO)_3SiCH_2 \cdot CH_2ND$ exhibit a sharply expressed effect of deshielding of the ethylene bridge.

The carbon chemical shifts of the $O\underline{C}H_3$ group in the pyrazole, imidazole, benzimidazole, and indazole derivatives span a narrow range of 47.9–50.6 ppm, and those of the $Si\underline{C}H_2$ group vary from 9.9 to 12.5 ppm. The NCH_2 carbon shifts vary in opposite directions.

The ^{29}Si NMR spectra correspond to the composition and structure of the synthesized *N*-[β-(tromethoxysilyl)ethyl]diazoles. The δ_{Si} values span a narrow range of 45.2– 47.0 ppm.

Thus we showed that the nucleophilic activity of diazolate anions is lower compared with aliphatic amine anions, being distributed between the C and N centers and decreasing activity of each of these centers. The example of diazoles (pyrazoles, imidazoles, benzodiazoles) was used to study in detail the N-silylethylation reaction of diazoles with trimethoxy (vinyl)silane. It was found that the formation of β-adducts is general in nature, and in the case of 3-methylpyrazole, 4-methylimidazole, and indazole the β-adducts are formed as mixtures of isomers with the silyl substituents on different nitrogen atoms of the diazole ring.

The authors are grateful to A.V. Kisin and M.G. Kuznetsova for measuring the NMR spectra.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{29}Si NMR spectra in $CDCl_3$ were registered on a Bruker AM-360 spectrometer with at 360.13 (^1H), 90.55 (^{13}C), and 71.58 MHz (^{29}Si), respectively, at room temperature. The chemical shifts are given on the δ scale. The two-dimensional spectra (COSY, NOESY, HMBC, HSQC) were measured on a Bruker AVANCE-600 spectrometer using standard pulse sequences. The spectra were processed by means of Bruker TopSpin 2.1 software.

Three-dimensional models of electrophilic and nucleophilic reagents were constructed and quantum-chemical computations were performed using HyperChem-9 software [13]. Geometry optimization was performed in two stages: first by molecular mechanics (MM+ parametrization) [14] and then by the semiempirical PM3 method [15], to the gradient norm less than 0.1 kcal mol^{-1} A^{-1}. The electronic characteristics were computed by the semiempirical AM1 method [16, 17].

1-[2-(Trimethoxysilyl)ethyl]-1*H*-imidazole (XIII). A three-necked flask equipped with a thermometer and a reflux condenser was charged with 68 g (1.00 mol) of imidazole, 149 g (1.01 mol) of trimethoxy(vinyl)-silane, and 0.05 g of metal lithium was heated under reflux for 20 h. A homogeneous reaction mass formed, and its temperature increased from 123 to 195°C by the end of the experiment. Distillation gave 117 g of compound **XIII.** ^1H NMR spectrum ($CDCl_3$) δ, ppm: 1.17 m (2H, $SiCH_2$), 3.53 s (9H, OCH_3), 4.01 m (2H, NCH_2), 6.89 d.d (1H, H^5, ^3J 1.3, ^4J 1.2 Hz), 7.00 d.d (1H, H^4, ^3J 1.3, ^4J 1.2 Hz), 7.45 т (1H, H^2, ^4J 1.2 Hz). ^{13}C NMR spectrum, ($CDCl_3$) δ_C, ppm: 11.8 ($SiCH_2$), 40.7 (NCH_2), 49.2 (3C, OCH_3), 117.2 (C^5), 128.0 (C^4), 135.4 (C^2). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –45.2 ppm.

Compounds **XIV–XXI** were obtained in a similar way.

3,5-Dimethyl-1-[2-(trimethoxysilyl)ethyl]-1*H*-pyrazole (XIV). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 m (2H, $SiCH_2$), 2.20 s (3H, C^3CH_3), 2.21 s (3H, C^5CH_3), 3.55 s (9H, OCH_3), 4.04 m (2H, NCH_2), 5.74 br.s (1H, H^4). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 10.4 (CH_3), 11.5 ($SiCH_2$), 13.0 (CH_3), 43.0 (NCH_2), 50.0 (3C, OCH_3), 104.4 (C^4), 137.6 (C^3), 146.6 (C^5). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –46.8 ppm.

2-Ethyl-1-[2-(trimethoxysilyl)ethyl]-1*H*-imidazole (XVII). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 m (2H, $SiCH_2$), 1.27 t (3H, $CH_2C\underline{H}_3$, ^3J 7.5 Hz), 2.61 q (2H, $C\underline{H}_2CH_3$, ^3J 7.5 Hz), 3.50 s (9H, OCH_3), 3.86 m (2H, NCH_2), 6.77 d (1H, H^5, ^3J 1.3 Hz), 6.85 d (1H, H^4, ^3J 1.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 10.7 ($\underline{C}H_3CH_2$), 11.6 ($SiCH_2$), 18.7 ($CH_3\underline{C}H_2$), 39.2 (NCH_2), 49.1 (3C, OCH_3), 116.9 (C^5), 125.8 (C^4), 147.2 (C^2). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –46.8 ppm.

1-[2-(Trimethoxysilyl)ethyl]-1*H*-pyrazole (XVIII). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.19 m (2H, $SiCH_2$), 3.42 s (9H, OCH_3), 4.10 m (2H, NCH_2), 6.07 d.d (1H, H^4, ^3J 2.3, ^3J 1.9 Hz), 7.26 d.d (1H, H^3, ^3J 2.3, ^4J 0.7 Hz), 7.34 d.d (1H, H^5, ^3J 1.9, ^4J 0.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.1 ($SiCH_2$), 46.0 (NCH_2), 49.3 (3C, OCH_3), 104.1 (C^4), 127.3 (C^3), 137.9 (C^5). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –45.8 ppm.

3-Methyl-1-[2-(trimethoxysilyl)ethyl]-1*H*-pyrazole (XVa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.22 m (2H, $SiCH_2$), 2.14 d.d (3H, CH_3, ^4J 0.5, ^5J 0.4 Hz), 3.50 s (9H, OCH_3), 4.05 m (2H, NCH_2), 5.95 d.q (1H, H^4, ^3J 2.1, ^4J 0.5 Hz), 7.56 d.q (1H, H^5, ^3J 2.1, ^5J 0.4 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 11.7 ($SiCH_2$), 13.2 (CH_3), 46.0 (NCH_2), 50.0 (3C, OCH_3), 104.2 (C^4), 129.5 (C^5), 146.6 (C^3). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –45.2 ppm.

5-Methyl-1-[2-(trimethoxysilyl)ethyl]-1*H*-pyrazole (XVb). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.16 m (2H, $SiCH_2$), 2.25 d.d (3H, CH_3, ^4J 0.8, ^5J 0.5 Hz), 3.49 s (9H, OCH_3), 4.04 m (2H, NCH_2), 5.97 d.q (1H, H^4, ^3J 1.7, ^4J 0.8 Hz), 7.27 d.q (1H, H^3, ^3J 1.7, ^5J 0.5 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 10.3 (CH_3), 11.3 ($SiCH_2$), 43.1 (NCH_2), 50.0 (3C, OCH_3), 104.7 (C^4), 136.9 (C^3), 137.3 (C^5). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –45.4 ppm.

4-Methyl-1-[2-(trimethoxysilyl)ethyl]-1*H*-imidazole (XVIa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.18 m (2H, $SiCH_2$), 2.07 d (3H, CH_3, ^4J 1.1 Hz), 3.50 s (9H, OCH_3), 3.92 m (2H, NCH_2), 6.86 d.q (1H, H^5, ^4J 1.4, ^4J 1.1 Hz), 7.47 d (1H, H^2, ^4J 1.4 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 12.5 ($SiCH_2$), 13.5 (CH_3), 41.0 (NCH_2), 50.0 (3C, OCH_3), 115.0 (C^5), 135.8 (C^2), 136.7 (C^4). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –46.6 ppm.

5-Methyl-1-[2-(trimethoxysilyl)ethyl]-1*H*-imidazole (XVIb). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.13 m (2H, $SiCH_2$), 2.16 d (3H, CH_3, ^4J 1.1 Hz), 3.50 s (9H, OCH_3), 3.90 m (2H, NCH_2), 6.60 d.q (1H, H^4, ^4J 1.3, ^4J 1.1 Hz), 7.53 d (1H, H^2, ^4J 1.3 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 8.5 (CH_3), 12.2 ($SiCH_2$), 38.8 (NCH_2), 50.0 (3C, OCH_3), 126.0 (C^5), 126.2 (C^4), 136.2 (C^2). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –46.6 ppm.

2-Methyl-1-[2-(trimethoxysilyl)ethyl]-1*H*-imidazole (XXI). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.96 m (2H, $SiCH_2$), 2.21 s (3H, CH_3), 3.40 s (9H, OCH_3), 3.76 m (2H, NCH_2), 6.67 d (1H, H^5, ^3J 1.4 Hz), 6.71 d (1H, H^4, ^3J 1.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 10.2 (CH_3), 10.3 ($SiCH_2$), 38.6 (NCH_2), 47.9 (3C, OCH_3), 116.1 (C^5), 124.6 (C^4), 141.3 (C^2). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –47.0 ppm.

1*H*-[2-(Trimethoxysilyl)ethyl]-1*H*-indazole (XIXa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.29 m (2H, $SiCH_2$), 3.48 s (9H, OCH_3), 4.46 m (2H, NCH_2), 7.12 d.d.d (1H, H^6, ^3J 7.9, ^3J 6.8, ^4J 0.8 Hz), 7.37 d.d.d (1H, H^7, ^3J 8.1, ^3J 6.8, ^4J 1.2 Hz), 7.60 d.d.d.d (1H, H^8, ^3J 8.1, ^5J 1.1, ^5J 1.0, ^4J 0.8 Hz), 7.75 d.d.d (1H, H^5, ^3J 7.9, ^4J 1.2, ^5J 1.1 Hz), 8.05 d (1H, H^3, ^5J 1.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 11.3 ($SiCH_2$), 43.7 (NCH_2), 50.5 (3C, OCH_3), 109.9 (C^8), 120.7 (C^6), 121.2 (C^5), 124.2 (C^4), 126.2 (C^7), 132.9 (C^3), 139.0 (C^9). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –45.3 ppm.

2*H*-[2-(Trimethoxysilyl)ethyl]-2*H*-indazole (XIXb). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.43 m (2H, $SiCH_2$), 3.52 s (9H, OCH_3), 4.48 m (2H, NCH_2), 7.01 d.d.d (1H, H^6, ^3J 8.4, ^3J 6.6, ^4J 0.8 Hz), 7.21 d.d.d (1H, H^7, ^3J 8.7, ^3J 6.6, ^4J 1.3 Hz), 7.61 d.d.d.d (1H, H^8, ^3J 8.7, ^5J 1.1, ^5J 0.9, ^4J 0.8 Hz), 7.68 d.d.d (1H, H^5, ^3J 8.4, ^4J 1.3, ^5J 1.1 Hz), 8.37 d (1H, H^3, ^5J 0.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 12.5 ($SiCH_2$), 48.5 (NCH_2), 50.6 (3C, OCH_3), 117.4 (C^8), 120.9 (C^5), 121.2 (C^6), 121.9 (C^4), 123.3 (C^3), 125.6 (C^7), 148.5 (C^9). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –46.1 ppm.

1-[2-(Trimethoxysilyl)ethyl]-1*H*-benzimidazole (XX). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 m (2H, $SiCH_2$), 3.47 s (9H, OCH_3), 4.18 m (2H, NCH_2), 7.18 (1H, H^7, $^3J_{AC}$ 8.2, $^3J_{AB}$ 7.1, $^4J_{AD}$ 1.2 Hz), 7.20

(1H, H^6, $^3J_{BD}$ 8.1, $^3J_{AB}$ 7.1, $^4J_{BC}$ 1.0 Hz), 7.31 (1H, H^8, $^3J_{AC}$ 8.2, $^4J_{BC}$ 1.0, $^5J_{CD}$ –0.8 Hz), 7.72 (1H, H^5, $^3J_{BD}$ 8.1, $^4J_{AD}$ 1.2, $^5J_{CD}$ –0.8 Hz), 7.83 s (1H, H^2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 9.9 ($SiCH_2$), 38.4 (NCH_2), 48.8 (3C, OCH_3), 108.2 (C^8), 118.6 (C^5), 120.2 (C^7), 121.0 (C^6), 132.1 (C^9), 141.3 (C^4), 142.7 (C^2). ^{29}Si NMR spectrum ($CDCl_3$): δ_{Si} –46.7 ppm

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