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Unusual Course of Diazolees Silylation and N-Siloxycarbonylation

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Abstract—The N-siloxycarbonylation and transamination reactions were studied by an example of diazoles. We found that because of insufficient nucleophilicity of the nitrogen atoms in the first case only the silylation process occurs, in the second case the low-boiling amine is replaced by the higher boiling one and the process is completed by the formation of *O*-silyluretans.

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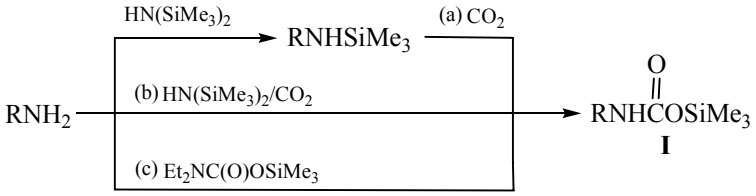
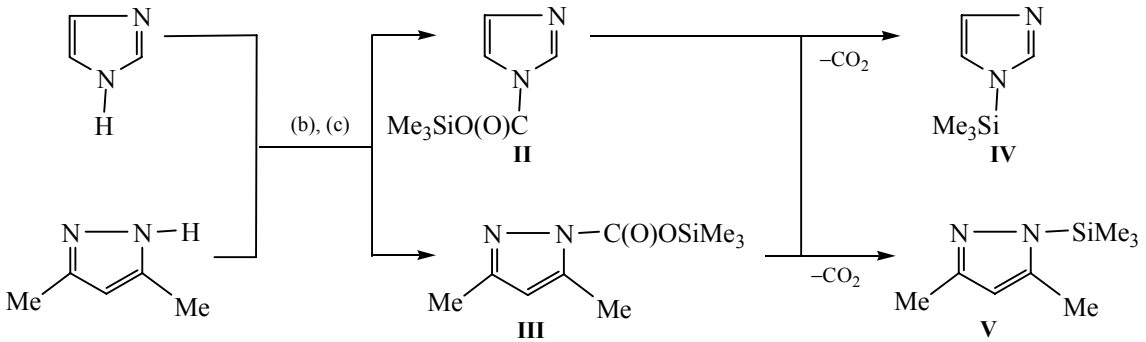
Earlier it was shown [1–3] that the *O*-silyluretans (**I**) can be obtained in the reactions of: (a) carboxylation, (b) *N*-siloxycarbonylation, and (c) transamination.



Synthesized by these routes compounds **I** are stable and do not decompose at heating up to 70–80°C. The analogous compounds of the $Et_2NC(O)OSiMe_3$ type completely substituted at the nitrogen atom are stable up to 108–113°C [4].

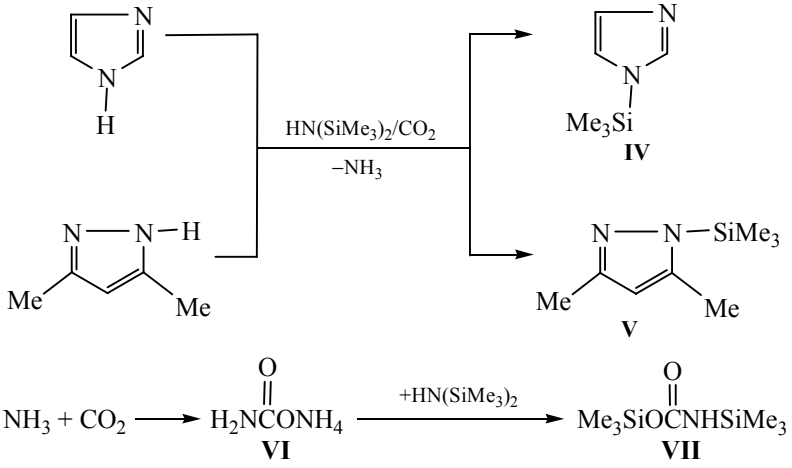
Only in the case of diazoles, which are formal analogs of the secondary amines, the *O*-silyluretans **II** by reactions (b) and (c), converting into the products of silylation **IV** and **V** [5].



(1)

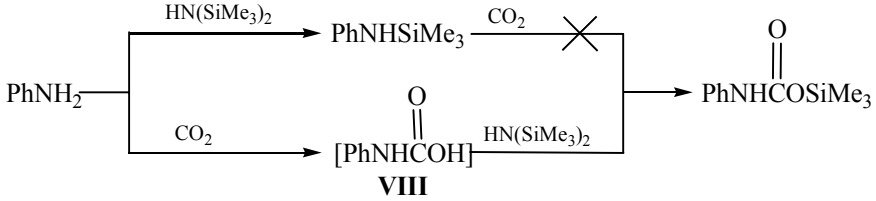
Since it is known that only thio analogs of *O*-silyluretans are unstable substances [1], we decided to study this process in detail. It turned out that the *O*-silyluretans **II** and **III** do not violate the established view of the thermal stability of these compounds. The mistaken belief [reaction (1)] is caused by the incorrect interpretation of the reaction results.

We found that the formation of products **IV** and **V** in the reaction (b) is not a consequence of elimination of carbon dioxide. In this case the silylation of diazoles unexpectedly occurs faster than their *N*-siloxycarbonylation [reaction (2)]. The released ammonia reacts with carbon dioxide to form ammonium carbamate, which under the reaction conditions undergoes silylation resulting in the *N*,*O*-bis(trimethylsilyl)carbamate **VII** by-product.



(2)

It is known that the reaction of N-siloxycarbonylation [2] proceeds through intermediate forma-tion of carbamic acid (**VIII**), whose proton is released from the carboxy group incomparably stronger than from the NH group. This leads to acceleration of the formation of *O*-silyluretanes and simultaneously reduces the impact of electronic and steric factors. This enables the formation of virtually any carbamates, even from aromatic amines.



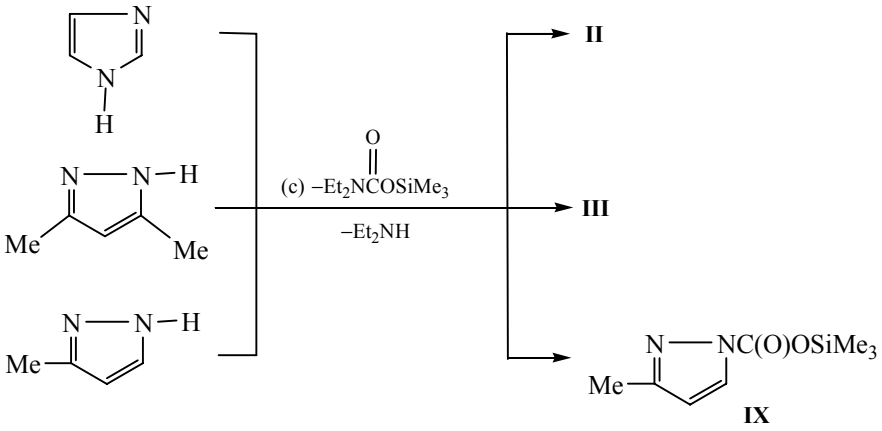
Therefore, obtaining the products of silylation rather than N-siloxycarbonylation in the reaction 2 suggests that this is caused by insufficient nucleophilicity of the diazole nitrogen atoms attacked by the electrophilic carbon atoms of the CO_2 molecule. Being, in turn, weak bases, the diazoles easily enter into silylation with hexamethyldisilazane, displacing ammonia which is a weaker base. The silylation process is accelerated due to the formation of ammonium carbamate **VI**, which catalyzes this process.

Note in particular that the use of imidazole, 3,5-dimethyl- and 3(5)-methylpyrazoles in transamination reaction is not accompanied, as previously stated [5], by release of carbon dioxide, and ends in the formation of *O*-silyluretans **II**, **III**, and **IX**.

In this case the nucleophilicity of the nitrogen atoms does not affect the course of process, since a transamination reaction of *O*-silyuretans proceeds accompanied by the displacement of low-boiling amine by a high-boiling one.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument. The ^{1}H NMR spectra were recorded on a Bruker WP-300 spectrometer with the operating frequency 300 MHz, solvent and internal reference trichloromethane-*d*.



All starting compounds and solvents were carefully purified and dried before use. Synthetic procedures and sampling for analysis of all the substances were carried out in the dry nitrogen atmosphere. The composition of reaction mixtures and pure compounds was monitored by GLC on a Shimadzu G-8 device (column 1500×3 mm of stainless steel, stationary phase SE-30 on Chromaton N-AW, carrier gas helium).

Trimethylsilyl 1*H*-imidazole-1-carboxylate (II). A mixture of 15 g of imidazole and 41.66 g of trimethylsilyl diethylcarbamate was heated at a complete reflux to complete release of diethylamine. By fractionation compound was isolated **II**, 36.88 g (91%), bp 100–101°C (2 mm Hg), n_D^{20} 1.4463. IR spectrum, ν, cm^{-1}: 3080 (C=CH), 1660 (C=O), 1520 (C=N). ^1H NMR spectrum, δ, ppm: 0.37 s (9H, $SiCH_3$), 6.95 s (2H, NCH), 7.6 s (1H, NCHN). Found, %: C 45.32; H 6.37; N 15.34. $C_7H_{12}N_2O_2Si$. Calculated, %: C 45.63; H 6.56; N 15.20.

Trimethylsilyl 3,5-dimethyl-1*H*-pyrazole-1-carboxylate (III). A mixture of 15g of 3,5-dimethylpyrazole and 29.56 g trimethylsilyl diethylcarbamate was heated at a complete reflux to the end of diethylamine release. By fractionation 30.81 g (93%) of compound **III** was isolated, bp 140–142°C (1 mm Hg), n_D^{20} 1.4483. IR spectrum, ν, cm^{-1}: 3180 (C=CH), 1690 (C=O), 1520 (C=N). ^1H NMR spectrum, δ, ppm: 0.44 s (9H, $SiCH_3$), 2.23 s (6H, CCH_3), 5.81 s (1H, CH). Found, %: C 50.92; H 7.55; N 13.31. $C_9H_{16}N_2O_2Si$. Calculated, %: C 50.91; H 7.60; N 13.19.

1-Trimethylsilyl-1*H*-imidazole (IV). Through a mixture of 15 g of imidazole and 19.20 g of hexamethyldisilazane was passed carbon dioxide for 20 h at 70°C. By fractionation 25.35 g (82%) of compound **IV** was isolated, bp 92–93°C (10 mm Hg), n_D^{20} 1.4745 [5].

3,5-Dimethyl-1-(trimethylsilyl)-1H-pyrazole (V). Through a mixture of 15 g of 3,5-dimethylpyrazole and 16.23 g of hexamethyldisilazane was passed carbon dioxide for 20 h at a temperature of 50–55°C. By fractionation 19.14 g (85%) of compound **V** was isolated, bp 77–78°C (10 mm Hg), n_D^{20} 1.4719 [5].

Trimethylsilyl-3(5)-methyl-1H-pyrazole-1-carboxylate (IX). A mixture of 20 g of 3(5)-methylpyrazole and 46.16 g of trimethylsilyl diethylcarbamate was heated at a complete reflux to the end of diethylamine release. By fractionation 44.47 g (92%) of compound **IX** was isolated, bp 93–95°C (10 mm Hg), n_D^{20} 1.4552. IR spectrum, ν, cm^{-1}: 3120 (C=CH), 1690 (C=O), 1520 (C=N). ^1H NMR spectrum, δ, ppm: 0.41 s (9H, $SiCH_3$), 2.29 s (6H, CCH_3), 6.01 s and 6.07 s (1H, CH), 7.43 s and 7.45 s (1H, CH). Found, %: C 48.65; H 7.23; N 14.41. $C_8H_4N_3O_2Si$. Calculated, %: C 48.46; H 7.12; N 14.13.

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