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Chemical Transformations of Diazoles in the Reactions of Carboxylation, *N*-Siloxycarbonylation, and Transsilylation

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Abstract—The behavior of 3,5-dimethylpyrazole, 3(5)-methylpyrazole, imidazole and their trimethyl-silyl derivatives in carboxylation, *N*-siloxycarbonylation, and transsilylation reactions was studied. A new *N*-siloxycarbonylation reagent, diazole trimethylsilyl derivative–carbon dioxide, was found. This reagent makes it possible to obtain easily *O*-silylurethanes starting from primary, secondary amines and hydrazine derivatives, as well as to develop a convenient one pot synthesis method for trimethylsiloxycarbonyldiazoles.

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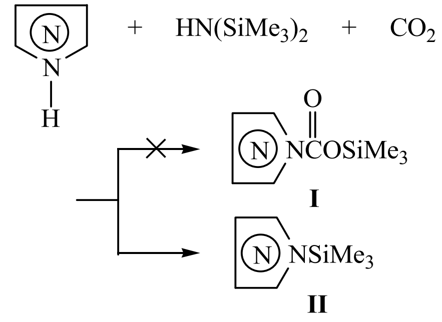
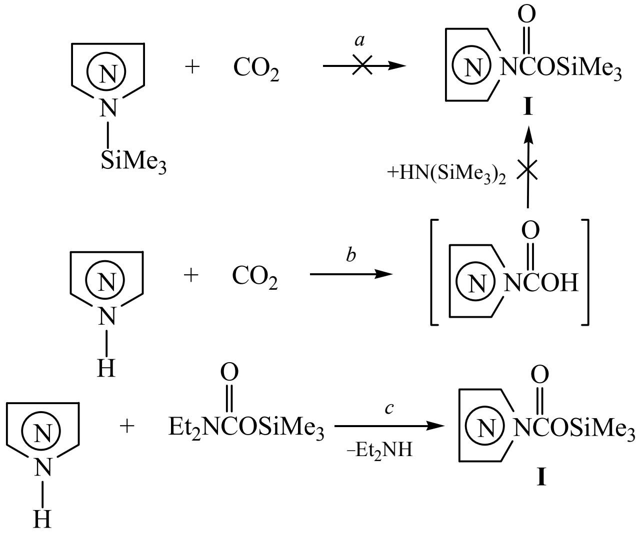
Previouslyit was shown that diazoles behaved unusually in *N*-siloxycarbonylation processes [1].

This universal reaction did not yield *O*-silylurethanes **I**: Always *N*-trimethylsilyl derivatives of diazoles **II** were obtained as the end products.



Impossibility to obtain *O*-silylurethanes **I** by carboxylation (*a*) and *N*-siloxycarbonylation (*b*) reactions was attributed to a low nucleophilicity of nitrogen atoms of diazoles attacked with electrophilic carbon atom of carbon dioxide.

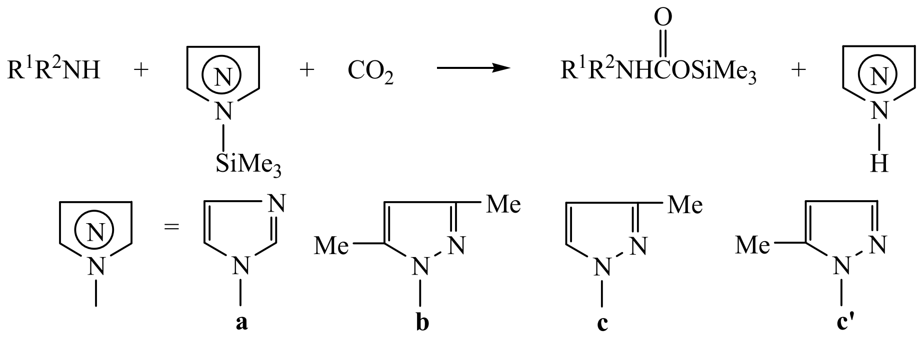
At the same time, these previously unavailable *O*-silylurethanes **I** were obtained via transamination of trimethylsilyl diethylcarbamate with diazoles (*c*) [2].



The inertness of *N*-trimethylsilyl-derived diazoles in the carboxylation reaction (*a*), along with their high silylating ability, allowed us discovering a new *N*-siloxycarbonylating agent.

It was found that not only the known systems HN $(SiMe_3)_2/CO_2$ [3] and R_3SiH/CO_2 [4] have *N*-siloxycarbonylating ability.

The system carbon dioxide–trimethylsilyl diazole derivative was found to easily provide *O*-silylurethanes from primary, secondary amines and hydrazine derivatives. Most importantly, this approach reduces the time of synthesis and increases the yield of the target

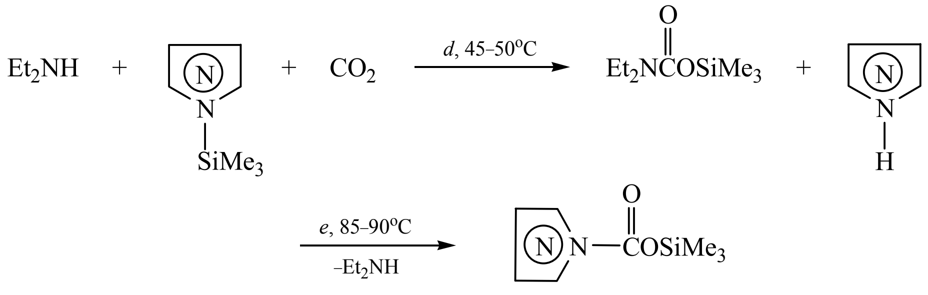


R^1 = Et, Ph, Me_2N; R^2 = H, Et.

product (see the table).

The first synthesis of *O*-silylurethanes **I** containing diazole fragments via the transamination reactions using trimethylsilyl diethylcarbamate and a discovery a new *N*-siloxycarbonylating reagent (*N*-trimethylsilyl diazole derivative–carbon dioxide) gave us an opportunity to develop a new method for synthesis of compounds **I**. This method involves two successive reactions taking place in one pot and excludes the need for intermediates isolation.

Since the trimethylsilyl derivatives of diazoles do not absorb carbon dioxide (reaction *a*), in the first stage the *N*-siloxycarbonylation reaction proceeds (*d*) using the system carbon dioxide–trimethylsilyl diazole derivative as the new *N*-siloxycarbonylating reagent to afford trimethylsilyl diethylcarbamate and the corresponding diazole.



Ia, Ib

The reaction temperature is 45–50°C, and the reaction time is 6–8 h.

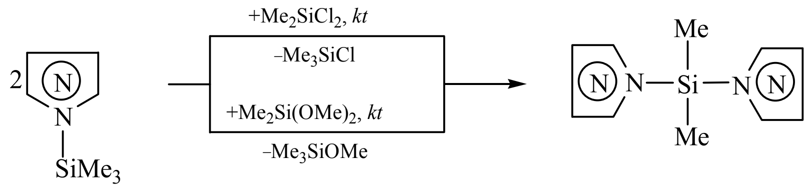
The formation of trimethylsilyl diethylcarbamate and diazole, the increase in the temperature to 85–90° C and removing diethylamine from the reaction zone favor the transamination process (*e*), which results in the formation of trimethylsilyl-1*H*-imidazole-1-carboxylate **Ia** and trimethylsilyl-3,5-dimethyl-1*H*-pyrazole-1-carboxylate **Ib** in high yields.

It should be noted that the proposed method excludes the preliminary synthesis and subsequent isolation of trimethylsilyl diethylcarbamate by *N*-siloxycarbonylation of diethylamine using a mixture $HN(SiMe_3)_2/CO_2$, which reduces the reaction time almost two times.

Trimethylsilyl group of diazoles is transsilylated

Conditions of the synthesis of *O*-silylurethanes using a mixture of *N*-siloxycarbonylating mixture 3(5)-methyl-1-trimethylsilyl-1*H*-pyrazole–carbon dioxide

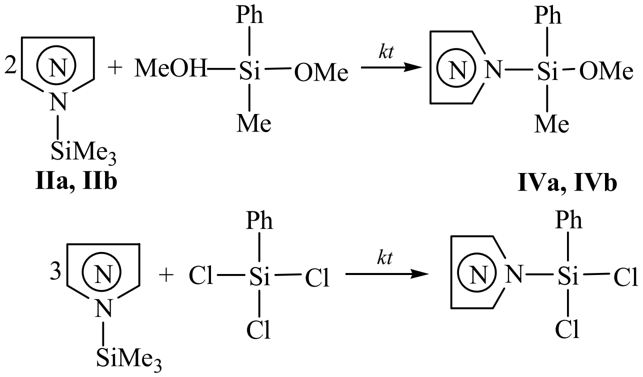
O-Silylurethane	Temperature, °C	Time, h	Yield, %	Yield, % with use of a mixture $HN(SiMe_3)_2$–CO_2
$Et_2NC(O)OSiMe_3$	50–55	1.5	97	87
$PhNHC(O)OSiMe_3$	60–65	2.5	93	41
$Me_2NNHC(O)OSiMe_3$	55–60	2.5	95	75



IIa, IIb **IIIa, IIIb**

with organochloro- and organoalkoxysilanes, allowing to obtain easily enough diazole-containing organosilicon products, like 1-[imidazol-1-yl(dimethyl)silyl]-1*H*-imidazole **IIIa** and 1-[(3,5-dimethyl-1-pyrazol-1-yl)dimethylsilyl]-3,5-dimethyl-1*H*-pyrazole **IIIb**.

At the same time, the use in this process of methylphenyldimethoxy- and phenyltrichlorosilane results in 1-[methoxy(methyl)phenylsilyl]-1*H*-imidazole **IVa**, 1-[methoxy(methyl)phenylsilyl]-3,5-dimethyl-1*H*-pyrazole **IVb**, 1-[dichloro(phenyl)silyl]-1*H*-imidazole **Va** and 1-[dichloro(phenyl) silyl]-3,5-dimethyl-1*H*-pyrazole **Vb**, i. e., in the reaction course only one chlorine atom or methoxy group is transsilylated.



IIa, IIb **IVa, IVb**

IIa, IIb **Va, Vb**

It should be noted that attempts to carry out an exhaustive transsilylation of alkoxysilanes **IVa**, **IVb** with the corresponding initial trimethylsilyl derivatives of diazoles **IIa**, **IIb** were not successful. In all cases, only starting compounds were isolated. Apparently, this is due to steric hindrances of phenyl substituent.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument. The ^{1}H NMR spectra were taken on a Bruker WP-300 spectrometer operating at 300 MHz in $CDCl_3$ solution using the residual proton signals as internal reference.

All starting materials and solvents were purified before use and thoroughly dried. Synthesis, isolation and sampling for analysis were performed in dry nitrogen atmosphere. Composition of the reaction mixtures and purity of compounds were monitored by GLC using a Shimadzu G-8 instrument (column 1500×3 mm, stainless steel, stationary phase SE-30 on Chromaton N-AW, carrier gas helium).

Trimethylsilyl-1*H*-imidazol-1-carboxylate (Ia). Through a mixture of 15 g of diethylamine and 28.77 g of 1-trimethylsilyl-1*H*-imidazole was bubbled carbon dioxide within 6 h at a temperature of 45–50°C. The mixture was then heated at 85–90°C for 5 h until the evolution of diethylamine completed. The target compound was isolated by fractionation. Yield 34.76 g (92% relative to the starting diethylamine), bp 100–102°C (2 mm Hg), n_D^{20} 1.4462 {published data [2]: bp 101–102°C (2 mm Hg), n_D^{20} 1.4463}.

Trimethylsilyl-3,5-dimethyl-1*H*-pyrazole-1-carboxylate (Ib) was prepared similarly from 15 g of diethylamine and 34.51 g of trimethylsilyl-1*H*-3,5-dimethylpyrazole. Yield 40.93 g (94% relative to the starting diethylamine), bp 140–141°C (1 mm Hg), n_D^{20} 1.4485 {published data [2]: bp 140–142°C (1 mm Hg), n_D^{20} 1.4483}.

1-[Imidazol-1-yl(dimethyl)silyl]-1*H*-imidazole (IIIa). A mixture of 18 g of trimethylsilyl-1*H*-imidazole **IIa** and 15.44 g of dimethyldimethoxysilane was heated in the presence of catalytic amounts of aluminum isopropoxide in a flask equipped with a full condensation distilling head until the evolution of trimethylmethoxysilane completed. The target compound was isolated by fractionation. Yield 16.29 g (81.2%), bp 107–109°C (1 mm Hg), n_D^{20} 1.4825. IR spectrum, ν, cm^{-1}: 3080 (C=CH), 1520 (C=N). ^{1}H NMR spectrum, δ, ppm: 0.47 s (6H, $SiCH_3$), 7.04 s (4H, CH), 7.61 s (2H, CH). Found, %: C 49.69; H 6.02; N 28.91. $C_8H_{12}N_4Si$. Calculated, %: C 49.97; H 6.29; N 29.14.

1-[(3,5-Dimethyl-1-pyrazol-1-yl)dimethylsilyl]-3,5-dimethyl-1*H*-pyrazole (IIIb) was prepared similarly from 11.80 g of trimethylsilyl-1*H*-3,5-dimethylpyrazole **IIb** and 9.03 g of dimethyldichlorosilane. $SnCl_4$ was used instead of aluminum isopropoxide. Yield 13.6 g (78.3%), bp 120–121°C (1 mm Hg), n_D^{20} 1.4943. IR spectrum, ν, cm^{-1}: 3140 (C=CH), 1540 (C=N). ^{1}H NMR spectrum, δ, ppm: 0.92 s (6H, $SiCH_3$), 2.24 s and 2.26 s (12H, CCH_3), 5.86 s (2H, CH). Found, %: C 57.84; H 8.17; N 22.48. $C_{12}H_{20}N_4Si$. Calculated, %: C 58.02; H 8.12; N 22.56.

1-[Methoxy(methyl)phenylsilyl]-1*H*-imidazole (IVa) was prepared similarly from 16 g of trimethylsilyl-1*H*-imidazole **IIa** and 10.39 g of methylphenyldimethoxysilane. Yield 10.67 g (85.7%), bp 94–96°C (2 mm Hg), n_D^{20} 1.5350. IR spectrum, ν, cm^{-1}: 3100 (C=CH), 1560 (C=N). ^{1}H NMR spectrum, δ, ppm: 0.75 s (3H, $SiCH_3$), 3.56 s (3H, OCH_3), 8.13 s, 7.39 s, 7.54 s (3H, CH), 7.47 t (1H, CH), 7.53 t (2H, CH), 8.01 t (2H, CH). Found, %: C 60.57; H 6.88; N 12.28. $C_{11}H_{14}N_2OSi$. Calculated, %: C 60.51; H 6.46; N 12.83.

1-[Methoxy(methyl)phenylsilyl]-3,5-dimethyl-1*H*-pyrazole (IVb) was prepared similarly from 15 g of trimethylsilyl-1*H*-3,5-dimethylpyrazole **IIb** and 9.74 g of methylphenyldimethoxysilane. Yield 10.6 g (84.4%), bp 128–130°C (2 mm Hg), n_D^{20} 1.5050. IR spectrum ν, cm^{-1}: 3110 (C=CH), 1540 (C=N). ^{1}H NMR spectrum, δ, ppm: 0.41 s (3H, $SiCH_3$), 2.28 s (6H, CCH_3), 3.58 s (3H, OCH_3), 5.52 m (1H, CH), 7.41 t (1H, CH), 7.55 t (2H, CH) and 8.06 t (2H, CH). Found, %: C 63.18; H 7.31; N 11.29. $C_{13}H_{18}N_2OSi$. Calculated, %: C 63.37; H 7.36; N 11.37.

1-[Dichloro(phenyl)silyl]-1*H*-imidazole (Va) was prepared similarly from 16.83 g of trimethylsilyl-1*H*-imidazole **IIa** and 8.47 g of phenyltrichlorosilane. $SnCl_4$ was used instead of aluminum isopropoxide. Yield 7.78 g (80%), mp 130–132°C. IR spectrum, ν, cm^{-1}: 3110 (C=CH), 1560 (C=N). ^{1}H NMR spectrum, δ, ppm: 7.29 s, 7.31 s, 8.79 s (3H, CH), 7.38 t (1H, CH), 7.33 t (2H, CH), 8.01 t (2H, CH). Found, %: C 44.39; H 3.12; N 11.44. $C_9H_8Cl_2N_2Si$. Calculated, %: C 44.45; H 3.32; N 11.52.

1-[Dichloro(phenyl)silyl]-3,5-dimethyl-1*H*-pyrazole (Vb) was prepared similarly from 20 g of trimethylsilyl-1*H*-3,5-dimethylpyrazole **IIb** and 8.38 g of phenyltrichlorosilane. $SnCl_4$ was used instead of aluminum isopropoxide. Yield 8.15 g (76%), bp 136–138°C (10 mm Hg), n_D^{20} 1.5482. IR spectrum, ν, cm^{-1}: 3120 (C=CH), 1590 (C=N). ^{1}H NMR spectrum, δ, ppm: 2.32 s and 2.38 s (6H, CCH_3), 6.01 s (1H, CH), 7.57 t (1H, CH), 7.59 t (2H, CH), 7.86 t (2H, CH). Found, %: C 48.57; H 4.41; N 10.24. $C_{11}H_{12}Cl_2N_2Si$. Calculated, %: C 48.71; H 4.46; N 10.33.

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