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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on the 65th Anniversary of His Birth

Synthesis of 5-Trimethylsilylethynyl-1,3,4-oxadiazoles

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Abstract—5-Trimethylsilylethynyl-2-R-1,3,4-oxadiazoles were synthesized for the first time by intramolecular cyclocondensation of unsymmetrical *N*-acyl-*N′*-(3-trimethylsilyl-2-propynoyl)hydrazines by the action of phosphoryl chloride.

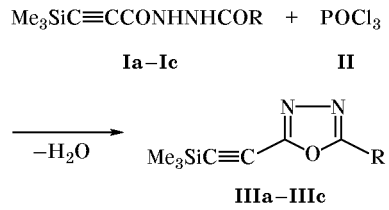
1,3,4-Oxadiazoles have found wide application in manufacture of dyes, pharmacology, and scintillation technique [1–3]. Polymeric oxadiazoles are used in the synthesis of heat-resistant materials [4], and liquid-phase lasers are developed on the basis of organic dyes [5–7]. The synthesis of picryl-substituted 1,3,4-oxadiazoles provides a way for utilization of trinitrotoluene [8]. Oxadiazoles are used as models for studying intramolecular interactions and structural–chemical design of new molecules with improved parameters [9]. Vigorous development of "Green Chemistry" has stimulated search for new methods of synthesis of 1,3,4-oxadiazoles under microwave irradiation [10, 11].

1,3,4-Oxadiazoles containing an acetylenic moiety were previously unknown. Introduction of a triple bond into the side chain of 1,3,4-oxadiazoles should considerably extend the spectrum of their chemical and physical properties and the range of their possible applications. Acetylenic 1,3,4-oxadiazoles can act as active dipolarophiles and electrophiles and monomers for the preparation of luminescent polymers. Removal of the C_{sp}-trimethylsilyl protection could lead to new 1,3,4-oxadiazoles with a terminal triple bond in the side chain.

Silylethynyl-substituted 1,3,4-oxadiazoles are potential biologically active substances and intermediate products for synthesis of new biologically active substances. We previously developed a procedure for the preparation of initial unsymmetrical trimethylsilylpropynoyl hydrazines [12]. Elaboration of a procedure for the synthesis of mono-silylethynyl-substituted 1,3,4-oxadiazoles will make it possible to synthesize their symmetric analogs, 2,5-bis(trimethylsilylethynyl)-1,3,4-oxadiazoles from 1,2-bis(trimethylsilylpropynoyl)hydrazines which were reported by us previously [13].

2-Substituted 5-trimethylsilylethynyl-1,3,4-oxadiazoles **IIIa**–**IIIc** were synthesized by cyclocondensation of *N*-acyl-*N′*-trimethylsilylpropynoylhydrazines **Ia**–**Ic** on heating with excess phosphoryl chloride (**II**) (Scheme 1).

Scheme 1.



R = Ph (**a**), 4-$O_2NC_6H_4$ (**b**), PhNH (**c**).

Crystalline oxadiazoles **IIIa**–**IIIc** were isolated in 45–56% yield by preparative chromatography on silica gel. When thionyl chloride was used as dehydrating agent, tarring of the reaction mixture occurred, and no target products were isolated. The structure of compounds **IIIa**–**IIIc** was confirmed by elemental analysis and IR and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. In the IR spectra of **IIIa**–**IIIc** we observed clearly defined absorption bands due to vibrations of the 1,3,4-oxadiazole ring [14]. Substituted 1,3,4-oxadiazoles **IIIa**–**IIIc** are characterized by almost the

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same set of IR absorption bands, in keeping with the experimental and calculated frequencies of unsubstituted 1,3,4-oxadiazole (**IV**): 1592, 1534, 1495, 1078, 951, and 650 cm^{-1} [14].

Vibrations of the Me_3Si group at the triple bond appear at 1240 and 840 cm^{-1} [15], and bands at 1530 and 1350 cm^{-1} belong, respectively, to asymmetric and symmetric stretching vibrations of the NO_2 group [16]. The aromatic fragment gives rise to a medium-intensity doublet at 1600/1585 cm^{-1}. Stretching vibrations of the triple C≡C bond are characterized by a weak band at 2170 cm^{-1} [15].

The presence of a nitro group in the *para*-position of the benzene ring $\{\sigma_I^*(NO_2) = 3.9$ [17, 18]$\}$ induces a high-frequency shift of the main absorption bands corresponding to vibrations of the oxadiazole ring. For example, the bands at 1592 and 1534 cm^{-1} in the IR spectrum of model oxadiazole **IV** are displaced to 1620 and 1550 cm^{-1}, respectively, in the spectrum of oxadiazole **IIIb**. The trimethylsilylethynyl fragment in molecules **IIIa**–**IIIc** is capable of participating in conjugation with unsaturated systems, and the experimental vibration frequencies depend on the overall contribution of inductive and mesomeric effects of the substituents in positions *2* and *5*.

The ^1H NMR spectra of **IIIa**–**IIIc** contain signals from protons of the trimethylsilyl group at δ 0.32–0.37 ppm and aromatic protons in the region δ 7.14–8.39 ppm with an intensity ratio of 2 : 2 : 1.

The C^5 and C^2 signals in the ^{13}C NMR spectrum of **IIIa** are located at δ_C 164.34 and 161.98 ppm, respectively. In going to compound **IIIb**, these signals shift upfield to δ_C 128.31 and 127.9 ppm, respectively, presumably due to the presence of a strong electron-acceptor substituent in the benzene ring. The silicon signals in the ^{29}Si NMR spectra appear at δ_{Si} –13.45 (**IIIb**) and –14.25 ppm (**IIIc**).

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrophotometer in KBr or mineral oil. The ^1H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker DPX-400 spectrometer from solutions in $CDCl_3$.

2-Phenyl-5-trimethylsilylethynyl-1,3,4-oxadiazole (IIIa). A mixture of 2 g (7.7 mmol) of diacylhydrazine **IIIa** and 6 g (39.1 mmol) of freshly distilled phosphoryl chloride was heated for 1 h at the boiling point. After cooling, the mixture was poured onto 150 g of finely crushed ice, and the precipitate was filtered off. The product was purified by preparative chromatography on Silpearl silica gel using chloroform–acetonitrile (10 : 1) as eluent. Yield 1.04 g (56%), beige crystals, mp 69–70°C. IR spectrum, ν, cm^{-1}: 2170, 1625, 1548, 1480, 1240, 1090, 930, 840, 685. ^1H NMR spectrum, δ, ppm: 8.13 d.d (2H, *o*-H), 7.53 m (3H, *m*-H, *p*-H), 0.32 s (9H, Me_3Si). ^{13}C NMR spectrum, δ_C, ppm: 164.34 (C^5), 161.98 (C^2), 130.03 (C^i,), 129.96 (C^o), 128.41 (C^p), 123.82 (C^m), –0.64 s (Me_3Si). Found, %: C 64.11; H 5.76; N 11.32; Si 11.34. $C_{13}H_{14}N_2OSi$. Calculated, %: C 64.43; H 5.82; N 11.55; Si 11.60.

2-(4-Nitrophenyl)-5-trimethylsilylethynyl-1,3,4-oxadiazole (IIIb) was synthesized in a similar way. Yield 52%, mp 153–154°C. IR spectrum, ν, cm^{-1}: 2170, 1620 w, 1550, 1530, 1475, 1350, 1240, 1090, 840, 690. ^1H NMR spectrum, δ, ppm: 8.39–8.30 m (4H, H_{arom}), 0.37 s (9H, Me_3Si). ^{13}C NMR spectrum, δ_C, ppm: 128. 34 (C^5), 127.90 (C^2), 128.23 (C^o), 128.09 (C^i), 124.56 (C^m), 124.3 (C^p, C^i), 107.61 (≡**C**C), 86.82 (Me_3Si**C**), –0.79 s (Me_3Si). ^{29}Si NMR spectrum: δ_{Si} –13.45 ppm. Found, %: C 54.38; H 4.82; N 14.30; Si 10.06. $C_{13}H_{13}N_3O_3Si$. Calculated, %: C 54.34; H 4.56; N 14.62; Si 9.77.

2-Phenylamino-5-trimethylsilylethynyl-1,3,4-oxadiazole (IIIc) was synthesized in a similar way. Yield 45%, mp 130–131°C. IR spectrum, ν, cm^{-1}: 3200, 2170, 1610 w, 1570, 1500, 1240, 1070, 900, 840, 690. ^1H NMR spectrum, δ, ppm: 7.98 br.s (1H, NH), 7.47 d.d (2H, *o*-H), 7.35 t (2H, *m*-H), 7.14 s (1H, *p*-H), 0.33 s (9H, Me_3Si). ^{13}C NMR spectrum, δ_C, ppm: 160.16 (C^5), 156.01 (C^2), 137.58 (C^i), 129.52 (C^o), 123.66 (C^p), 118.21 (C^m), 104.52 (≡**C**C), 87.24 (Me_3Si**C**), –0.84 s (Me_3Si). ^{29}Si NMR spectrum: δ_{Si} –14.25 ppm. Found, %: C 60.54; H 5.71; N 16.18; Si 10.79. $C_{13}H_{15}N_3OSi$. Calculated, %: C 60.67; H 5.88; N 16.32; Si 10.91.

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