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Synthesis of Unsymmetrical *N*-Acyl-*N′*-(3-trimethylsilylpropynoyl)hydrazines

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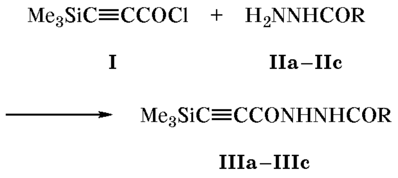
Abstract—Previously unknown unsymmetrical *N*-acyl-*N′*-(3-trimethylsilylpropynoyl)hydrazines were synthesized by reactions of 3-trimethylsilylpropynoyl chloride with aroylhydrazines and 4-phenylsemicarbazide.

Hydrazides are key starting compounds for synthesis of amines, aldehydes, diazo compounds, and heterocycles; they also exhibit versatile biological activity [1]. Some hydrazides were found as toxic components of *Gyromitra eskulenta* [2]. Tarasova and Moskva [3] recently revealed a new class of phosphinoylacetohydrazides which showed neurotropic activity; these include such preparations as *SARAN* and *Fosfabenzid*. Hydrazides are used as bidentate ligands in coordination compounds which are promising high-energy materials [4].

Silicon-containing α,β-acetylenic acylhydrazides have been studied poorly. Previously, we made attempts to synthesize monoacylhydrazines from 3-trimethylsilylpropynoic esters and hydrazine hydrate or phenylhydrazine, as well as by the action of 3-trimethylsilylpropynoyl chloride (**I**) on monosubstituted hydrazines. However, reactions of trimethylsilylpropynoates with hydrazines resulted in heterolytic cleavage of the $Si-C_{sp}$ bond and nucleophile addition at the triple bond to form pyrazol-5-one (from hydrazine hydrate) or ethyl 3-phenylhydrazonopropanoate (in the reaction with phenylhydrazine) [5]. Chloride **I** reacted with monoalkylhydrazines to give symmetrical 1,2-bis(trimethylsilylpropynoyl)hydrazines [6].

Scheme 1.



$$\underset{\textbf{I}}{Me_3SiC{\equiv}CCOCl} + \underset{\textbf{IIa–IIc}}{H_2NNHCOR} \longrightarrow \underset{\textbf{IIIa–IIIc}}{Me_3SiC{\equiv}CCONHNHCOR}$$

R = C_6H_5 (**a**), 4-$NO_2C_6H_4$ (**b**), NHC_6H_5 (**c**).

In the present work we examined the possibility for preparation of unsymmetrical diacylhydrazines of the general formula $Me_3SiC{\equiv}CCONHNHCOR$ (**IIIa**–**IIIc**, R = C_6H_5, 4-$NO_2C_6H_4$, NHC_6H_5) by acylation with trimethylsilylpropynoyl chloride **I** of less basic aroylhydrazines **IIa** and **IIb** and 4-phenylsemicarbazide (**IIc**). The reactions were carried out in methylene chloride or acetonitrile at 0–25°C, and the target diacylhydrazines were obtained in 68–87% yield (Scheme 1).

Compounds **IIIa**–**IIIc** were isolated as colorless crystalline substances, soluble in polar organic solvents (chloroform, acetonitrile, alcohol, and dimethyl sulfoxide). Their yields, melting points, and analytical data are given in Table 1. The structure of compounds **IIIa**–**IIIc** was confirmed by IR and NMR (^{1}H, ^{13}C, and ^{29}Si) spectroscopy (Tables 2, 3).

The IR spectra of crystalline products **IIIa**–**IIIc** (in KBr or mineral oil) contain bands typical of functional groups present in their molecules (Table 2). The bands were assigned on the basis of published data [1, 7–9]. The high-frequency carbonyl band (1675 cm^{-1}) was assigned to the aroyl fragment, in keeping with the known data for benzamides and anilides [7]. The low-frequency band at 1630 cm^{-1} was attributed to the $C{=}O$ bond conjugated with the triple bond; an analogous band was observed by us in the spectra of trimethylsilylpropynamides [10]. It should be noted that the carbonyl bands of **III** have complex shapes, presumably due to conformational isomerism and hydrogen bonding [11, 12]. The relatively low frequencies of NH stretching vibrations, observed for crystalline samples (3200–3250 cm^{-1}), considerably increase in going to solution (to 3380–3460 cm^{-1}). These data indicate participation of the

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Table 1. Yields, melting points, and elemental analyses of compounds **IIIa**–**IIIc**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	N	Si		C	H	N	Si
IIIa	87	178	59.92	6.44	10.62	10.46	$C_{13}H_{16}N_2O_2Si$	59.97	6.19	10.75	10.78
IIIb	68	144	50.82	4.76	13.76	8.82	$C_{13}H_{15}N_3O_4Si$	51.14	4.95	13.75	9.20
IIIc	74	173–174	57.03	6.25	14.95	10.13	$C_{13}H_{17}N_3O_2Si$	56.70	6.22	15.25	10.20

Table 2. IR spectra of compounds **IIIa**–**IIIc**, ν, cm^{-1}

Comp. no.	NH	C≡C	C=C$_{arom}$, δNH	Amide II (C=O), δNH	Amide I C=O	C–N, N–N	ν$_{as}$ SiMe$_3$	ν$_s$SiMe$_3$
IIIa	3200	2170	1600, 1590	1540	1675, 1630	1325, 1300	1250	840
IIIb	3250	2170	1600, 1580	1530	1675, 1650	1350, 1305	1255	850
IIIc	3200 3500	2170	1600, 1605	1550	1670, 1640	1330, 1305	1250	850

Table 3. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of compounds **IIIa**–**IIIc**, δ, ppm (DMSO-d_6, TMS)

Comp. no.	^{1}H	^{13}C	^{29}Si
IIIa	10.61 br.s (1H, NH), 10.42 s (1H, NH), 7.89 d (2H, *o*-H, Ph), 7.62 d.d (1H, *p*-H, Ph), 7.54 d.d (2H, *m*-H), 0.30 s (9H, SiMe$_3$)	165.20 (Ph**C**O), 151.21 (≡C**C**O), 132.15 (C^i), 131.97 (C^p), 128.49 (C^o), 127.46 (C^m), 97.10 (≡**C**CO), 92.50 (≡CSiMe$_3$), –0.82 (SiMe$_3$)	–10.70
IIIb	10.80 br.s (1H, NH), 8.90, 8.37 (4H, *AB* system, H$_{arom}$), 0.27 s (9H, SiMe$_3$)	163.82 (Ph**C**O), 151.16 (≡C**C**O), 149.52 (C^p), 137.75 (C^i), 128.94 (C^m), 123.73 (C^o), 96.93 (≡**C**CO), 92.96 (≡**C**SiMe$_3$), –0.85 (SiMe$_3$)	–13.76
IIIc	10.32 br.s (1H, NH), 8.80 br.s (1H, NH), 8.16 br.s (1H, NH), 7.44 d (2H, *o*-H), 7.27 d.d (2H, *m*-H), 6.97 d.d (1H, *p*-H), 0.26 s (9H, SiMe$_3$)	154.72 (Ph**C**O), 152.09 (≡C**C**O), 139.50 (C^i), 128.64 (C^o), 121.97 (C^p), 118.50 (C^m), 97.40 (≡**C**CO), 92.58 (≡**C**SiMe$_3$), –0.81 (SiMe$_3$)	–10.80

NH groups in formation of hydrogen bonds in crystal, which are broken on dissolution. Compounds **IIIa**–**IIIc** displayed no molecular ion peaks in the mass spectra. The most abundant peak is that from the rearranged $[Me_3SiNHNHCO]^+$ ion with *m/z* 151.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples pelleted with KBr, dispersed in mineral oil, or dissolved in chloroform. The ^{1}H, ^{13}C, and ^{29}Si spectra were obtained on a Bruker DPX-400 spectrometer in DMSO-d_6; the chemical shifts were measured relative to tetramethylsilane (TMS) as internal reference. The mass spectra were recorded on an LKB-2091 GC–MS system (SE-54 30-m capillary column; oven temperature programming at 16 deg/min; injector temperature 250°C; ion source temperature 240°C; accelerating voltage 2.33 kV; energy of ionizing electrons 60 eV). TLC analysis was performed on Silufol UV-254 plates using chloroform–methanol (10 : 1) as eluent, development with iodine vapor. The products were isolated by column chromatography on silica gel L, 40/100 μm (Chemapol), eluent chloroform–methanol (10 : 1). All solvents were preliminarily dehydrated.

***N*-Acyl-*N′*-(3-trimethylsilylpropynoyl)hydrazines IIIa–IIIc.** 3-Trimethylsilylpropynoyl chloride (**I**), 20 mmol, and triethylamine, 20 mmol, were added from different dropping funnels to a solution of compound **IIa**–**IIc**, 20 mmol, in acetonitrile. The mixture was stirred for 4 h and poured onto ice. The crystals were separated and purified by recrystallization or column chromatography on silica gel.

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