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(Butylsulfanyl)ethanal and 3-(Organylsulfanyl)butanal 1,1-Dimethylhydrazones

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Abstract — Previously unknown (butylsulfanyl)ethanal and 3-(organylsulfanyl)butanal 1,1-dimethylhydrazones were synthesized. Their reactivity toward methyl iodide was studied.

Certain N-substituted hydrazones have exhibited spasmolytic, hypotensive, and antitumor activity. Their use for treatment of schizophrenia, leprosy, and other diseases is being studied [1]. Over the past few years much attention has been given to 1,1-dimethylhydrazones, i.e. derivatives of 1,1-dimethylhydrazine, a component of rocket fuels [2–4]. In particular, certain 1,1-dimethylhydrazones serve as key starting materials in the synthesis of azapeptides [5, 6], antibiotics, such as cirzathiomycin [7], anthrimycin [8], azinothricyn [9], citropeptin [10], methamycin [11], as well as biologically active pyrazole derivatives [12] and muscarinic antagonists [13].

Proceeding with the research into aldehyde 1,1-dimethylhydrazones [14], as well as trialkoxysilyl and silatranyl derivatives of alkyl organyl sulfides [15–18], we have synthesized previously unknown (butylsulfanyl)ethanal 1,1-dimethylhydrazone (**II**) and 3-(organylsulfanyl)butanal 1,1-dimethylhydrazones **IV**–**XIV** and studied their reactions with methyl iodide. The yields, physicochemical properties, and elemental analyses of compounds **II**–**XIV** are listed in Table 1 and their structural formulas and spectral characteristics, in Table 2.

(Butylsulfanyl)ethanal 1,1-dimethylhydrazone (**II**) was synthesized by reaction of (butylsulfanyl)ethanal (**I**) with 1,1-dimethylhydrazine [scheme (1)].

$$\begin{aligned} &{}^{1}CH_3{}^{2}CH({}^{3}CH_2{}^{4}CH{=}NN({}^{5}CH_3)_2)\\ &\quad\quad|\\ &\quad\quad SH\\ &\longrightarrow BuSCH_2CH{=}NNMe_2 + H_2O. \quad (1)\\ &\quad\quad\textbf{II} \end{aligned}$$

The reaction was accomplished by mixing equimolar reagent amounts in benzene or with no solvent. It is accompanied by heat release and is complete within 10–15 min. The yield of hydrazone **II** attains 85% in both cases.

3-(Organylsulfanyl)butanal 1,1-dimethylhydrazones **V**–**XII** were synthesized by thiylation of the C=C bond in crotonaldehyde 1,1-dimethylhydrazone (**III**) with organic thiols, thiolcarboxylic acids, (sulfanylalkyl)trialkoxysilanes, and 1-(sulfanylalkyl)silatranes [scheme (2)]. The most vigorous reaction was observed with thiolcarboxylic acids. Mixing of thiolacetic or thiolbenzoic acids with 1,1-dimethylhydrazone **III** gives rise to a vigorous exothermic reaction that results in an almost quantitative formation of hydrazones **VII** and **VIII**, respectively. The reaction of hydrazone **III** with benzenethiol occurred less vigorously but still with heat release. The latter reaction involved an induction period of about 2 min and then exothermal reaction developed to form hydrazone **VI**. Ethanethiol could be added to crotonaldehyde 1,1-dimethylhydrazone (**III**) only under prolonged reflux (reagent molar ratio 1 : 3) or UV irradiation. However, the yield of product **V** in both cases was no higher than 40%.

$$\begin{aligned} &RSH + MeCH{=}CH{-}CH{=}NNMe\\ &\quad\quad\textbf{III} \quad (2)\\ &\longrightarrow MeCH(SR)CH_2CH{=}NNMe_2,\\ &\quad\quad\textbf{V}–\textbf{XII} \end{aligned}$$

R = Et (**V**), Ph (**VI**), MeCO (**VII**), PhCO (**VIII**), CH_2CH_2OH (**IX**), CH_2COOEt (**X**), $CH_2Si(OMe)_3$ (**XI**), $CH_2CH_2Si(OMe)_3$ (**XII**).

Successful thiylation of crotonaldehyde 1,1-dimethylhydrazone (**III**) with 2-sulfanylethanol, ethyl sulfanylacetate, trimethoxy(sulfanylmethyl)silane, trimethoxy(2-sulfanylethyl)silane, 1-(sulfanylmethyl)-silatrane, and 1-(2-sulfanylethyl)silatrane could only be effected by heating of a mixture of the corresponding reagents at 135–140°C for 2.5–3 h. Under these conditions, adducts **IX**–**XII** formed in high yields (Table 1). At the same time, the same reactions under UV irradiation at 35–40°C for 6 h gave no more than 10–15% of adducts **IX**–**XII**.

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Table 1. Physicochemical characterisitics and elemental analyses of hydrazones **II** and **IV**–**XIV**

Comp. no.	Yield, %	bp, °C (*p*, mm Hg)	n_D^{20}	Found, %				Formula	Calculated, %			
				C	H	N	S		C	H	N	S
II	85	80–81 (1.5)	1.4960	54.93	10.43	15.85	18.03	$C_8H_{18}N_2S$	55.13	10.41	16.07	18.39
IV	83	85–86 (9.0)	1.4990	49.37	9.21	19.01	21.56	$C_6H_{14}N_2S$	49.27	9.64	19.15	21.92
V	37	70–71 (1.5)	1.4965	54.81	10.18	15.88	18.02	$C_8H_{18}N_2S$	55.13	10.41	16.07	18.39
VI	78	117–119 (2.5)	1.5657	64.31	7.88	12.47	14.22	$C_{12}H_{18}N_2S$	64.82	8.16	12.60	14.42
VII	90	95–96 (1.5)	1.5018	50.78	8.23	14.47	16.78	$C_8H_{16}N_2OS$	51.03	8.56	14.88	17.02
VIII	92	115–116 (1.5)	1.5675	61.86	6.94	10.87	12.65	$C_{13}H_{18}N_2OS$	62.37	7.25	11.19	12.81
IX	87	120–121 (1.5)	1.5180	50.02	9.14	14.28	16.37	$C_8H_{18}N_2OS$	50.49	9.53	14.72	16.85
X	85	115–116 (1.0)	1.4920	51.36	8.43	11.88	13.62	$C_{10}H_{20}N_2O_2S$	51.69	8.68	12.06	13.80
XI	78	135–136 (1.5)	1.4760	42.31	8.27	9.62	11.09	$C_{10}H_{24}N_2O_3SSi$	42.82	8.63	9.99	11.41
XII	70	147–148 (1.5)	1.4730	44.31	8.41	9.36	10.39	$C_{11}H_{26}N_2O_3SSi$	44.86	8.90	9.51	10.89
XIII	96	80–82[a]	–	46.38	7.87	12.36	9.36	$C_{13}H_{27}N_3O_3SSi$	46.82	8.16	12.60	9.61
XIV	94	[b]	–	48.01	8.17	11.87	9.06	$C_{14}H_{29}N_3O_3SSi$	48.38	8.41	12.09	9.22

[a] Melting point. [b] Viscous oil.

3-[2-(Trimethoxysilyl)ethylsulfanyl]butanal 1,1-dimethylhydrazone (**XII**) was also synthesized by addition of 3-sulfanylbutanal 1,1-dimethylhydrazone (**IV**) to trimethoxy(vinyl)silane [scheme (3)].

$$\mathbf{IV} + CH_2{=}CHSi(OMe)_3 \longrightarrow \mathbf{XII}. \quad (3)$$

The reaction was accomplished by heating of equimolar reagent mixture at 135–140°C. However, the yield of thus obtained adduct **XII** after 3 h was no higher 35%.

Previously unknown 3-sulfanylbutanal 1,1-dimethylhydrazone (**IV**) was synthesized from acetylsulfanyl derivative **VII** in methanol under reflux in the presence of a catalytic amount of sodium methylate.

Hydrazones **II** and **IV**–**XII** are viscous colorless or light yellow liquids with a characteristic strong unpleasant odor.

Silatranes **XIII** and **XIV** were synthesized by transetherification of 3-(trimethoxysilyl)methylsulfanyl)- and 3-[2-(trimethoxysilyl)ethylsulfanyl]butanals (**XII**, **XIII**) with tris(2-hydroxyethyl)amine [scheme (4)]. The reaction was accomplished by heating (120–130°C) of equimolar reagent mixture of the corresponding reagents in the presence of a catalytic amount of sodium methylate.

$$\mathbf{XI, XII} + (HOCH_2CH_2)_3N \longrightarrow \mathbf{XIII, XIV} + 3MeOH. \quad (4)$$

3-(Silatranylmethylsulfanyl)butanal 1,1-dimethylhydrazone (**XIII**) is a colorless crystalline substance, whereas its homolog **XIV** was obtained as a thick light yellow syrup that could not be crystallized even upon prolonged handling in the cold.

The ^1H and ^{13}C NMR spectra of silatranyl derivative **XIV** show that it contains a small admixture of the starting compounds. On attempted purification by vacuum distillation hydrazone **XIV** decomposed to form 1-(2-sulfanylethyl)silatrane (**XV**) [scheme (5)–(7)].

$$\mathbf{XIV} \xrightarrow{\Delta} MeCHCH_2CH{=}NNMe_2 + \dot{S}(CH_2)_2Si(OCH_2CH_2)_3N, \quad (5)$$

$$Me\dot{C}HCH_2CH{=}NNMe_2 \longrightarrow \underset{\mathbf{III}}{[MeCH{=}CHCH{=}NNMe_2]} + H^{\cdot}, \quad (6)$$

$$H^{\cdot} + \dot{S}(CH_2)_2Si(OCH_2CH_2)_3N \longrightarrow \mathbf{XV}. \quad (7)$$

This reaction occurs above 200°C, probably, by a free-radical mechanism. Along with 1-(2-sulfanylethyl)silatrane (**XV**), crotonaldehyde 1,1-dimethylhydrazone (**III**) is formed and undergoes tarring under the reaction conditions.

Because of the thermal instability of 1,1-dimethylhydrazone **XIV**, we failed to synthesize it by adding (2-sulfanylethyl)silatrane (**XV**) to the C=C bond in hydrazone **III**. Heating of equimolar reagent mixture at 145–150°C for 3 h resulted in no adduct **XIV** formation, and at 180–200°C tarring of the reaction mixture was observed. For qualitative assessment of the ability of the S and N atoms in organic (**II**, **V**–**X**) and organosilicon (**XI**–**XIV**) 3-sulfanylbutanal 1,1-

Table 2. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of hydrazones **II**–**XIV**

Comp. no.	Structure	^{1}H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
II	$^{1}CH_3{}^{2}CH_2{}^{3}CH_2{}^{4}CH_2S{}^{5}CH_2{}^{6}CH{=}NN(^{7}CH_3)_2$	0.82 t (3H, C^1H_3), 1.33 sextet (2H, C^2H_2), 1.48 sextet (2H, C^3H_2), 2.42 t (2H, C^4H_2), 2.70 s (6H, $2C^7H_3$), 3.19, 3.2 d [2H, C^5H_2, J(C^5H_2–C^6H) 6.5 Hz)], 6.44 t (1H, C^6H)	13.74 (C^1), 21.99 (C^2), 30.51 (C^3), 31.64 (C^4), 34.05 (C^5), 43.71 (C^7), 133.30 (C^6)
III	$^{1}CH_3{}^{2}CH{=}{}^{3}CH–{}^{4}CHNN(^{5}CH_3)_2$	1.78, 1.79 d (3H, C^1H_3, J 6.80 Hz), 2.78 s (6H, $2C^5H_3$), 5.78 m [1H, C^2H_3, J(C^1H_3–C2H) 6.8, J_{gem} 15.5 Hz], 6.18 m (1H, C^3H), 6.97, 6.99 d (1H, C^4H, J 8.85 Hz)	18.15 (C^1), 42.90 (C^5), 130.11 (C^2), 130.38 (C^3), 136.83 (C^4)
IV	$^{1}CH_3{}^{2}CH(SH){}^{3}CH_2{}^{4}CH{=}NN(^{5}CH_3)_2$	1.19, 1.20 (d, 3H, C^1H_3), 1.52, 1.54 d (1H, SH), 2.29 (*A*), 2.32 (*B*) m (2H, *AB*), C^3H_2), 2.59 s (6H, $2C^5H_3$), 2.97 sextet (1H, C^2H), 6.45 t (1H, C^4H)	24.71 (C^1), 33.80 (C^2), 43.51 (C^3), 42.83 (C^5), 134.49 (C^4)
V	$^{1}CH_3{}^{2}CH(S{}^{6}CH_2{}^{7}CH_3){}^{3}CH_2{}^{4}CH{=}NN(^{5}CH_3)_2$	1.24 t (3H, C^7H_3), 1.28, 1.29 d (3H, C^1H_3), 2.42 (*A*), 2.46 (*B*) m (2H, *AB*), C^3H_2), 2.56 q (2H, C^6H2), 2.73 s (6H, $2C^5H_3$), 2.94 sextet (1H, C^2H), 6.65 t (1H, C^4H)	14.68 (C^7), 19.49 (C^1), 24.12 (C^3), 38.28 (C^2), 39.86 (C^6), 43.02 (C^5), 135.41 (C^4)
VI	$^{1}CH_3{}^{2}CH(S{}^{6}C_6H_5){}^{3}CH_2{}^{4}CH{=}NN(^{5}CH_3)_2$	1.33, 1.35 d (3H, C^1H_3), 2.44 (*A*), 2.52 (*B*) m (2H, *AB*), C^3H_2), 2.71 s (6H, $2C^5H_3$), 3.38 sextet (1H, C^2H), 6.62 t (1H, C^4H), 7.19–7.41 m (5H, C^6H5)	20.78 (C^1), 39.82 (C^3), 42.10 (C^2), 43.02 (C^5), 126.80 (C^9), 128.72 (C^7, C^{11}), 132.13 (C^8, C^{10}), 134.79 (C^6), 135.02 (C^4)
VII	$^{1}CH_3{}^{2}CH(S{}^{6}C(=O){}^{7}CH_3){}^{3}CH_2{}^{4}CH{=}NN(^{5}CH_3)_2$	1.30, 1.31 d (3H, C^1H_3), 2.28 s (3H, C^7H_2), 2.47 pseudotriplet (2H, C^3H_2), 2.72 s (6H, $2C^5H_3$), 3.71 sextet (1H, C^2H), 6.52 t (1H, C^4H)	20.71 (C^1), 30.62 (C^2), 37.98 (C^3), 39.78 (C^7), 43.04 (C^5), 134.20 (C^4), 195.31 (C^6)
VIII	$^{1}CH_3{}^{2}CH(S{}^{6}C(=O)C_6H_5){}^{3}CH_2{}^{4}CH{=}NN(^{5}CH_3)_2$	1.39, 1.41 d (3H, C^1H_3), 2.59 pseodo-triplet (2H, C^3H_2), 2.70 s (6H, $2C^5H_3$), 3.95 m (1H, C^2H), 6.60 t (1H, C^4H), 7.38–7.91 m (5H, C^6H5)	20.73 (C^1), 37.89 (C^2), 39.80 (C^3), 42.91 (C^5), 126.96 (C^9, C^{11}), 128.36 (C^8, C^{12}), 133.08 (C^{10}), 134.51 (C^4), 136.96 (C^7), 191.34 (C^6)
IX	$^{1}CH_3{}^{2}CH(S{}^{6}CH_2{}^{7}CH_2OH){}^{3}CH_2{}^{4}CH{=}NN(^{5}CH_3)_2$	1.29, 1.30 d (3H, C^1H_3), 2.44 (*A*), 2.47 (*B*) m (4H, *AB*), C^3H_2 and C^6H_2), 2.73 s (6H, $2C^5H_3$), 2.99 m (1H, C^2H), 3.69 t (2H, C^7H_2), 6.65 t (1H, C^4H)	21.41 (C^1), 33.24 (C^3), 38.81 (C^2), 39.91 (C^6H2), 43.21 (C^5), 61.40 (C^7), 135.88 (C^4)

Table 2. (Contd.)

Comp. no.	Structure	^{1}H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
X	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H{=}NN(\overset{5}{C}H_3)_2$ $\mid$ $S\overset{6}{C}H_2\overset{7}{C}OO\overset{8}{C}H_2\overset{9}{C}H_3$	1.26 t (3H, C^9H_3), 1.29, 1.30, d (3H, C^1H_3), 2.44 (*A*), 2.51 (*B*) m (2H, *AB*, C^3H_2), 2.74 s (6H, $2C^5H_3$), 3.12 pseudo-sextet (1H, C^2H), 3.26 s (2H, C^6H_2), 4.18 q (2H, C^8H_2), 6.62 t (1H, C^4H)	14.23 (C^9), 20.73 (C^1), 32.56 (C^3), 39.48 (C^2), 43.23 (C^5), 60.35 (C^8), 134.84 (C^4), 170.69 (C^7), 39.64 (C^6)
XI[a]	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H{=}NN(\overset{5}{C}H_3)_2$ $\mid$ $S\overset{6}{C}H_2Si(O\overset{7}{C}H_3)_3$	1.28, 1.29 d (3H, C^1H_3), 1.88 s (2H, C^6H_2), 2.41 (*A*), 2.48 (*B*) m (2H, *AB*, C^3H_2), 2.74 s (6H, $2C^5H_3$), 2.87 m (1H, C^2H), 3.60 s (9H, $3C^7H_3$), 6.65 t (1H, C^4H)	8.60 (C^6), 20.16 (C^1), 39.14 (C^3), 41.36 (C^2), 43.26 (C^5), 51.08 (C^7), 135.52 (C^4)
XII[b]	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H{=}NN(\overset{5}{C}H_3)_2$ $\mid$ $S\overset{6}{C}H_2\overset{7}{C}H_2Si(O\overset{8}{C}H_3)_3$	0.96 m (2H, C^7H_2), 1.28, 1.29 d (3H, C^1H_3), 2.43 (*A*), 2.47 (*B*) m (2H, *AB*, C^3H_2), 2.64 m (2H, C^6H_2), 2.73 s (6H, $2C^5H_3$), 2.95 pseudo-sextet (1H, C^2H), 3.58 s (9H, $3C^8H_3$), 6.65 t (1H, C^4H)	10.31 (C^7), 20.78 (C^1), 24.14 (C^3), 38.50 (C^2), 39.75 (C^6), 42.90 (C^5), 50.27 (C^8), 135.19 (C^4)
XIII[c]	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H{=}NN(\overset{5}{C}H_3)_2$ $\mid$ $S\overset{6}{C}H_2Si(O\overset{7}{C}H_2\overset{8}{C}H_2)_3N$	1.25, 1.28 d (3H, C^1H_3), 1.76 s (2H, C^6H_2), 2.35 (*A*), 2.42 (*B*) m (2H, *AB*, C^3H_2), 2.74 s (6H, $2C^5H_3$), 2.80 m (1H, C^2H), 2.85 t (6H, $3C^8H_2$), 3.85 t (6H, $3C^7H_2$), 6.72 t (1H, C^4H)	16.05 (C^6), 19.62 (C^1), 39.06 (C^3), 40.84 (C^2), 43.07 (C^5), 50.65 (C^7), 57.25 (C^8), 136.99 (C^4)
XIV[d]	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H{=}NN(\overset{5}{C}H_3)_2$ $\mid$ $S\overset{6}{C}H_2\overset{7}{C}H_2Si(O\overset{8}{C}H_2\overset{9}{C}H_2)_3N$	0.67 m (2H, C^2H_2), 1.21, 1.24 d (3H, C^1H_3), 2.35 (*A*), 2.42 (*B*) m (2H, *AB*, C^3H_2), 2.61 m (2H, C^6H_2), 2.65, 2.67 d (6H, C^5H_3), 2.87 pseudo-sextet (1H, C^2H), 6.65 t (1H, C^4H)	17.42 (C^7), 20.88 (C^1), 27.45 (C^3), 38.01 (C^2), 39.99 (C^6), 43.15 (C^5), 50.94 (C^8), 57.46 (C^9), 137.03 (C^4)

[a] δ_{Si} –48.7 ppm. [b] δ_{Si} –45.2 ppm. [c] δ_{Si} –75.3 ppm. [d] δ_{Si} –69.9 ppm.

dimethylhydrazones to form the corresponding onium derivatives, we studied their reaction with methyl iodide in a 1 : 1 molar ratio [schemes (8) and (9)]. It was found that the most active reaction center in organylsulfanyl derivatives **II** and **V**–**X** is the terminal nitrogen atom. (Butylsulfanyl)ethanal hydrazone **II** fairly fast reacts with methyl iodide already at room temperature both in the absence of solvents and in ether or methanol. However, reaction (8) fails to come to completion. The yield of 1,1,1-trimethylhydrazinium iodide **XVI** is no higher than 50%, even though the reaction time is increased from 1 to 6 h. Under similar conditions, hydrazones **VI**–**VIII** much faster react with methyl iodide (~10 min). Therewith, respective 1,1,1-trimethylhydrazonium iodides **XVIII**–**XX** are formed in an almost quantitative yeild. Even though hydrazones **V** and **IX**–**XII** slowly reacted with methyl iodide under the same conditions (8–10 h), the yields of 1,1,1-trimethylhydrazinium iodides **XVII** and **XXI**–**XXIV** were no higher than 70%. The yields, physicochemical properties, and elemental analyses of compounds **XVI**–**XXXIII** are listed in Table 3 and their structural formulas and spectral characteristics, in Table 4.

$$\textbf{II} + \text{MeI} \longrightarrow \textbf{XVI}, \qquad (8)$$

$$\textbf{V–XII},\ \textbf{XIV} + \text{MeI} \longrightarrow \textbf{XVII–XXIV}. \qquad (9)$$

With hydrazones **V** and **XII**, both the nitrogen and sulfur atoms could be iodomethylated at a hydrazone:

Table 3. Physicochemical characteristics and elemental analyses of 1,1,1-trimethylhydrazinium iodides **XVI**–**XXIV, XXXI**, and **XXXIII** and diiodomethylates **XXV, XXVI**, and **XXX**

Comp. no.	Yield, %	mp, °C	Found, %					Formula	Calculated, %				
			C	H	I	N	S		C	H	I	N	S
XVI	42	117–119 (decomp.)	33.76	6.42	39.63	8.81	9.74	$C_9H_{21}IN_2S$	34.16	6.69	40.11	8.85	10.13
XVII	72	84–85	33.95	6.51	40.11	8.79	9.93	$C_9H_{21}IN_2S$	34.16	6.69	40.11	8.85	10.13
XVIII	87	74–76 (decomp.)	42.51	5.58	34.87	7.89	8.86	$C_{13}H_{21}IN_2S$	42.86	5.81	34.84	7.68	8.80
XIX	96	147–148	32.14	5.63	37.90	8.04	9.34	$C_9H_{19}IN_2OS$	32.73	5.80	38.42	8.48	9.71
XX	91	148–149	42.43	6.88	31.79	5.16	7.78	$C_{14}H_{21}IN_2OS$	42.86	7.14	32.36	5.40	8.17
XXI	72	[a]	32.35	6.12	37.75	8.18	9.16	$C_9H_{21}IN_2OS$	32.53	6.37	38.19	8.43	9.65
XXII	75	[a]	35.24	6.10	33.18	7.56	9.34	$C_{11}H_{23}IN_2O_2S$	35.28	6.19	33.89	7.48	8.56
XXIII	78	[a]	30.91	6.11	29.73	6.33	7.39	$C_{11}H_{27}IN_2O_3SSi$	31.26	6.44	30.03	6.63	7.58
XXIV	81	[a]	32.89	6.32	25.94	6.13	7.11	$C_{12}H_{29}IN_2O_3SSi$	33.03	6.70	29.31	6.42	7.34
XXV	89	140–142	26.01	5.62	54.97	6.03	6.83	$C_{10}H_{24}I_2N_2S$	26.19	5.28	55.35	6.11	6.99
XXVI	96	[a]	26.49	5.78	42.18	7.12	5.08	$C_{13}H_{32}I_2N_2O_3SSi$	26.99	5.58	43.87	7.27	5.54
XXX	95	145–146 (decomp.)	29.62	6.05	40.25	6.32	4.87	$C_{15}H_{33}I_2N_3O_3SSi$	29.16	5.38	41.08	6.80	5.18
XXXI	97	[a]	36.32	6.18	25.18	8.17	6.14	$C_{15}H_{32}IN_3O_3SSi$	36.81	6.59	25.92	8.58	6.55
XXXIII	98	185–187	33.15	6.17	49.24	10.87	–	$C_7H_{15}IN_2$	33.08	5.95	49.94	11.02	–

[a] Oily material.

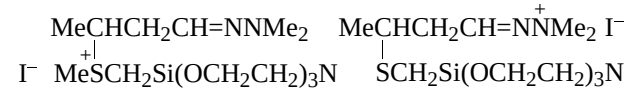
MeI molar ratio of 1:2 [scheme (10)]. The reaction was accomplished under short reflux in methanol.

$$\mathbf{V, XII} + 2MeI \longrightarrow \underset{\mathbf{XXV, XXVI}}{[MeCH(Me\overset{+}{S}R)CH_2CH{=}NNMe_3]_2\ I^-}, \quad (10)$$

R = Et (**XXV**), $CH_2CH_2Si(OMe)_3$ (**XXVI**).

At the same time, hydrazones **IX** and **X** react by the terminal nitrogen atom even with excess MeI. After 6-h refluxing in methanol, 1,1,1-trimethylhydrazinium iodides **XXI** and **XXII**, as well as 1,1,1-trimethylhydrazinium iodide $Me_3\overset{+}{N}NH_2$ (**XXVII**) were isolated. The latter product (yield ~20%) is probably formed by partial hydrolysis or methanolysis of 1,1,1-trimethylhydrazinium iodides **XXI** and **XXII**.

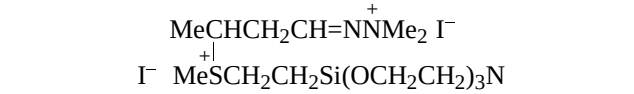
3-(Silatranylmethylsulfanyl)butanal and 3-[2-(silatranylethylsulfanyl)butanal] 1,1-dimethylhydrazones (**XIII**, **XIV**) in which the sulfur and silicon atoms are intervened by one (**XIII**) or two (**XIV**) methylene units were of particular interest in view of the presence in their molecules of a superelectron-donor group $Si(OCH_2CH_2)_3N$ (σ^* –3.49 [19]). Previously we found that 1-(organylsulfanylmethyl)silatranes extremely easily react with methyl iodide to form dimethylsilatranylmethylsulfonium iodides [20]. Therefore, it might be expected that the reaction of hydrazone **XIII** with MeI at a 1:1 molar ratio would lead to methylsulfonium iodide **XXVIII** rather than 1,1,1-trimethylhydrazinium iodide **XXIX**.



XXVIII **XXIX**

However, we failed to obtain unambiguous experimental evidence for this suggestion. The reaction in chloroform gave a hardly separable mixture of sodides **XXVIII**–**XXX**. The reaction in methanol at a 1:≥2 **XIII**:CH_3I molar ratio gave bisiodomethylate **XXX**.

Unlike compound **XIII**, the reaction of hydrazone **XIV** with MeI at a ~1:1 molar ratio in ether gave primarily 1,1,1-trimethylhydrazinim iodide **XXXI** (yield ~90%).



XXXI

Attempted synthesis of bisiodomethylate **XXXII** by reaction of hydrazone **XIV** with excess methyl

Table 4. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of 1,1,1-trimethylhydrazinium iodides **XVI**–**XXIV, XXXI**, and **XXXIII** and diiodomethylate **XXX**

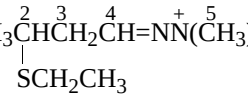
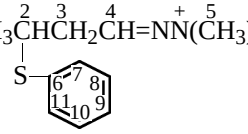
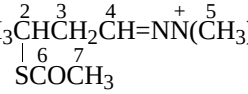
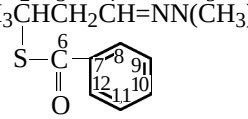
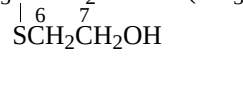
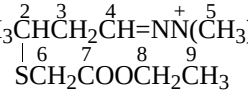
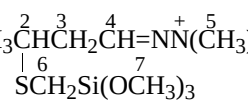
Comp. no.	Structure	^{1}H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
XVI	$CH_3^1CH_2^2CH_2^3CH_2^4SCH_2^5CH^6{=}N^+N^7(CH_3)_3\,I^-$	0.94 t (3H, C^1H_3), 1.43 sextet (2H, C^3H_2), 1.56 m (2H, C^2H_2), 2.55 t (2H, C^4H_2), 3.43, 3.45 d [2H, C^5H_2, ^3J(CH2=CH) 6.14 Hz], 3.47 s (9H, $3C^7H_3$), 8.35 t (1H, C^6H)	14.29 (C^1), 23.07 (C^2), 32.28 (C^3), 32.54 (C^4), 32.80 (C^5), 56.28 (C^6), 165.67 (C^7)
XVII		1.24 t (3H, C^7H_3), 1.35, 1.38 d (3H, C^1H_3), 2.55 (*A*), 2.58 (*B*) m (4H, *AB*, C^3H_2 and C^6H_2), 3.35 sextet (1H, C^2H), 3.72 s (9H, $3C^5H_3$), 8.99 t (1H, C^4H)	14.60 (C^7), 21.68 (C^1), 23.79 (C^3), 35.90 (C^6), 38.24 (C^8), 55.68 (C^5), 168.40 (C^4)
XVIII		1.37, 1.39 d (3H, C^1H_3), 2.69 (*A*), 2.82 (*B*) m (2H, *AB*, C^3H_2), 3.67 s (9H, $3C^5H_3$), 3.81 sextet (1H, C^2H), 7.24–7.48 m (5H, C^6H_5), 9.06 t (1H, C^4H)	21.43 (C^1), 39.20 (C^3), 39.57 (C^2), 55.75 (C^5), 127.57 (C^9), 129.08 (C^7, C^{11}), 132.69 (C^8, C^{10}), 133.12 (C^6), 168.52 (C^4)
XIX		1.42, 1.44 d (3H, C^1H_3), 2.32 s (3H, C^7H_3), 2.73 (*A*), 2.89 (*B*) m (2H, *AB*, C^3H_2), 3.74 s (9H, $3C^5H_3$), 3.84 sextet (1H, C^2H), 8.85 t (1H, C^4H)	20.97 (C^1), 30.98 (C^2), 36.19 (C^3), 39.80 (C^7), 55.73 (C^5), 167.64 (C^4), 196.06 (C^6)
XX		1.53, 1.55 d (3H, C^1H_3), 2.76 (*A*), 3.08 (*B*) m (2H, *AB*, C^3H_2), 3.66 s (9H, $3C^5H_3$), 4.07 pseudo-sextet (1H, C^2H), 7.44–7.87 m (5H, C^6H_5), 8.84 t (1H, C^4H)	21.14 $(C1), 36.28 ($C^3$), 40.33 ($C^2$), 55.45 ($C^5$), 127.21 ($C^9$, C^{11}), 128.97 (C^8, C^{12}), 134.05 (C^{10}), 136.38 (C^7), 166.91 (C^4), 192.13 (C^6)
XXI		1.37, 1.39 d (3H, C^1H_3), 2.75 m (4H, C^6H_2 and C^3H_2), 3.35 pseudo-sextet (1H, C^2H), 3.52 s (9H, $3C^5H_3$), 3.70 t (2H, C^7H_2), 8.85 t (1H, C^4H)	22.24 (C^1), 26.50 (C^3), 37.72 (C^2), 39.84 (C^6), 56.05 (C^5), 62.43 (C^7), 169.00 (C^4)
XXII		1.28 t (3H, C^9H_3), 1.41 d (3H, C^1H_3), 2.70 (*A*), 2.85 (*B*) m (2H, *AB*, C^3H_2), 3.34 s (2H, C^6H_2), 3.43 m (1H, C^2H), 3.74 s (9H, $3C^5H_3$), 9.00, 8.99 d.d	13.81 (C^9), 21.42 (C^1), 32.15 (C^6), 37.28 (C^2), 37.86 (C^3), 55.50 (C^5), 61.23 (C^8), 161.71 (C^4), 170.00 (1H, C^4H) (C^7)
XXIII[a]		1.22, 1.25 d (3H, C^1H_3), 1.71 s (2H, C^6H_2), 2.65 (*A*), 2.75 (*B*) m (2H, *AB*, C^3H_2), 3.25 m (1H, C^2H), 3.44 s (9H, 3 C^5H_3), 3.58 s (9H, $3C^7H_3$), 8.80 t (1H, C^4H)	6.61 (C^6), 20.08 (C^1), 36.75 (C^3), 37.53 (C^2), 50.46 (C^7), 55.21 (C^5), 167.54 (C^4)

Table 4. (Contd.)

Comp. no.	Structure	^1H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
XXIV[b]	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H{=}N\overset{+}{N}(\overset{5}{C}H_3)_3I^-$ $\vert\ \overset{6}{S}CH_2\overset{7}{C}H_2Si(O\overset{8}{C}H_3)_3$	1.30, 1.32 d (3H, C^1H_3), 0.89 m (2H, C^7H_2), 2.60, 2.73 centers of two overlapping multiplets (4H, C^3H_2 and C^6H_2), 3.28 m (1H, C^2H), 3.49 s (9H, $3C^5H_3$), 3.68 s (9H, $3C^8H_3$), 8.94 t (1H, C^4H)	10.04 (C^7), 21.51 (C^1), 23.73 (C^3), 36.18 (C^2), 38.27 (C^6), 50.41 (C^8), 55.64 (C^5), 168.31 (C^5)
XXX	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H{=}N\overset{+}{N}(\overset{5}{C}H_3)_3I^-$ $I^-\ \overset{6}{C}H_3\overset{+\vert}{S}\overset{7}{C}H_2Si(O\overset{8}{C}H_2CH_2)_3N$	1.47 d. d. (3H, C^1H_3), 1.95 (*A*), 2.10 (*B*) (2H, *AB*, C^7H_2, $^2J_{AB}$ 7.6 Hz), 2.76, 2.82 d (3H, C^3H_3), 3.00 t (6H, C^8H_2), 3.49 s (9H, $3C^5H_3$), 3.81 t (6H, C^9H_2), 4.02 pseudo-sextet (1H, C^2H), 8.60 t (1H, C^4H)	21.33 (C^1), 27.82 (C^7), 29.07 (C^6), 42.16 (C^2), 43.92 (C^6), 50.01 (C^9), 54.44 (C^5), 56.90 (C^8), 167.59 (C^4)
XXXI	$\overset{1}{C}H_3\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H{=}N\overset{+}{N}(\overset{5}{C}H_3)_3I^-$ $\overset{+\vert\ 6}{S}CH_2\overset{7}{C}H_2Si(O\overset{8}{C}H_2\overset{9}{C}H_2)_3N$	0.90 m (2H, C^7H_2), 1.08 center of a doublet (3H, C^1H_3)	17.54 (C^5), 21.84 (C^1), 26.77 (C^3), 35.86 (C^2), 38.60 (C^6), 50.54 (C^8), 55.46 (C^5), 57.09 (C^9), 167.55 (C^4)
XXXIII	$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H{=}N\overset{+}{N}(\overset{5}{C}H_3)_3\ I^-$	2.00 d (3H, C^1H_3), 3.47 s (9H, $3C^5H_3$), 6.31 m (1H, C^2H), 6.94 m (1H, C^3H), 8.72 d (1H, C^4H)	19.59 (C^1), 56.59 (C^5), 126.66 (C^2), 153.34 (C^3), 166.61 (C^4)

iodide in methanol or by transetherification of trimethoxysilyl derivative **XXVI** with tris(2-hydroxyethyl)amine proved unsuccessful. In both cases, complex product mixtures formed. In the first case we could only isolate (2-hydroxyethyl)amine hydroiodide and in the second, tris(2-hydroxyethyl)amine hydroiodide and 2-(but-2-enylidene)-1,1,1-trimethylhydrazinium iodide (**XXXIII**).

Attempted quaternization of the nitrogen atom in hydrazones **VII** and **VIII** with 1-(iodomethyl)silatrane in methanol under reflux or in DMF also failed.

The composition and structure of the synthesized compounds were proved by ^1H, ^{13}C, and ^{29}Si NMR and IR spectroscopy and elemental analysis (Tables 3 and 4).

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument. The ^1H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker DPX-400 instrument at 400.13, 100.61, and 79.49 MHz (^1H, ^{13}C, and ^{29}Si, respectively). Most compounds were studied as 10–15% solutions in $CDCl_3$. The NMR spectra of iodides **XVI**, **XXI**, and **XXVII**, as well as of bisiodomethylate **XXX** were obtained for 10–15% solutions in CD_3OD.

(Butylsulfanyl)ethanal 1,1-dimethylhydrazone (II). To a stirred solution of 9.0 g of (butylsulfanyl)ethanal (**I**) in 25 ml of benzene, 6.0 g of 1,1-dimethylhydrazine was added dropwise. Therewith, the temperature of the reaction mixture was maintained at 20–25°C. The mixture was stirred for 1 h at that temperature, transferred into a separatory funnel, left to stand for 1 h, and the aqueous layer was separated. The organic layer was freed of water admixture (by azeotropic distillation with benzene), after which benzene was distilled off at atmospheric pressure. The residue was fractionated in a vacuum to obtain 10.1 g (85%) of compound **II** as a colorless oily liquid with a characteristic unpleasant odor of aminosulfide. IR spectrum, ν, cm^{-1}: 1590 (C=N).

A similar simplified procedure was used to prepare the starting (known) crotonaldehyde 1,1-dimethylhydrazone (**III**). From 14.0 g of crotonaldehyde and

12.0 g of 1,1-dimethylhydrazine in 25 ml of benzene we obtained 11.5 g (51%) of compound **III** as a colorless oily liquid with a strong unpleasant odor, bp 62–63°C (20 mm Hg), n_D^{20} 1.5120 {published data [21]: bp 65–68°C (16 mm Hg)}.

3-(Ethylsulfanyl)butanal 1,1-dimethylhydrazone (V). A mixture of 8.3 g of crotonaldehyde 1,1-dimethylhydrazone (**III**) and 7.0 ml of ethanethiol was heated under reflux for 6 h. Excess ethanethiol was removed from the reaction mixture by distillation. The residue was fractionated in a vacuum to isolate 4.7 g (37%) of compound **V** as a colorless oily liquid. IR spectrum, ν, cm^{-1}: 1610 (C=N).

3-(Phenylsulfanyl)butanal 1,1-dimethylhydrazone (VI). Benzenethiol, 2.2 g, was added to 2.3 of crotonaldehyde 1,1-dimethylhydrazone (**III**). Within 1–2 min, the temperature of the reaction mixture raised from 20 to 50°C. The mixture was heated for 1 h at 100°C and fractionated in a vacuum to obtain 3.4 g (78%) of compound **VI** as a colorless oily liquid.

3-(Acetylsulfanyl)butanal 1,1-dimethylhydrazone (VII). Thiolacetic acid, 4.0 g, was added dropwise to 5.5 g of hydrazone **III**. Therewith, the temperature of the reaction mixture was maintained at 20–25°C. The mixture was fractionated in a vacuum to obtain 8.3 g (90%) of compound **VII** as a colorless oily liquid. IR spectrum, ν, cm^{-1}: 1595 (C=N), 1680 (C=O).

A similar procedure was used to obtain **3-(benzoylsulfanyl)butanal 1,1-dimethylhydrazone (VIII)** from 5.5 g of hydrazone **III** and 7.0 g of thiolbenzoic acid. Yield 10.1 g (82%). IR spectrum, ν, cm^{-1}: 1580 ($C–C_{arom}$), 1590 (C=N), 1650 (C=O).

3-Sulfanylbutanal 1,1-dimethylhydrazone (IV). Methanolic MeONa, 5–6 drops, was added to a solution of 5.4 g of 3-(acetylsulfanyl)butanal 1,1-dimethylhydrazone (**VII**) in 50 ml of CH_3OH, and the mixture was refluxed for 6 h. The solvent was distilled off at atmospheric pressure, and the residue was fractionated in a vacuum to obtain 3.5 g (83%) of compound **IV** as a colorless oily liquid. IR spectrum, ν, cm^{-1}: 1600 (C=N), 2550 (SH).

3-[(2-Hydroxyethyl)sulfanyl]butanal (IX). Equimolar mixture of 4.8 g of hydrazone **III** and 3.4 g of 2-sulfanylethanol was heated for 3 h at 140–150°C and then fractionated in a vacuum to isolate 7.1 g (87%) of compound **IX** as a colorless oily liquid. IR spectrum, ν, cm^{-1}: 1600 (C=N), 3400 (OH).

In a similar way, from 5.5 g of hydrazone **III** and 6.0 g of (ethoxycarbonyl)methanethiol we obtained 9.9 g (85%) of **3-(ethoxycarbonylsulfanyl)butanal 1,1-dimethylhydrazone (X)** [IR spectrum, ν, cm^{-1}: 950, 1050 (C?O), 1610 (C=N), 1720 (C=O)], and from 5.0 g of hydrazone **III** and 7.5 g of trimethoxy(sulfanylmethyl)silane, 9.7 g (78%) of **3-[(trimethoxysilyl)methylsulfanyl]butanal 1,1-dimethylhydrazone (XI)** [IR spectrum, ν, cm^{-1}: 790, 810, 1090, 1190 (Si–O–C), 1600 (C=N)].

3-[2-(Trimethoxysilyl)ethylsulfanyl]butanal 1,1-dimethylhydrazone (XII). *a*. Compound **XII** was obtained similarly to compound **XI** from 5.0 g of hydrazone **III** and 8.1 g of trimethoxy(2-sulfanylethyl)silane. Yield 9.2 g (70%). IR spectrum, ν, cm^{-1}: 800, 1090, 1190 (Si–O–C), 1600 (C=N).

b. A mixture of 2.5 g of hydrazone **IV** and 2.2 g of trimethoxy(vinyl)silane was heated at 140–145°C for 3 h and then fractionated in a vacuum to isolate 1.5 g (35%) of compound **XII**.

3-(Silatranylmethylsulfanyl)butanal 1,1-dimethylhydrazone (XIII). A solution of 2.3 g of tris(2-hydroxyethyl)amine in 5 ml of methanol and 2 drops of 10% methanolic MeONa were added to a solution of 4.1 g of compound **XI** in 5 ml of methanol. The reaction mixture was refluxed for 2 h. Methanol was distilled off at atmospheric pressure. The syrupy residue crystallized within 1 day in a refrigerator. Yield 4.8 g (96%). IR spectrum, ν, cm^{-1}: 780, 800, 1090, 1120 (Si–O–C), 1600 (C=N).

In a similar way, from 5.0 g of compound **XII** and 2.5 g of tris(2-hydroxyethyl)amine we obtained 5.5 g (94%) of **3-(2-silatranylethylsulfanyl)butanal 1,1-dimethylhydrazone (XIV)** as a thick light yellow syrup.

2-[2-(Butylsulfanyl)ethylidene]-1,1,1-trimethylhydrazinium iodide (XVI). A mixture of 1.55 g of hydrazone **II** and 1.26 g of methyl iodide was allowed to stand at room temperature for ~24 h. Colorless crystals formed and were filtered off, washed with ether, and dried in a vacuum to obtain 1.18 g (42%) of iodide **XVI**. IR spectrum, ν, cm^{-1}: 1630 (C=C).

2-[3-(Ethylsulfanyl)butylidene]-1,1,1-trimethylhydrazinium iodide (XVII). A solution of 1.3 g of methyl iodide in 5 ml of ether was added to 1.6 g of hydrazone **II**. The mixture was allowed to stand at room temperature in the dark for ~24 h. A precipitate formed and was filtered off, washed with ether, and dried in a vacuum to obtain 2.4 g (83%) of iodide **XVII** as light yellow flakes. IR spectrum, ν, cm^{-1}: 1620 (C=N).

2-[3-(Phenylsulfanyl)butylidene]-1,1,1-trimethylhydrazinium iodide (XVIII). Hydrazone **VI**, 1.5 g, and 1.5 g were mixed at room temperature.

After ~5 min the mixture warmed up from 25 to 40°C. It was cooled to room temperature and allowed to stand for 2 h in the dark. A precipitate formed and was filtered off, washed with ether, and dried in a vacuum to obtain 2.14 g (87%) of compound **XVIII**.

In a similar way, from 1.9 g of hydrazone **VII** and 2.0 g of methyl iodide we obtained 3.2 g (96%) of **2-[3-(acetylsulfanyl)butylidene]-1,1,1-trimethylhydrazinium iodide (XIX)** [IR spectrum, ν, cm^{-1}: 1630 (C=N), 1680 (C=O)] and from 2.5 g of hydrazone **VIII** and 2.5 g of methyl iodide, 3.6 g (91%) of **2-[3-(benzoylsulfanyl)butylidene]-1,1,1-trimethylhydrazinium iodide (XX)** [IR spectum, ν, cm^{-1}: 1580 ($C=C_{arom}$), 1600 (C=N), 1660 (C=O)].

2-[3-[2-(Hydroxyethyl)sulfanyl]butylidene]-1,1,1-trimethylhydrazinium iodide (XXI). A solution of 2.0 g of hydrazone **IX** in 5 ml of ether was mixed with a solution of 1.5 g of methyl iodide in 5 ml of ether. The reaction mixture was allowed to stand in the dark for 24 h. The ether layer was decanted, and the syrupy residue was treated with ether (3.5 ml) and exposed to a vacuum of 1–2 mm Hg for ~1 h to obtain 2.5 g (72%) of compound **XXI** as a viscous yellowish oil.

In a similar way, from 2.0 g of hydrazone **X** and 1.2 g of methyl iodide we synthesized 2.1 g (75%) of **2-[3-(ethoxycarbonylmethylsulfanyl)butylidene]-1,1,1-trimethylhydrazinium iodide (XXII)** (viscous yellowish oil), from 2.0 g of hydrazone **XI** and 1.3 g of methyl iodide, 3.9 g (78%) of **2-[3-[(trimethoxysilyl)methylsulfanyl]butylidene]-1,1,1-trimethylhydrazinium iodide (XXIII)** (viscous yellowish oil), and from 2.5 g of hydrazone **XII** and 1.2 g of methyl iodide, 2.8 g (76%) of **2-[3-[2-(trimethoxysilyl)ethylsulfanyl]butylidene]-1,1,1-trimethylhydrazinium iodide (XXIV)** (viscous yellowish oil).

2-[3-(2-Silatranylethylsulfanyl)butylidene]-1,1,1-trimethylhydrazinium iodide (XXXI). Methyl iodide, 0.5 g, was added at 20°C to a stirred solution of 1.2 g of hydrazone **XIV** in 5 ml of chloroform. The mixture was allowed to stand at room temperature in the dark for 2 h, after which the solvent was removed in a vacuum to obtain 1.55 g (97%) of compound **XXXI** as a viscous yellowish oil.

3-(Ethylsulfanyl)butanal 1,1-dimethylhydrazone diiodomethylate (XXV). Methyl iodide, 3.5 g, was added to a stirred solution of 2.1 g of hydrazone **V** in 5 ml of CH_3OH. The mixture was allowed to stand for 24 h in the dark, and the solvent and excess methyl iodide were removed. The syrupy residue was subjected to a vacuum (2 mm) at 50°C until it crystallized. The solid reaction product was thoroughly ground, washed with ether, and dried in a vacuum to obtain 4.9 g (89%) of diiodomethylate **XXV** as light yellow fine crystals. IR spectrum, ν, cm^{-1}: 1630 (C=N).

3-[2-(Trimethoxysilyl)ethylsulfanyl]butanal 1,1-dimethylhydrazone diiodomethylate (XXVI). Methyl iodide, 3.5 g, was added to a solution of 3.0 g of hydrazone **XII** in 5 ml of CH_3OH. The mixture was allowed to stand for 24 h in the dark. The solvent and excess methyl iodide were removed in a vacuum. The residue was washed with ether and then subjected to a vacuum (1–2 mm Hg) for ~1 h to obtain 5.6 g (96%) of diiodomethylate **XXVI** as a light yellow syrup.

Reaction of 3-[2-(trimethoxysilyl)ethylsulfanyl]butanal 1,1-dimethylhydrazone diiodomethylate (XXVI) with tris(2-hydroxyethyl)amine. A solution of 0.8 g of tris(2-hydroxyethyl)amine in 2 ml of CH_3OH was added to a stirred solution of 3.0 g of diiodomethylate **XXVI** in 3 ml of CH_3OH. When slight heat release ceased (~5 min), the mixture was cooled to 0°C. White fine crystals formed and were filtered off, washed with ether, and dried in a vacuum to obtain 1.3 g of tris(2-hydroxyethyl)amine hydroiodide (mp 166–167°C). The mother liquor was diluted with ether to isolate 0.9 g of 2-(but-2-enylidene)-1,1,1-trimethylhydrazinium iodide (**XXXIII**).

2-(But-2-enylidene)-1,1,1-trimethylhydrazinium iodide (XXXIII). Methyl iodide, 7.1 g, was added to a stirred solution of 5.6 g of hydrazone **III** in 5 ml of isopropanol. When slight heat release ceased (~5 min), fine crystals formed and were washed with ether and dried in a vacuum to obtain 12.4 g (98%) of iodide **XXXIII**.

Reaction of 1,1,1-trimethylhydrazonium iodide (XXI) with methyl iodide. Methyl iodide, 2.5 g, was added to a solution of 2.5 g of iodide **XXI** in 3 ml of CH_3OH. The mixture was allowed to stand for 72 h in the dark. Fine crystals formed and were separated, washed with ether, and dried in a vacuum to obtain 0.7 g (46%) of 1,1,1-trimethylhydrazinium iodide (**XXVII**), mp 236°C (decomp.). Found, %: C 18.08; H 5.12; I 62.30; N 13.27. $C_3H_{11}IN_2$. Calculated, %: C 17.83; H 5.48; I 62.80; N 13.86. ^1H NMR spectrum (CD_3OD), δ, ppm: 3.38 s (9H, $3CH_3$).

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REFERENCES

1. Kitaev, Yu.P. and Buzykin, B.I., *Gidrazony* (Hydrazones), Moscow: Nauka, 1974.
2. Belyaev, E.Yu., *N,N-Dimetilgidrazin v organicheskom sinteze* (*N,N*-Dimethylhydrazine in Organic Synthesis), Krasnoyarsk: Sib. Gos. Tekh. Univ., 1999.
3. Lopyrev, V.A., Dolgushin, G.V., and Laskin, B.M., *Ros. Khim. Zh.*, 2001, vol. 45, nos. 5–6, p. 149.
4. Lopyrev, V.A., Dolgushin, G.V., and Voronkov, M.G., *Zh. Prikl. Khim.*, 1998, vol. 71, no. 8, p. 1233.
5. Gante, J. and Weitzel, R., *Ann. Chem.*, 1990, no. 4, p. 349.
6. Limal, D., Grand, V., Wandiresse, R., and Marraud, H., *Tetrahedron Lett.*, 1994, vol. 35, no. 22, p. 3711.
7. Shiroza, T., Ebisawa, N., Furihata, K., and Endo, T., *Agric. Biol. Chem.*, 1982, vol. 46, p. 1891.
8. Morimoto, K., Shimada, N., Naganawa, H., and Takita, T., *J. Antibiotics*, 1982, vol. 35, no. 3, p. 378.
9. Maher, H., Liu, C.M., Pelleroni, N.J., Smallheer, J., Todaro, L. Williams, T.H., and Blount, J.F., *J. Antibiotics*, 1986, vol. 39, no. 1, p. 17.
10. Hayakawa, Y., Nakagawa, M., Toda, Y., and Seto, H., *Agric. Biol. Chem.*, 1990, vol. 54, no. 4, p. 1007.
11. Shibahara, S., Kondo, S., Maeda, K., and Umezawa, H., *J. Am. Chem. Soc.*, 1972, vol. 94, no. 12, p. 4353.
12. Hart, T.W. and Vacher, B., *Tetrahedron Lett.*, 1992, vol. 33, no. 47, p. 7215.
13. Tsukamoto, S., Fujii, M., Yasunaga, T., Matsuda, K., Wanibuchi, F., Hidaka, K., Furuya, T., and Tamura, T., *Chem. Pharm. Bull.*, 1995, vol. 43, no. 5, p. 842.
14. Elokhina, V.N., Nakhmanovich, A.S., Karnaukhova, R.V., Larina, L.I., and Lopyrev, V.A., *Zh. Org. Khim.*, 2000, vol. 36, no. 4, p. 502.
15. Sorokin, M.S. and Voronkov, M.G., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 12, p. 1988.
16. Voronkov, M.G. and Sorokin, M.S., *Zh. Obshch. Khim.*, 1984, vol. 54, no. 9, p. 2020.
17. Voronkov, M.G., Sorokin, M.S., and D'yakov, V.M., *Zh. Obshch. Khim.*, 1979, vol. 49, no. 3, p. 605.
18. Voronkov, M.G., Sorokin, M.S., D'yakov, V.M., and Sigalov, M.V., *Zh. Obshch. Khim.*, 1975, vol. 45, no. 8, p. 1807.
19. Voronkov, M.G., Brodskaya, E.I., Belyaeva, V.V., Kashik, T.V., Baryshok, V.P., and Yarosh, O.G., *Zh. Obshch. Khim.*, 1986, vol. 56, no. 3, p. 621.
20. Voronkov, M.G. and Sorokin, M.S., *Zh. Obshch. Khim.*, 1979, vol. 49, no. 12, p. 2671.
21. Duhamel, L. and Valnot, J.Y., *C. R. Acad. Sci., Ser. C*, 1978, vol. 286, no. 1, p. 47.