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Nitrimines: VII.[1] Reaction of *S*,*S*′-Dimethyl-*N*-nitroimidodithiocarbonate with Alkali. Synthesis of *S*-Methyl-*N*-nitrothiocarbamate and Its Salts

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Abstract—Reaction of *S,S*′-dimethyl-*N*-nitroimidodithiocarbonate with alkali in aqueous-alcoholic solution results in salts of *S*-methyl-*N*-nitrothiocarbamate. In anhydrous ethanol a salt of nitrouretane is obtained. By the reaction of *S*-methyl-*N*-nitrothiocarbamate salts with hydrazine 4-nitrosemicarbazide salts were prepared.

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Nitrimines are interesting as energy rich [2–4] and biologically active compounds [5–8]. A classic method of such compounds preparation is *N*-nitration of the corresponding imino derivatives [2, 9]. However, a number of compounds that may be obtained by this method is limited. Another path of synthesis of target nitrimines is to use the substitution reaction of compounds that already possess nitrimine function and, besides that, group easily leaving under the action of nucleophilic agents (Scheme 1).

Such compounds, convenient for the preparation of nitrimines of different structure are, for example, *S*-methyl-*N*-nitroisothiourea **1** and *S*,*S*′-dimethyl-*N*-nitroimidodithiocarbonate **2**, whose molecules contain one or two methylsulfanyl groups respectively.

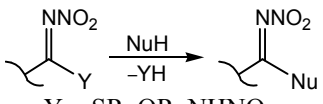
Published data exist on reactions of compounds **1** and **2** with different mono- and diamines [10, 11], hydrazine [4, 12], and hydroxylamine [13].

Previously we demonstrated that although the reaction of compound **1** with alkali occurred with the substitution of methylsulfanyl group it resulted not in the expected nitrourea salts, but in salts of nitrocyanamide [14] (Scheme 2).

In this connection in was interesting to investigate the reaction with alkali of compound **2**. Due to the insolubility of the latter in water we applied aqueous-alcoholic solutions as the reaction medium. To a solution of compound **2** in ethanol aqueous solution was added with calculated amount of NaOH and the reaction solution was heated till reflux.

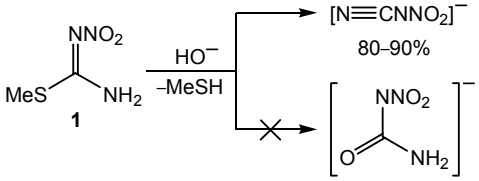
One of the reaction products is sodium carbonate whose yield depends on the ratio compound **2**–sodium

Scheme 1.



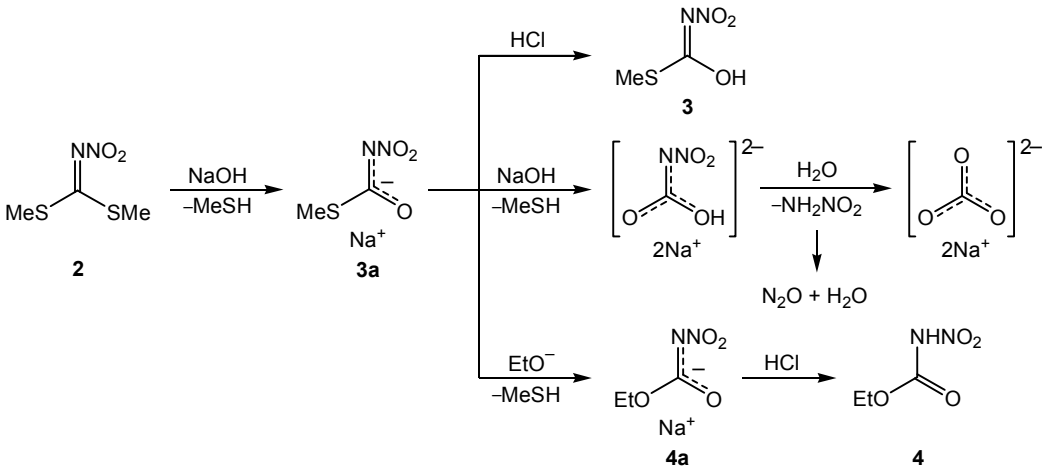
Y = SR, OR, $NHNO_2$.

Scheme 2.



[1] For communication VI, see [1].

Scheme 3.



hydroxide. Increasing the alkali concentration and the reaction time leads to an increased yield of sodium carbonate. For instance, at the molar ratio of components 1 : 2 the yield of sodium carbonate is ~90% after 2 h from the beginning of the reaction. At the molar ratio of components in the range from 1 : 1 to 1 : 2 a compound was isolated possessing an absorption maximum in the UV spectrum at 280 nm that turned out to be a previously unknown sodium salt of *S*-methyl-*N*-nitrothiocarbamate **3a**. Also along with compound **3a** and sodium carbonate we isolated from the reaction mixture the unreacted initial compound **2**. The optimization of reaction conditions allowed increasing the yield of compound **3a** to 65%.

Free *S*-methyl-*N*-nitrothiocarbamate **3** is easily isolated quantitatively from its salts by treating with HCl (Scheme 3).

At replacing 95% ethanol with anhydrous ethanol compound **3a** was not obtained, however besides sodium carbonate from reaction mixture a compound was isolated possessing an absorption maximum in the UV spectrum at 260 nm. It was identified as a sodium salt of nitrocarbamic acid ethyl ether **4a**, which at treating with HCl provided nitrouretane **4** in a 60% yield. Similary from compound **2** and KOH we obtained a potassium salt of *S*-methyl-*N*-nitrothiocarbamate **3b**.

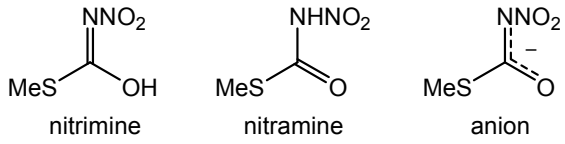
The formation of salts **3a** and **3b** evidences that alkaline hydrolysis of nitrimine **2** occurs through nucleophilic substitution of methylsulfanyl group with the hydroxide anion. The formation of carbonates is due to the substitution of the second methylsulfanyl group, probably, with the intermediate formation of a hydrolytically unstable salt of nitrocarbamic acid whose hydrolysis eventually leads to carbonate.

In anhydrous ethanol the reaction with alkali also probably occurs with the primary formation of compound **3** salt. The subsequent nucleophilic substitution of the second methylsulfanyl group by ethoxide anion explains the formation of nitrouretane salt **4a** (Scheme 3).

The composition and structure of previously unknown compound **3** were confirmed by elemental analysis, high resolution mass-spectrometry, IR, UV, and NMR spectra.

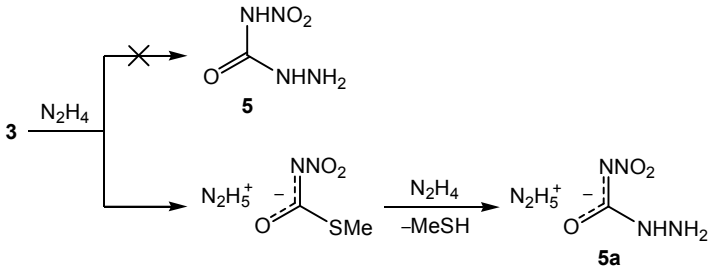
Essentially there are two possible structures of compound **3**: nitrimine and primary nitramine, distinguished by the place of localization of the hydrogen atom (Scheme 4).

Scheme 4.



We believe that compound **3** possesses a nitrimine structure. Particularly it is evidenced by the lack of a typical for a carbonyl group strong absorption band in the range 1700 cm^{-1} (for example, for nitrouretane 1739 cm^{-1}) in the IR spectrum. The probable attribution of IR spectra is described in the experimental part, it is made by comparison with the other nitrimines and nitramines [15]. Thus, the strong band at 1632 cm^{-1} is assigned to the stretching vibrations of the CN bond, and bands at 1408 and 1316 cm^{-1}, to the stretching

Scheme 5.



vibrations of nitro group (ν_{as} and ν_{s} respectively), which is close to the data on IR spectra of nitroguanidine [16]. In alkali salts **3a**, **3b** the absorption bands at 1311–1301 and 918–927 cm^{-1} are attributed to vibrations of nitro group (ν_{as} and ν_{s}). Such a shift of vibration frequencies of nitro group at ionization is typical of *N*-nitrocompounds [15].

The coincidence of UV spectra of compound **3** with the spectra of its salts **3a** and **3b** evidences that compound **3** in aqueous solution also exists as an anion. Meanwhile regardless of the initial structure of compound **3** its anion should have a similar structure in both cases with a general delocalization of electron density.

^{1}H, ^{13}C, and ^{15}N NMR spectra do not allow distinguishing between nitramine and nitrimine structures, moreover that also in DMSO the formation of anion and fast proton exchange are possible. Yet the NMR spectra confirm the formation of compound **3**. In the ^{1}H NMR spectrum two signals are present: the singlet of the methyl group at 2.30 ppm and a broadened signal at 10.76 ppm of the OH proton. In the ^{13}C NMR spectrum the signal of the methyl atom appears at 12.0 ppm, and of the second carbon atom, at 167.3 ppm. The chemical shift value of the latter is typical of nitrimine carbon atom C=NNO_2, however the signal of carbonyl atom C=O may appear in the same range. In ^{15}N NMR spectrum the signal at –39.7 ppm corresponds to nitrogen atom of nitro group, the second nitrogen atom appears at –164.3 ppm. In this case it is also difficult to determine the localization place of the hydrogen atom.

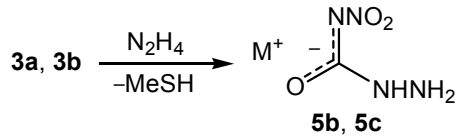
The methylsulfanyl group in compound **3** and its salts can be substituted as well with other nucleophiles, in particular, in reaction of compounds **3** and **3a** and **3b** with hydrazine we have obtained salts of 4-nitrosemicarbazide.

4-Nitrosemicarbazide **5** and its derivatives, promising as energy rich compounds and as initial substances for the synthesis of other compounds [17–22] previously were obtained in the reaction of hydrazine with *N*,*N*′-dinitrourea [17].

In the reaction of equimolar amounts of compound **3** and hydrazine only hydrazinium salt forms quantitively, while the substitution of methylsulfanyl group does not occur. At the same time at the action of 2 mol of hydrazine on compound **3** mercaptan is liberated and hydrazinium salt **5a** forms. It allows an assumption that in the reaction with hydrazine the anion of compound **3** takes part (Scheme 5).

This assumption was confirmed at investigation of reaction with hydrazine of salts **3a** and **3b**. In both cases for the formation of the corresponding salts of nitrosemicarbazide it was enough to add 1 mol of hydrazine (Scheme 6).

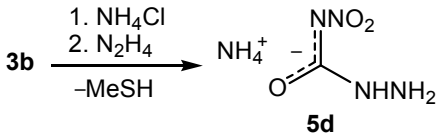
Scheme 6.



M = Na (**b**), K (**c**).

The ammonium salt **5d** was obtained from salt **3b** at treating with ammonium chloride and hydrazine without isolation of intermediate ammonium salt (Scheme 7).

Scheme 7.



At increasing the excess of hydrazine the rate of reaction of compound **3** with salts increases, however at the same time increases the yield of the side product,

1,3-diaminourea, the formation of which from compound **5** has been demonstrated previously [22]. The side product is well soluble in ethanol, unlike salts of nitrosemicarbazide, which in course of reaction precipitate from the reaction mixture.

The method we have developed for the preparation of nitrosemicarbazide salts has a number of benefits comparing to the method of obtaining them from *N*,*N*′-dinitrourea [17]. In particular, the process occurs in ethanol where final target products are insoluble, but the initial and side substances are well soluble. Nitrosemicarbazide salts **5a–5d** formed in course of reaction crystallize directly from the reaction solution and may be used in further reactions without additional purification. Yet the preparation of salts of nitrosemicarbazide by the method [17] is performed in aqueous solution because at application of alcohols *N*,*N*′-dinitrourea quickly enough reacts with them even at low temperatures with the formation of nitrouretanes [17].

EXPERIMENTAL

UV spectra were recorded on a spectrophotometer Shimadzu UV-1601 from aqueous solutions. Vibration spectra were taken on a spectrometer Nicolet AVATAR 380 from tablets with KBr. Elemental analysis was carried out on an automatic CHN-analyzer Vario EL III. ^{1}H, ^{13}C, and ^{15}N NMR spectra are recorded on a spectrometer Bruker AV-600 (600, 150, and 60 MHz respectively) at room temperature in DMSO-d_6, internal reference TMS (for ^{15}N chemical shifts δ are reported in CH_3NO_2 scale). Mass spectrum was measured on a high resolution spectrometer Thermo Electron DFS with direct input of sample (ionization energy 70 eV).

***S*-Methyl-*N*-nitrothiocarbamate (3).** To solution of 0.50 g (2.8 mmol) of salt **3b** in 10 mL of acetone was added 0.6 mL of 30% HCl, the precipitate was filtered off, the filtrate was evaporated till dryness, the residue was recrystallized from benzene. Yield 0.36 g (94%), mp 93–95°C. UV spectrum: λ_{max} 280 nm, logε 4.10. IR spectrum, ν, cm^{-1}: 3121, 2980, 2799, 1632, 1605, 1408, 1337, 1316, 1276, 1192, 1039, 971, 785, 731, 697, 637, 573, 446. ^{1}H NMR spectrum, δ, ppm: 2.30 s (3H, CH_3), 10.76 br.s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 12.0 (SCH_3), 167.3 ($C{=}NNO_2$). ^{15}N NMR spectrum, δ, ppm: –164.3 ($\underline{N}NO_2$), –39.7 ($N\underline{N}O_2$). Mass spectrum: *m*/*z* 135.9938. Found, %: C 17.81; H 3.01; N 20.16. $C_2H_4N_2O_3S$. Calculated, %: C 17.65; H 2.96; N 20.58. *M* 135.9937.

Sodium salt of *S*-methyl-*N*-nitrothiocarbamate (3a). To solution of 0.50 g (3 mmol) of *S*,*S*′-dimethyl-*N*-nitroimidodithiocarbonate **2** in 5 mL of ethanol was added 5 mL of aqueous solution containing 0.12 g (3 mmol) of NaOH, the mixture was heated till reflux in a round bottom flask equipped with a reflux condenser and was maintained for 2 h. After that the reaction mixture was evaporated till dryness and extracted with acetone (3 × 15 mL). The extract was evaporated, the residue was recrystallized from acetone. Yield 0.31 g (65%), mp 149–150°C. UV spectrum: λ_{max} 280 nm, logε 4.10. IR spectrum, ν, cm^{-1}: 2983, 2924, 2852, 1650, 1391, 1311, 1203, 1099, 1066, 960, 927, 784, 735, 710, 662. Found, %: C 15.96; H 2.199; N 17.52. $C_2H_3N_2NaO_3S$. Calculated, %: C 15.19; H 1.91; N 17.72.

Potassium salt of *S*-methyl-*N*-nitrothiocarbamate (3b) was obtained similarly from compound **2** and 0.17 g of KOH. Yield 0.32 g (62%), mp 112°C. UV spectrum: λ_{max} 280 nm, logε 4.10. IR spectrum, ν, cm^{-1}: 2972, 2927, 2849, 1631, 1405, 1301, 1197, 918, 780, 732, 710, 661. Found, %: C 14.05; H 1.88; N 16.54. $C_2H_3KN_2O_3S$. Calculated, %: C 13.79; H 1.74; N 16.08.

Ethyl ether of carbamic acid (nitrouretane) (4). To a solution of 0.50 g (3 mmol) of compound **2** in 5 mL of anhydrous ethanol was added 5 mL of ethanol solution containing 0.24 g (6 mmol) of NaOH. The reaction mixture was heated till reflux in a round bottom flask equipped with a reflux condenser and was maintained for 1 h, after that it was evaporated till dryness and extracted with acetone (3 × 15 mL). To the extract 0.25 mL of 30% HCl was added. The precipitate was filtered off, the filtrate was evaporated till dryness, the residue was recrystallized from benzene. Yield 0.28 g (60%), mp. 62–63°C (64°C [23]). UV spectrum: λ_{max} 260 nm, logε 4.01. IR spectrum, ν, cm^{-1}: 3235, 3006, 2989, 1739, 1605, 1456, 1393, 1368, 1331, 1240, 1117, 1018, 998, 879, 799, 769, 730, 605 (full coincidence of spectrum with the spectrum of an authentic sample).

Hydrazinium salt of 4-nitrosemicarbazide (5a). To a solution of 0.25 g (1.8 mmol) of compound **3** in 5 mL of ethanol was added 0.16 mL (3.6 mmol) of 75% hydrazine hydrate. The reaction mixture was heated till reflux in a round bottom flask equipped with a reflux condenser and was maintained for 2 h. The precipitated crystals were filtered off, washed with a small amount of ethanol and dried in open air. Yield 0.23 g (82%), mp 130°C (130°C [17]). UV spectrum: λ_{max} 256 nm, logε 3.91. IR spectrum, ν, cm^{-1}: 3325,

3229, 3001, 2924, 2845, 2801, 2644, 1667, 1619, 1548, 1513, 1382, 1349, 1271, 1182, 1107, 971, 849, 776, 759. Found, %: C 8.07; H 5.11; N 55.62. $CH_8N_6O_3$. Calculated, %: C 7.90; H 5.30; N 55.25.

Sodium salt of 4-nitrosemicarbazide (5b). To a solution of 0.30 g (1.9 mmol) of salt **3a** in 5 mL of ethanol was added 0.10 mL (2.25 mmol) of 75% hydrazine hydrate and the mixture was stirred for 2 h at reflux with a reflux condenser. The precipitated crystals were filtered off, washed with a small amount of ethanol, and dried in open air. Yield 0.20 g (73%), mp 151°C (with decomposition). UV spectrum: λ_{max} 255 nm, logε 3.91. IR spectrum, ν, cm^{-1}: 3314, 3253, 3207, 2923, 2856, 1661, 1606, 1502, 1376, 1320, 1158, 1032, 929, 786, 686. Found, %: C 8.40; H 2.35; N 38.44. $CH_3N_4O_3Na$. Calculated, %: C 8.46; H 2.13; N 39.44.

Potassium salt of 4-nitrosemicarbazide (5c) was obtained similarly from salt **3b**. Yield 0.23 g (76%), mp 139–140°C (with decomposition) {130°C (with decomposition) [17]}. UV spectrum: λ_{max} 255.5 nm, logε 3.91. IR spectrum, ν, cm^{-1}: 3325, 3228, 3018, 2925, 2852, 1667, 1619, 1535, 1359, 1263, 1187, 1048, 1029, 957, 825, 781, 689. Found, %: C 7.38; H 1.86; N 35.48. $CH_3KN_4O_3$. Calculated, %: C 7.59; H 1.91; N 35.42.

Ammonium salt of 4-nitrosemicarbazide (5d). To a solution of 0.50 g (2.9 mmol) of salt **3b** in 10 mL of water was added 0.19 g (3.45 mmol) of ammonium chloride. After a full dissolution 0.13 mL (2.9 mmol) of 75% hydrazine-hydrate was added and the reaction mixture was stirred for 30 min at 30°C. Then 10 mL of ethanol was added, the reaction mixture was cooled to –15°C, the precipitate was filtered off, washed with a small amount of ethanol, and dried in open air. Yield 0.27 g (70%), mp 145°C (with decomposition). UV spectrum: λ_{max} 255 nm, logε 3.91. IR spectrum, ν, cm^{-1}: 3318, 3260, 3017, 1778, 1656, 1615, 1545, 1405, 1351, 1315, 1257, 1180, 1114, 1028, 950, 867, 822, 781, 732. Found, %: C 9.12; H 5.17; N 51.44. $CH_7N_5O_3$. Calculated, %: C 8.76; H 5.15; N 51.08.

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