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SHORT COMMUNICATIONS

Reaction of Potassium 2-(1-Adamantyl)ethynethiolate with Nitrilimines

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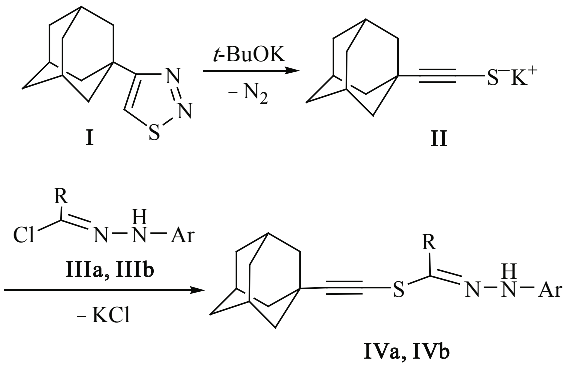
Nitrilimines are the most active donor Huisgen 1,3-dipoles that readily are brought into the [2+3]-cycloaddition reactions with thiocarbonyl compounds. The simplest method of nitrilimines generation is the reaction of hydrazonoyl chlorides with bases [1]. It was formerly established that potassium 2-arylethynethiolates form with nitrilimines products of [2+3]-cycloaddition, 1,3,4-thiadiazolines [2]. It was proved that this reaction could proceed both as a concerted 1,3-dipolar cycloaddition and in two stages. First a linear product formed resulting from the nucleophilic attack of the thiolate on the electrophilic site of the nitrilimine that at the treatment with a methanol solution of KOH quantitatively converted into thiadiazolidine. The reaction of potassium 2-arylethynethiolates with the initial compounds for nitrilimines synthesis (hydrazonoyl chlorides) occurred exclusively as the nucleophilic substitution of the halogen by the thiolate residue [2]. At the same time the reaction of potassium 2-*tert*-butylethynethiolate with nitrilimines afforded only the linear product of the nucleophilic attack of the thiolate on the electrophilic site of the nitrilimine. This product did not undergo the intramolecular cyclization under the treatment with bases evidently due to the geometry of the molecule [3].

Potassium 2-(1-adamantyl)ethynethiolate (**II**) obtained by the treatment with such a strong base as potassium *tert*-butylate of 4-(1-adamantyl)-1,2,3-thiadiazole (**I**) [4] readily reacted with hydrazonoyl chlorides **IIIa–IIIc**. However the direction of the reaction is ambiguous and depends on the character of the substituents in hydrazonoyl chlorides **IIIa–IIIc**. For instance, the reaction of potassium 2-(1-adamantyl)-ethynethiolate (**II**) with hydrazonoyl chlorides **IIIa, IIIb** containing strond electron-withdrawing substituents MeC=O (**IIIa**) and CO_2Me (**IIIb**) takes two routes. The first direction consists in the nucleophilic substitution of the halogen in hydrazonoyl chlorides **IIIa, IIIb by** thiolate **II**.

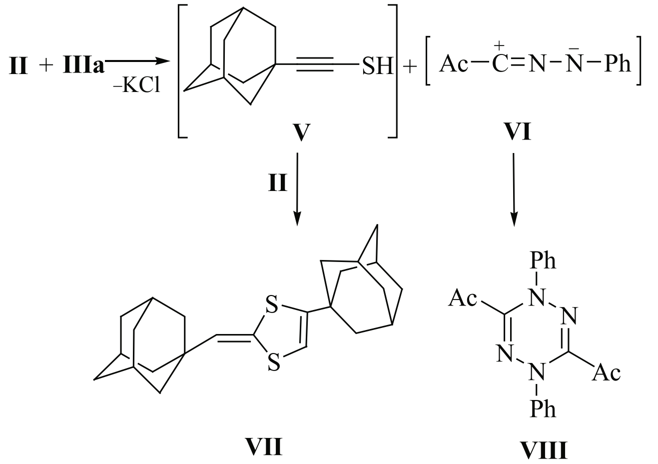


R = Ac, Ar = Ph (**a**); R = CO_2Me, Ar = 4-ClC_6H_4 (**b**).

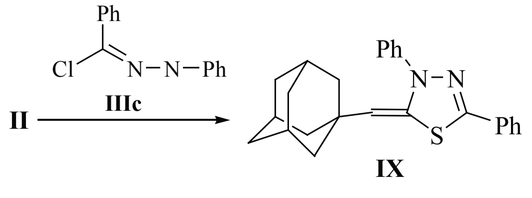
The structure of isolated products of the nucleophilic substitution 1-(1-adamantylethynethio)-1-phenylhydrazono-2-oxopropane (**IVa**) and methyl (1-adamantylethynethio)[(4-chlorophenyl)hydrazono] acetate (**IVb**) was proved by the IR, ^1H, ^{13}C NMR, and mass spectra. The IR spectra of hydrazones **IVa, IVb** contain the absorption bands of the stretching vibrations of the NH bonds in the region 3195 (**IVa**) and 3245 (**IVb**) cm^{-1}, no absorption bands of the stretching vibrations of the triple bonds, strong bands of the stretching vibrations of C=O [1708 (**IVa**), 1688 (**IVb**)] and C=N bonds [1520 (**IVa**), 1527 (**IVb**) cm^{-1}]. In the ^1H NMR spectra the signals of amine protons are present at δ_{NH} 10.53 (**IVa**) and 9.12 (**IVb**) ppm. The ^{13}C NMR spectra contain the signals of the carbon atoms of the triple bond SC≡ [61.22 (**IVa**), 59.45 (**IVb**)] and ≡C–C [103.3 (**IVa**), 107.1 (**IVb**) ppm]. In the mass spectra of hydrazones **IVa, IVb** fairly intensive peaks of molecular ions were observed.

The chromatographic separation of the reaction mixtures showed that alongside the formation of the products of nucleophilic substitution a second route of the reaction led to the formation of nitrilimine **VI** from hydrazonoyl chloride **IVa**. Here potassium 2-(1-adamantyl)ethynethiolate (**II**) played the role of a base. From this reaction "dimers" of thiolate (**II**) [2-(1-adamantyl)-methylene-4-(1-adamantyl)-2*H*-dithiol (**VII**)] and of nitrilimine **VI** [3,6-diacetyl-1,4-diphenyl-1*H*,4*H*-1,2,4,5-tetrazine (**VIII**)] were obtained.

The structure of tetrazine **VIII** and dithiol **VII** was proved by the comparison with the previously obtained samples [5, 6].



The change of the character of substituent to the electron-donor phenyl resulted in the reaction of [2+3]-cycloaddition of potassium 2-(1-adamantyl) ethynethiolate (**II**) to hydrazonoylchloride **IIIc**. Thus 2-(1-adamantyl)methylene-3,5-diphenyl-2*H*-1,3,4-thiadiazoline (**IX**) was obtained.



The structure of 2-(1-adamantyl)methylene-3,5-diphenyl-2*H*-1,3,4-thiadiazoline (**IX**) was proved with IR, ^{1}H, ^{13}C, and mass spectra. Its IR spectrum lacks the band of the stretching vibrations of NH bond and contains the characteristic bands of the stretching vibrations of CH=C bonds (3051 cm^{-1}). In the ^{1}H NMR spectrum the signal of amine proton is absent, the signal of the methylene proton appears at $\delta_{CH=C}$ 7.26 ppm. The ^{13}C NMR spectrum lacks the signals of the carbon atoms of triple bonds and contains the signals of the methine carbon atom C=<u>CH</u> (110.44 ppm) and atoms C^5 (127.31) and C^2 (155.88 ppm) of the heterocycle. A weak peak of the molecular ion is detected in the mass. The structure of the isolated thiadiazoline **IX** is confirmed by further fragmentation of the molecular ion. In contrast to hydrazones **IVa, IVb** the heterocyclic ring of compound **IX** is sufficiently stable, and the decomposition of adamantyl radical known by publications occurs with the ejection of C_4H_9 radical [7].

The obtained results of the study of the reaction between potassium 2-(1-adamantyl)ethynethiolate (**II**) and hydrazonoyl chlorides **IIIa–IIIc** and comparison with the published data on similar reactions with *tert*-butyl-substituted ethynethiolates [2, 3] show an essential difference in the effect on these reactions of the adamantyl and *tert*-butyl residues.

1-(Adamantan-1-ylethynylsulfanyl)-1-(*N*^{1}-phenylhydrazono)propan-2-one (IVa). To a solution of 0.5 g (2.2 mmol) of thiadiazole **I** in 25 ml of anhydrous THF was added 0.26 g (2.4 mmol) of potassium *tert*-butylate under an argon atmosphere at room temperature. The reaction mixture was stirred for 5 min till complete end of gas liberation; therewith a precipitate of potassium thiolate **II** separated from the reaction mixture. Then 0.43 g (2.2 mmol) of hydrazonoyl chloride **IIIa** was added. The reaction mixture was stirred for 3 h, the solvent was distilled off in a vacuum. The precipitate was washed with water, dried, dissolved in 20 ml of chloroform, and boiled with 5 g of silica gel for 0.5 h, the solvent was distilled off in a vacuum. The residue was crystallized from ethanol. Yield 0.1 g (13%). Colorless crystals, mp 154–155°C, R_f 0.45 (ethyl acetate–hexane, 1:8). IR spectrum, ν, cm^{-1}: 3195, 2927, 2901, 2892, 2848, 1708, 1597, 1520, 1471, 1435, 1245, 1185, 1065, 821, 756. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.56 m ($6H_{Ad}$), 1.72 m ($6H_{Ad}$), 1.83 m ($3H_{Ad}$), 2.43 s (3H, CH_3CO), 7.03 d (H^4_{Ph}, *J* 7 Hz), 7.34 t (H^3, H^5_{Ph}, *J* 7.5 Hz), 7.46 t (H^2, H^6_{Ph}, *J* 7 Hz), 10.53 s (NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 25.31 (CH_3), 27.21 (CH_{Ad}), 30.47 (C^1_{Ad}), 35.60, 41.96 (CH_{2Ad}), 61.22 (S<u>C</u>≡C), 103.30 (SC≡<u>C</u>), 115.06 ($C^{2,6}_{Ph}$), 123.09 (C^4_{Ph}), 126.78 (SC=N), 129.30 ($C^{3,5}_{Ph}$), 142.44 (C^1_{Ph}), 191.64 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 352 (12) $[M]^+$, 135

(74) $[Ad]^+$, 92 (100), 77 (21) $[Ph]^+$, 65 (45), 51 (9), 43 (75) $[CH_3CO]$. Found, %: C 71.38, 71.25; H 6.55, 6.72. $C_{21}H_{24}N_2OS$. Calculated, %: C 71.56; H 6.86. *M* 352.49.

3,6-Diacetyl-1,4-diphenyl-1*H*,4*H*-[1,2,4,5]-tetrazine (VIII). The precipitate after the reaction from the previous experiment was subjected to chromatography on a column (3 × 20 cm) packed with silica gel L 100/160, eluent ethyl acetate–hexane, 1:8, the fraction with R_f 0.36 was collected. The solvent was distilled off. Yield 0.15 g (35%). Red crystals, mp 161–162°C (mp 162–163°C [5]). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.53 s (6H, CH_3CO), 7.13m ($4H_{Ph}$), 7.28 m ($6H_{Ph}$).

From the fraction with R_f 0.81 on removing the solvent we obtained **2-(1-adamantyl)methylene-4-(1-adamantyl)-[1,3]dithiol (VII)**. Yield 0.15 g (41%). Colorless crystals, mp 252–255°C (mp 250–255°C [6]). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.80 m ($6H_{Ad}$), 2.02 m ($9H_{Ad}$), 5.11 s (*E*, H^4_{Ht}), 5.15 d (*Z*, H^4_{Ht}, *J* 2 Hz), 5.66 d (*Z*, CH=, *J* 2 Hz), 5.70 s (*E*, CH=).

Compounds **IVb, IX** were similarly obtained.

Methyl (1-adamantylethynylsulfanyl)[(4-chlorophenyl)hydrazono]acetate (IVb) was obtained from 0.5 g (2.2 mmol) of thiadiazole **I**, 0.26 g (2.4 mmol) of potassium *tert*-butylate, and 0.54 g (2.2 mmol) of hydrazonoyl chloride **IIIb**. The precipitate was subjected to chromatography on a column (3 × 20 cm) packed with silica gel L 100/160, eluent chloroform–hexane, 1 : 10, the fraction with R_f 0.41 (ethyl acetate–hexane, 1:8) was collected. The solvent was distilled off. Yield 0.29 g (33%). Light-yellow needle crystals, mp 153–154°C. IR spectrum, ν, cm^{-1}: 3245, 2927, 2904, 2849, 1688, 1602, 1527, 1491, 1450, 1235, 1024, 753, 688. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.63 m ($6H_{Ad}$), 1.78 m ($6H_{Ad}$), 1.91 m ($3H_{Ad}$), 3.89 s (3H, CH_3O), 7.21 d (H^3, H^5_{Ar}, *J* 7 Hz), 7.30 d (H^2, H^6_{Ar}, *J* 7 Hz), 9.12 s (NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 27.63 (CH_{Ad}), 31.07 (C^1_{Ad}), 35.02 + 42.28 (CH_{2Ad}), 52.99 (CH_3O), 59.45 ($S\underline{C}\equiv C$), 107.1 ($SC\equiv\underline{C}$), 115.64 (C^2, C^6_{Ar}), 119.2 (C^4_{Ar}), 128.12 (C^1_{Ar}), 129.4 (C^3, C^5_{Ar}), 140.41 (C=N), 162.65 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 402 (12) $[M]^+$, 135 (27) $[Ad]^+$, 126 (100), 111 (18), 99 (56), 91 (51), 79 (34), 63 (30), 53 (24), 41 (70). Found, %: C 62.78, 62.87; H 5.43, 5.39. $C_{21}H_{23}ClN_2O_2S$. Calculated, %: C 62.60; H 5.75. *M* 402.94.

2-(1-Adamantyl)methylene-3,5-diphenyl-2*H*-1,3,4-thiadiazoline (IX) was obtained from 0.5 g (2.2 mmol) of thiadiazole **I**, 0.26 g (2.4 mmol) of potassium *tert*-butylate, and 0.5 g (2.2 mmol) of the corresponding hydrazonoyl chloride **IIIc**. The precipitate was dissolved in 20 ml of chloroform, and boiled with 3 g of silica gel for 0.5 h, the solvent was distilled off in a vacuum. The residue was crystallized from ethanol. Yield 0.36 g (41%). Yellow-orange needle crystals, mp 210– 211°C, R_f 0.6 (ethyl acetate–hexane, 1:8). IR spectrum, ν, cm^{-1}: 3051, 3024, 2929, 2896, 2843, 1538, 1449, 1342, 1296, 1225, 1136, 736, 683, 591. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.88 m ($6H_{Ad}$), 2.17 m ($3H_{Ad}$), 2.30 m ($6H_{Ad}$), 7.23 m (H^3, H^5_{NPh}), 7.26 s (CH=), 7.48 m, 7.93 m ($8H_{Ar}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 28.66 (CH_{Ad}), 33.48 (C^1_{Ad}), 36.81, 42.60 (CH_{2Ad}), 110.44 ($C{=}\underline{CH}$), 112.70 (C^2_{Ht}), 119.91 + 120.25 ($C^{2,6}_{Ph}$), 126.46 (C^4_{N-Ph}), 127.31 ($C^1_{=C-Ph}$), 127.74 (C^1_{N-Ph}), 128.76 ($C^4_{=C-Ph}$), 130.37 + 130.66 ($C^{3,5}_{Ph}$), 155.88 (C^5_{Ht}). Масс-спеqtр, *m*/*z* (I_{rel}, %): 386 (7) $[M]^+$, 384 (96) $[M-2]^+$, 327 (100) $[M-2-C_4H_9]^+$, 290 (12), 263 (9), 250 (11), 223 (21), 186 (18), 165 (24), 135 (15) $[Ad]^+$, 128 (25), 121 (14), 103 (34), 91 (29), 77 (32) $[Ph]^+$, 67 (10), 51 (15), 41 (47). Found, %: C 77.47, 77.51; H 6.42, 6.81. $C_{25}H_{26}N_2S$. Calculated, %: C 77.68; H 6.78. *M* 386.55.

Melting points were measured on a Boëtius heating block. IR spectra were recorded on a spectrophotometer Shimadzu FTIR 84000S from pellets with KBr. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker AMX-400 (400 and 100 MHz respectively), the signals of residual protons (^1H) and carbon atoms (^{13}C) of deuterated solvents served as internal references. Mass spectra were taken on an instrument Finnigan INCOS MAT 95 with the direct admission of the sample into the ion source, ionizing electrons energy 70 eV, ionizing chamber temperature 200°C. The reaction progress was monitored by TLC on Silica Gel 60 F_{254} plates, development under UV irradiation or in iodine vapor. All solvents used in the study were purified and dried by standard procedures.

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