Regioselective reduction of 2-cyanoprop-2-enethioamides with sodium borohydride

V. V. Dotsenko[a,b]* *and S. G. Krivokolysko*[a]

[a]*ChemEx Laboratory, V. Dal´ East-Ukranian National University, 20A Molodyozhny kv., 91034 Lugansk, Ukraine. E-mail: Victor_Dotsenko@bigmir.net*
[b]*State Enterprise "Luganskstandartmetrologiya", 50 ul. Timiryazeva, 91021 Lugansk, Ukraine*

Treatment of 2-cyanoprop-2-enethioamides with $NaBH_4$ in EtOH gave C-alkylated cyanothioacetamides in 62—69% yields.

Key words: cyanothioacetamide, 2-cyanoprop-2-enethioamides, reduction, the Hantzsch thiazole synthesis, 2-(1-cyanoalkyl)thiazoles.

Reductive alkylation is a very popular method of C—C and C—N bond formation in various organic compounds.[1—3] In the case of active methylene compounds, C-alkylation is usually effected in two steps: (1) the Knoevenagel condensation with a carbonyl compound and (2) reduction of the resulting electron-deficient alkene using a wide range of reducing agents. This approach has been used to obtain monoalkylated derivatives of malononitrile,[4,5] ethyl cyanoacetate,[5,6] cyanoacetamide,[7] barbituric acid,[8] Meldrum´s acid,[9] ethyl acetoacetate,[10] ethyl malonate,[6,11] indane-1,3-dione,[12] and other 1,3-diketones.[10a,13] It allows selective and high-yielding synthesis of C-alkylation products from active methylene compounds and is especially useful when direct alkylation is not selective or gives C,C-dialkylation products. As a rule, direct C-alkylation of active methylene thioamides is also hindered by regiospecific alkylation at the S atom of the thioamide group. Known exceptions include successful syntheses of γ,β-unsaturated thioamides by tandem alkylation of thioamide dianions with allylic electrophiles followed by the thio-Claisen rearrangement of the resulting S-alkylated derivatives[14] and formal C-alkylation in the formation of stable acyclic adducts under the conditions of the Michael reaction.[15,16] Despite an obviously convenient introduction of an alkyl fragment into active methylene thioamides by a tandem process involving the Knoevenagel condensation/reduction of the C=C bond, we found only one example of such a transformation in the literature.[17]

In the present work, we tried to study the possibility of obtaining C-alkylated derivatives of cyanothioacetamide *via* reduction of products of its condensation with carbonyl compounds. It turned out that reduction of 2-cyanoprop-2-enethioamides **1** with $LiAlH_4$ in boiling diethyl ether proceeds nonselectively to give a complex mixture of products, regardless of the reaction conditions and the ratio of the reagents. However, unsaturated thioamides **1** and **2** smoothly and selectively react with excess $NaBH_4$ in EtOH to form the expected thioamides **3** and **4** in good yields (Scheme 1). The compounds obtained can be used in the Hantzsch condensation with α-halo ketones. This was illustrated with the synthesis of 2-(1-cyanoethyl)-thiazole **5** from thioamide **3a** and 4-methylphenacyl bromide.

It should be noted that reduction of compounds **1e**,**f** with excess $NaBH_4$ in EtOH did not produce thioamides **3e**,**f**: acidification of the reaction mixture results in its resinification. Apparently, when compounds contain reducible substituents, the reduction is not selective and proceeds any further. Compounds **3** and **4** are pale yellow fine crystalline solids that are well soluble in DMSO, ethyl acetate, acetone, and hot EtOH but are insoluble or poorly soluble in benzene and water. The structures of the compounds obtained were confirmed by IR and ^1H NMR spectroscopy as well as by HPLC/MS and elemental analysis.

The ^1H NMR spectra of compounds **3** show a characteristic ABX pattern: a multiplet for the diastereotopic methylene $C(3)H_2$ protons at δ 3.09—3.43 and a doublet of doublets for the C(2)H proton at δ 4.20—4.33 (^3J = 7.2—8.6 Hz). The signals for the protons of the thioamide group appear as two broadened peaks at δ 9.46—9.57 and 9.80—9.92. The IR spectra of compounds **3** and **4** contain no absorption bands due to conjugated cyano groups at 2200±30 cm^{-1}; the low-intensity bands at 2244—2256 cm^{-1} correspond to the stretching vibrations of the nonconjugated C≡N group.

To sum up, reactions of easily accessible derivatives of 2-cyanoprop-2-enethioamide with excess $NaBH_4$ in EtOH

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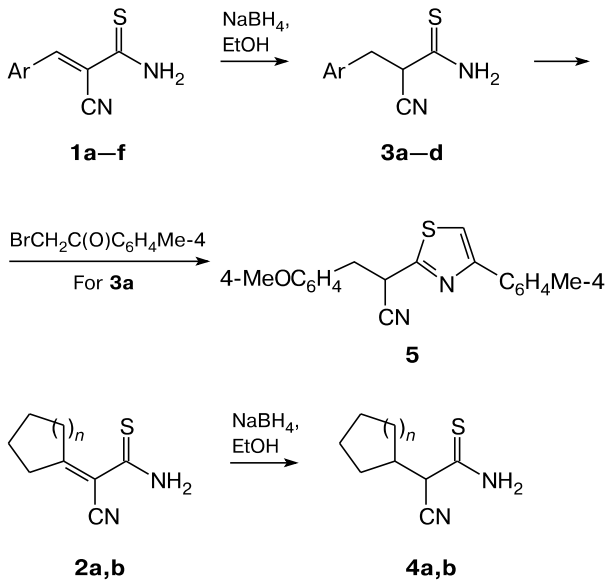
Scheme 1



Ar = 4-$MeOC_6H_4$ (**1a**, **3a**), 3,4-$(MeO)_2C_6H_3$ (**1b**, **3b**), 2-furyl (**1c**, **3c**), 2-ClC_6H_4 (**1d**, **3d**), 5-nitro-2-furyl (**1e**), 1-benzylbenzimidazol-2-yl (**1f**)
n = 1 (**2a**, **4a**), 2 (**2b**, **4b**)

allow reduction of the C=C bond to C-monoalkylated cyanothioacetamides, which hold promise as low-molecular-weight building blocks for the synthesis of heterocyclic compounds.

Experimental

^{1}H NMR spectra were recorded on Bruker Avance DPX-300 (300.16 MHz) (for **1e**), Bruker DRX-500 (500.13 MHz) (**1f**), and Bruker DPX-400 instruments (400.40 MHz) (the other compounds) in DMSO-d_6 with Me_4Si as the internal standard. The ^{13}C NMR spectrum of compound **1f** was recorded on a Bruker DRX-500 instrument (125.76 MHz) in DMSO-d_6, with Me_4Si as the internal standard. IR spectra were recorded on an Infralum FT-801 FTIR spectrometer (KBr pellets) (for **3a**), a Magna-IR 750 spectrophotometer (KBr) (**4a**), and an IKS-29 spectrophotometer (Nujol) (the other compounds). HPLC/MS analysis of compound **3b** was carried out using an Agilent 1200 instrument (Rapid Resolution HT Cartridge column, 4.6×30 mm, 1.8 μm, Zorbax SB-C18, ES-API ionization mode) equipped with DAD and MS detectors. The other compounds were analyzed with a Shimadzu LC-10AD liquid chromatograph equipped with Shimadzu SP D-10A UV-Vis (254 nm) and Sedex 75 ELSD detectors; the chromatograph was combined with a Perkin—Elmer SCIEX API 150EX mass spectrometer. Elemental analysis was carried out on a Carlo Erba Strumentazione 1106 analyzer. The individuality of the compounds was checked by TLC on Silufol UV-254 plates with acetone—hexane (1 : 1) as an eluent; spots were visualized with the iodine vapor and under UV light. Melting points were measured on a Kofler hot stage and are given uncorrected. The starting reagents 3-aryl-2-cyanoprop-2-enethioamides **1a**—**d** (see Ref. 18) and (cyano)(cycloalkylidene)thioacetamides **2a**,**b** (see Ref. 19) were prepared by condensation of cyanothioacetamide[20] with carbonyl compounds according to known procedures.

(*E*)-2-Cyano-3-(5-nitro-2-furyl)prop-2-enethioamide (1e). A mixture of cyanothioacetamide (1.00 g, 10 mmol) and 5-nitrofurfural (1.41 g, 10 mmol) in EtOH (15 mL) was stirred at ~30 °C to complete homogenization. Then one drop of *N*-methylmorpholine was added to the vigorously stirred resulting solution. A precipitate of the product formed within 1—2 min. The mixture was stirred for an additional 1 h and kept at 20 °C for 4 h. The precipitate was filtered off and washed with EtOH. Yield 1.97 g (88%), brown powder, m.p. 195—200 °C (decomp.) (*cf.* Ref. 21: m.p. 218 °C). Found (%): C, 43.19; H, 2.38; N, 18.60. $C_8H_5N_3O_3S$. Calculated (%): C, 43.05; H, 2.26; N, 18.83. IR (Nujol), ν/cm^{-1}: 3366, 3263, 3150 (N—H); 2214 (C≡N); 1458, 1377 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 7.59 (d, 2 H, C(3)H_{fur}, ^3J = 3.9 Hz); 7.84 (d, 2 H, C(4)H_{fur}, ^3J = 3.9 Hz); 8.00 (s, 1 H, —CH=); 9.70, 10.27 (both br.s, 1 H each, C(S)NH_2). MS, *m/z* (ES-API): 224.3 $[M + H]^+$.

(*E*)-3-(1-Benzyl-1*H*-benzimidazol-2-yl)-2-cyanoprop-2-enethioamide (1f) was obtained from 1-benzyl-1*H*-benzimidazole-2-carbaldehyde (1.11 g, 4.71 mmol) and cyanothioacetamide (0.47 g, 4.70 mmol) as described for thioamide **1e**. Yield 1.16 g (78%), brick-red powder, m.p. 192—194 °C, R_f 0.61 (acetone—hexane, 1 : 1). Found (%): C, 67.79; H, 4.53; N, 17.74. $C_{18}H_{14}N_4S$. Calculated (%): C, 67.90; H, 4.43; N, 17.60. IR (Nujol), ν/cm^{-1}: 3399, 3259, 3148 (N—H); 2208 (C≡N). ^{1}H NMR (500 MHz, DMSO-d_6), δ: 5.77 (s, 2 H, C$\underline{H}_2$Ph); 7.17 (d, 2 H, Ar, ^3J = 7.3 Hz); 7.27—7.40 (m, 5 H, Ar); 7.66 (d, 1 H, Ar, ^3J = 7.8 Hz); 7.83 (d, 2 H, Ar, ^3J = 7.8 Hz); 8.19 (s, 1 H, —CH=); 9.80, 10.29 (both br.s, 1 H each, C(S)NH_2). ^{13}C NMR (125 MHz, DMSO-d_6), δ: 46.90 ($\underline{C}H_2$Ph); 112.05 (=$\underline{C}$—CN); 115.58 (C_{Ar}); 116.63 (C≡N); 121.01 (C_{Ar}); 124.27 (C_{Ar}); 125.63 (C_{Ar}); 127.18 (C_{Ar}); 128.30 (C_{Ar}); 129.35 (C_{Ar}); 131.09 (C_{Ar}); 136.03 (C_{Ar}); 137.22 (C_{Ar}); 143.55 (C_{Ar}); 145.53 (C_{Ar}); 192.12 (—$\underline{C}$H=C—CN); 194.59 (C=S).

Reduction of unsaturated thioamides 1 and 2 (general procedure). Sodium borohydride (302 mg, 8 mmol) was added to a stirred suspension of an unsaturated thioamide **1a**—**f** or **2a**,**b** (4 mmol) in 96% EtOH (10—15 mL). A brief induction period was followed by an exothermic reaction (cooling on an ice water bath is required!) accompanied by evolution of H_2 and H_2S, dissolution of the starting thioamide, and decoloration of the solution. The reaction mixture was stirred for 1.5 h and diluted with water (10 mL). Then dilute (1 : 1) HCl was added dropwise to pH ~3—4. The reaction mixture was left for 2—4 days for completion of crystallization. The product was filtered and washed with water, 50% aqueous EtOH, and benzene (for **4a**,**b**, with benzene—light petroleum, 1 : 2) to complete decoloration of the filtrate. Compounds **3a**—**d** and **4a**,**b** were obtained in the analytically pure state. Reduction of thioamides **1e**,**f** followed by acidification with HCl resulted in strong resinification precluding isolation of the target products **3e**,**f**.

2-Cyano-3-(4-methoxyphenyl)propanethioamide (3a). Yield 69%, light yellow powder, m.p. 156—158 °C (subl.), R_f 0.60 (acetone—hexane, 1 : 1). Found (%): C, 60.18; H, 5.33; N, 12.94. $C_{11}H_{12}N_2OS$. Calculated (%): C, 59.97; H, 5.49; N, 12.72. MS, *m/z* (ES-API): 221.3 $[M + H]^+$, 238.1 $[M + NH_4]^+$, 441.4 $[2 M + H]^+$, 458.3 $[2 M + NH_4]^+$. IR (KBr), ν/cm^{-1}: 3366.6, 3281.9, 3165.6 (N—H); 2914.3, 2836.8 (C—H); 2247.1 (C≡N).

^{1}H NMR (400 MHz, DMSO-d_6), δ: 3.09—3.15 (m, 2 H, C(3)H_2); 3.76 (s, 3 H, MeO); 4.20 (dd, 1 H, C(2)H, ^3J = 8.6 Hz, ^3J = 8.6 Hz); 6.86, 7.22 (both d, 2 H each, Ar, ^3J = 8.9 Hz); 9.46, 9.80 (both br.s, 1 H each, C(S)NH_2).

2-Cyano-3-(3,4-dimethoxyphenyl)propanethioamide (3b). Yield 66%, pale yellow powder, m.p. 171.5—173.5 °C (acetone—toluene), R_f 0.60 (acetone—hexane, 1 : 1). Found (%): C, 57.39; H, 5.78; N, 11.30. $C_{12}H_{14}N_2O_2S$. Calculated (%): C, 57.58; H, 5.64; N, 11.19. MS, *m/z* (ES-API): 151.1 [3,4-$(MeO)_2C_6H_3CH_2]^+$, 251.1 $[M + H]^+$. IR (Nujol), ν/cm^{-1}: 3391, 3312, 3240 (N—H); 2256 (C≡N). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 3.09—3.19 (m, 2 H, C(3)H_2); 3.73, 3.74 (both s, 3 H each, MeO); 4.29 (dd, 1 H, C(2)H, ^3J = 7.5 Hz, ^3J = 7.8 Hz); 6.81 (d, 1 H, Ar, ^3J = 8.0 Hz); 6.89 (d, 2 H, Ar, ^3J = 8.0 Hz); 6.94 (s, 1 H, Ar); 9.53, 9.92 (both br.s, 1 H each, C(S)NH_2).

2-Cyano-3-(2-furyl)propanethioamide (3c). Yield 62%, fine crystalline beige powder, m.p. 135—137 °C (subl.). Found (%): C, 53.45; H, 4.61; N, 15.47. $C_8H_8N_2OS$. Calculated (%): C, 53.31; H, 4.47; N, 15.54. IR (Nujol), ν/cm^{-1}: 3355, 3285, 3145 (N—H); 2250 (C≡N). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 3.22—3.35 (m, 2 H, C(3)H_2); 4.33 (dd, 1 H, C(2)H, ^3J = 7.6 Hz, ^3J = 7.7 Hz); 6.27 (d, 1 H, C(3)H_{fur}, ^3J = 3.0 Hz); 6.35—6.37 (m, 1 H, C(4)H_{fur}); 7.51—7.52 (m, 1 H, C(5)H_{fur}); 9.54, 9.90 (both br.s, 1 H each, C(S)NH_2).

3-(2-Chlorophenyl)-2-cyanopropanethioamide (3d). Yield 66%, pale yellow needles, m.p. 139.5—141 °C (subl.), R_f 0.53 (acetone—hexane, 1 : 1). Found (%): C, 53.58; H, 4.03; N, 12.54. $C_{10}H_9ClN_2S$. Calculated (%): C, 53.45; H, 4.04; N, 12.47. MS, *m/z* (ES-API): 226.6 $[M + H]^+$, 451.5 $[2 M + H]^+$. IR (Nujol), ν/cm^{-1}: 3372, 3262, 3159 (N—H); 2248 (C≡N). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 3.30—3.43 (m, 2 H, C(3)H_2); 4.32 (dd, 1 H, C(2)H, ^3J = 7.2 Hz, ^3J = 8.3 Hz); 7.29—7.33, 7.41—7.45 (both m, 2 H each, Ar); 9.57, 9.91 (both br.s, 1 H each, C(S)NH_2).

2-Cyano-2-cyclopentylethanethioamide (4a). Yield 66%, pale yellow small needles, m.p. 113—115 °C (subl.). Found (%): C, 57.18; H, 7.27; N, 16.60. $C_8H_{12}N_2S$. Calculated (%): C, 57.11; H, 7.19; N, 16.65. MS, *m/z* (ES-API): 169.1 $[M + H]^+$, 337.3 $[2 M + H]^+$. IR (KBr), ν/cm^{-1}: 3361.3, 3284.2, 3162.7 (N—H); 2957.4, 2913.0, 2867.7 (C—H); 2243.8 (C≡N). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 1.16—1.28, 1.38—1.45 (both m, 1 H each, CH); 1.49—1.72 (m, 6 H, CH); 1.80—1.88 (m, 1 H, CH); 3.90 (d, 1 H, C(2)H, ^3J = 8.6 Hz); 9.50, 9.90 (both br.s, 1 H each, C(S)NH_2).

2-Cyano-2-cyclohexylethanethioamide (4b). Yield 69%, pale yellow fine crystalline powder, m.p. 134—137 °C (subl.). Found (%): C, 59.48; H, 7.87; N, 15.45. $C_9H_{14}N_2S$. Calculated (%): C, 59.30; H, 7.74; N, 15.37. MS, *m/z* (ES-API): 183.3 $[M + H]^+$, 365.3 $[2 M + H]^+$. IR (Nujol), ν/cm^{-1}: 3337, 3285, 3127 (N—H); 2247 (C≡N). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 0.95—1.29 (m, 5 H, CH); 1.61—1.75 (m, 4 H, CH); 1.90—2.02 (m, 2 H, CH); 3.83 (d, 1 H, C(2)H, ^3J = 8.3 Hz); 9.46, 9.92 (both br.s, 1 H each, C(S)NH_2).

3-(4-Methoxyphenyl)-2-[4-(4-methylphenyl)thiazol-2-yl]-propanenitrile (5). 4-Methylphenacyl bromide (0.258 g, 1.21 mmol) was added to a solution of thioamide **3a** (0.267 g, 1.21 mmol) in DMF (2 mL). The reaction mixture was brought to boiling and left at 20 °C for 72 h. Then the mixture was treated with water (10 mL) and left at 20 °C for 24 h. The aqueous layer was poured out by decantation and the resinous oily residue was recrystallized from EtOH. The colorless crystalline product was filtered off and washed with EtOH and light petroleum. Yield 54%, m.p. 102.5—104.5 °C. Found (%): C, 71.68; H, 5.47; N, 8.50. $C_{20}H_{18}N_2OS$. Calculated (%): C, 71.83; H, 5.42; N, 8.38. IR (Nujol), ν/cm^{-1}: 2249 (C≡N). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 2.34 (s, 3 H, Me); 3.28—3.39 (m, 2 H, C(3)H_2); 3.72 (s, 3 H, MeO); 3.83 (dd, 1 H, C(2)H, ^3J = 6.7 Hz, ^3J = 8.3 Hz); 6.88, 7.24 (both d, 2 H each, Ar, ^3J = 8.6 Hz); 7.27, 7.86 (both d, 2 H each, Ar, ^3J = 7.9 Hz); 8.04 (s, 1 H, C(5)$H_{thiazolyl}$).

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