Transformations of *N*-ethylamines into amide derivatives under the action of sulfur monochloride

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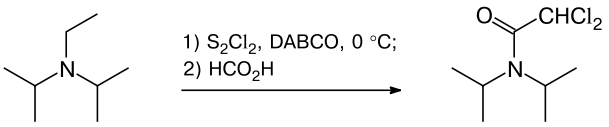
Tertiary *N*-ethylamines were converted into amide derivatives by reactions with sulfur monochloride and DABCO at 0 °C. Depending on the nature of the substituents in the amine, the reaction can be accompanied by unexpected transformations.

Key words: sulfur monochloride, tertiary amines, dichloroacetamides, 1,2-dithiol-3-ones.

Reactions of *N*-substituted diisopropylamines, especially commercial and inexpensive *N*-ethyl-*N*,*N*-diisopropylamine (**1a**) (Hünig base), with sulfur monochloride have been intensively studied by us for more than 10 years. It was believed for a long period of time that such reactions involve only the isopropyl groups of these compounds, which allowed the synthesis of complex S,N-containing heterocycles, *e.g.*, bis[1,2]dithiolo[1,4]thiazines,[1] bis[1,2]dithiolopyrroles,[2] and bis[1,2]dithiolylamines.[3] In our further investigations in this field, we found the conditions for the reaction to stop at the formation of monocyclic 1,2-dithioles.[4] Tests of these compounds for anticancer activity at the US National Cancer Institute have revealed their appreciable effects against certain types of cancer.[5]

Recently,[6] we have demonstrated that the pathway of the reaction of Hünig base **1a** with S_2Cl_2 and 1,4-diazabicyclo[2.2.2]octane (DABCO) dramatically changes at a lower temperature (0 °C) so that the transformation selectively occurs at the *N*-ethyl group to give *N*,*N*-diisopropyldichloroacetamide (**2**), the isopropyl groups remaining intact (Scheme 1).

Scheme 1



1a **2**

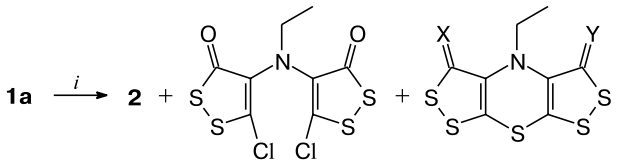
The discovered transformation of the *N*-ethyl group into a dichloroacetamido one has not been documented hitherto and opens up new possibilities for functionalization of *N*-alkyl groups in compounds that can be of interest for fine organic synthesis.

Here we studied reactions of tertiary amines containing ethyl or β-substituted ethyl groups with sulfur monochloride and the influence of the structures of the starting reagents on the reaction outcome.

Results and Discussion

A study of a reaction of *N*-ethyl-*N*,*N*-diisopropylamine (**1a**) with S_2Cl_2 and DABCO in chloroform (Scheme 2) and an analysis of the previous results (Table 1) showed that amide **2** is formed on keeping the reaction mixture at 0 °C. At room temperature, tricyclic bis[1,2]dithiolo[1,4]thiazines **4** were the major reaction products, while at −20 °C, the reaction proceeded slowly to give dithiolothiazines **5** and **6** in low yields. The amounts of S_2Cl_2 and DABCO have no substantial effect on the reaction pathway; with an increase in their amounts, the yield of amide **2** decreased only slightly. Selected data on optimization of the synthesis of amide **2** from the Hünig base are given in Table 1.

Scheme 2



3 **4—6**

i. 1) S_2Cl_2, DABCO; 2) HCO_2H.

X = Y = O (**4**); X = S, Y = O (**5**); X = Y = S (**6**)

The best conditions for the synthesis of amide **2** are as follows: chloroform as a solvent, 0 °C, 3 days, further

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1135—1140, June, 2007.

Table 1. Conditions (amounts of the reagents and the reaction temperature) and the yields of the products for the reaction of Hünig base **1a** with S_2Cl_2 and DABCO

Entry	Amounts of the reagents*/mmol		*T* /°C	Yields of the reaction products (%)				
	S_2Cl_2	DABCO		**2**	**3**	**4**	**5**	**6**
1[1]	10	10	20	—	—	42	—	—
2[3]	8	6	20	—	10	8	—	—
3	5	5	20	19	—	—	20	—
4	5	5	0	41	—	—	—	—
5	7	7	0	34	—	—	—	—
6	10	5	0	12	17	20	—	—
7	5	5	–20	—	—	—	11	6

* Per millimole of compound **1a**.

treatment with formic acid. The yield of product **2** was 41%.

Apparently, the key step of the reaction is oxidation of the tertiary amine with S_2Cl_2 into iminium ion **7** or **8** (Scheme 3). The final reaction outcome (formation of compounds **3**—**6** or amide **2**) depends on which of the ions (**7** or **8**) will have a higher concentration under the reaction conditions. At 0 °C, the conditions seem to be more favorable for oxidative abstraction of the sterically less blocked α-H atom of the ethyl group rather than the proton of the isopropyl group; this process yields kinetically controlled iminium ion **7** rather than more stable ion **8**. Ion **7** probably undergoes a transformation into enamine **9**, which then oxidizes to give tetrachloride **10**. The latter is transformed in the presence of formic acid into the final amide **2** (see Scheme 3). Apparently, the isopropyl groups in intermediates **7**—**10** are deactivated and inert to electrophilic species. For instance, *N*,*N*-diisopropyldichloroacetamide (**2**) is inert in the reaction with S_2Cl_2 and DABCO even at room temperature. Earlier,[1] we have shown that neither *N*-acetyl- nor *N*-cyano(diisopropyl)amines reacts with S_2Cl_2 under analogous conditions.

Possible selective formation of iminium ion **7** rather than its isomer **8** has been illustrated[7] with oxidation of Hünig base **1a** with trifluoroacetic anhydride in CH_2Cl_2 at 0 °C; no products of the oxidation of the isopropyl group were detected.

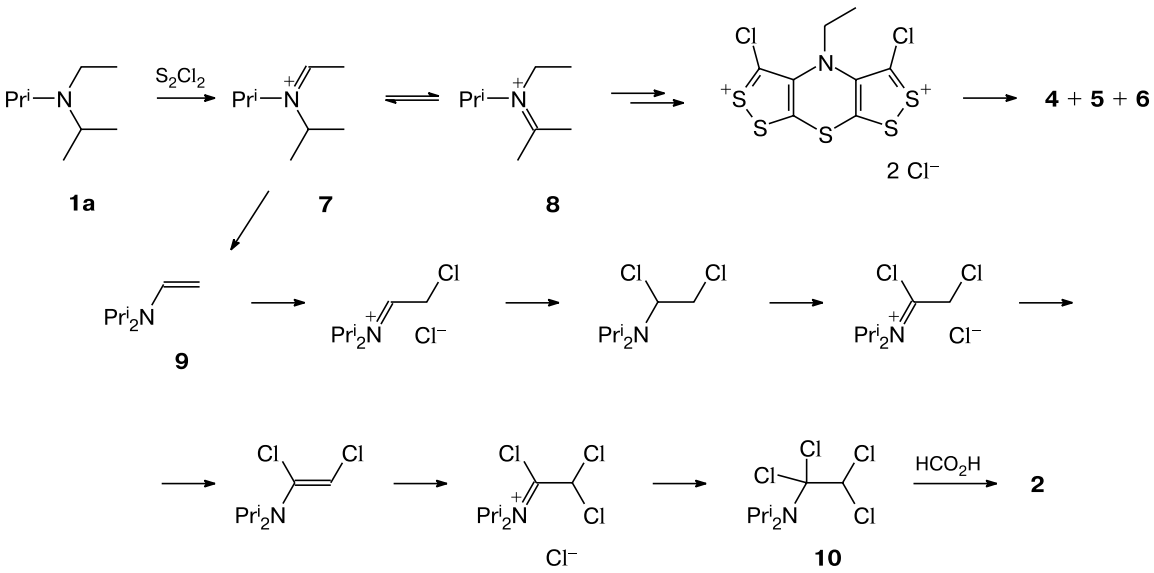
Thus, our study revealed that the reaction of the Hünig base with S_2Cl_2 and DABCO at 0 °C involves the ethyl group to give dichloroacetyl derivative **2**, while at room temperature, the isopropyl group transformation leads to 1,2-dithioles.

Since analogous transformations of the *N*-ethyl group have not been documented, in a search for an area of their application we studied reactions of a number of *N*-(2-R-ethyl)-*N*,*N*-diisopropylamines with S_2Cl_2 and DABCO under the conditions of the synthesis of amide **2**. It turned out that the reaction outcomes substantially depend on the nature of the substituent R and that the reactions can be complicated by unexpected rearrangements.

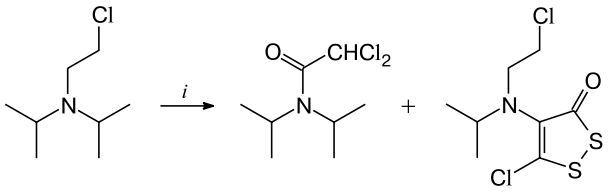
A reaction of *N*-(2-chloroethyl)-*N*,*N*-diisopropylamine (**1b**) with S_2Cl_2 and DABCO at 0 °C followed by treatment with formic acid gave two products: dichloroacetyl derivative **2** and 1,2-dithiol-3-one **11b** (Scheme 4). Note that the corresponding dithiolone **11a** was not detected among the products obtained from Hünig base **1a** under analogous conditions.

Obviously, the chloroethyl group in amine **1b** oxidizes like the ethyl group but the oxidation rate is lower, which

Scheme 3



Scheme 4



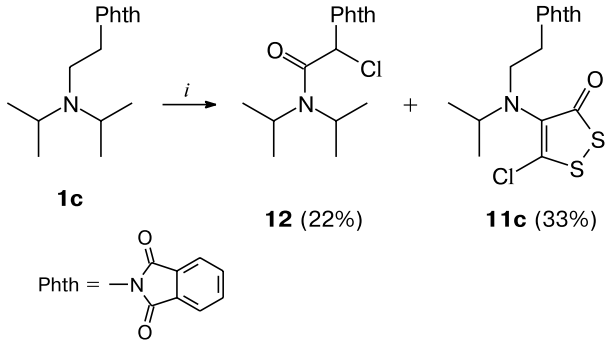
1b **2** (21%) **11b** (34%)

i. 1) S_2Cl_2, DABCO, 0 °C; 2) HCO_2H.

allows the isopropyl group to participate in a competitive reaction leading to dithiolone **11b**. Based on the reaction mechanism (see Scheme 3) and the results summarized in Table 1, we concluded that the transformation of the isopropyl group should be favored by an increased reaction temperature, while the formation of dichloroacetamide, by the lowered temperature. This was additionally confirmed by the reaction of amine **1b** with S_2Cl_2 and DABCO in boiling chloroform, giving a mixture of bis[1,2]dithiolo[1,4]thiazines[8] (although in low yields), while compound **2** was detected only in trace amounts (TLC). An analogous reaction at −20 °C selectively afforded dichloroacetamide **2**; however, its yield was low (12%).

N-(2-Phthalimidoethyl)diisopropylamine (**1c**) reacted like chloro analog **1b** to give chloroacetamide **12** and dithiolone **11c**, respectively, in virtually the same yields (Scheme 5).

Scheme 5

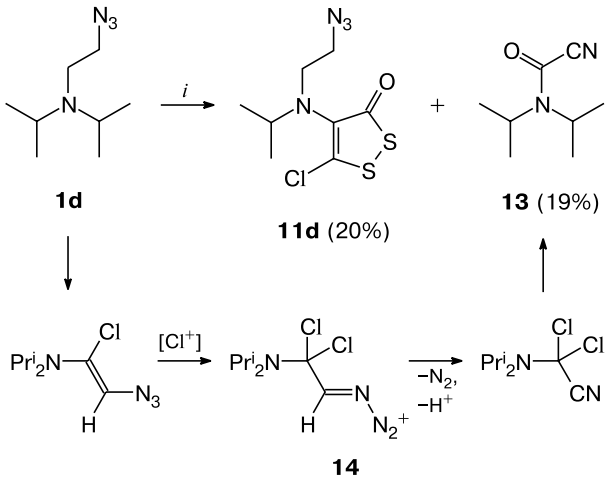


1c **12** (22%) **11c** (33%)

i. 1) S_2Cl_2, DABCO, 0 °C; 2) HCO_2H.

Reactions of *N*-(2-azidoethyl)diisopropylamine (**1d**) with S_2Cl_2 and DABCO at 0 °C also gave dithiolone **11d** as the result of a transformation at the isopropyl group. The ethyl group is also involved but the product was cyanoformyl derivative **13** rather than the expected azidoacetyl one (Scheme 6). It is known[9] that the azidomethyl group can be transformed into a cyano group in the presence of palladium catalysts or bromine trifluoride. However, no transformation of the azidoethyl group into a C(O)CN group has been observed hitherto. The formation of this compound can be explained in terms of the general mechanism (see Scheme 3) by elimination of a nitrogen molecule from an intermediate (most likely, **14**) followed by formation of a triple CN bond (see Scheme 6).

Scheme 6



1d **11d** (20%) **13** (19%)

14

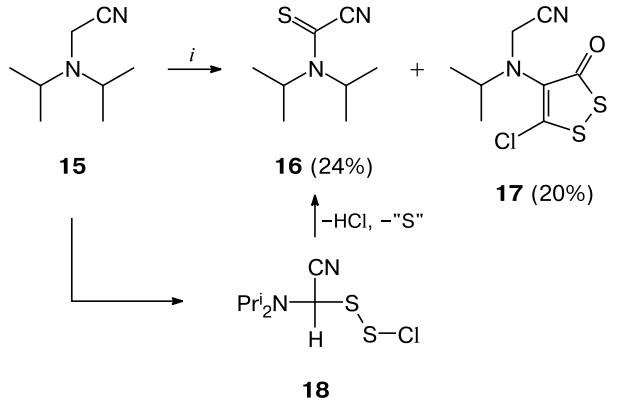
i. 1) S_2Cl_2, DABCO, 0 °C; 2) HCO_2H.

The formation of cyanoformamide **13** from azidoethyl derivative **1d** prompted us to use *N*-cyanomethyl-*N*,*N*-diisopropylamine **15** in the reaction with S_2Cl_2 and DABCO. We expected that the same compound **13** would be obtained, possibly in a higher yield. However, along with dithiolone **17** (20%), we isolated from the reaction mixture cyanothioformamide **16** (24%). The formation of compound **16** instead of carboxamide **13** suggested an alternative mechanism of the reaction with S_2Cl_2, probably, because of the presence of the cyano group in the starting amine **15**. Apparently, in this case, S_2Cl_2 adds to the activated methylene group to give S—S—Cl derivative **18** (analogous addition has been described earlier[10]), which is followed by elimination of an S atom and an HCl molecule (Scheme 7).

The possibility of this reaction pathway for acetonitrile derivatives was indirectly confirmed by a reaction of *N*-(2-cyanoethyl)-*N*,*N*-diisopropylamine (**1e**) with S_2Cl_2 and DABCO at 0 °C. Apart from chlorodithiolone **11e** (24%), we isolated a yellow crystalline product. Its molecular formula ($C_{18}H_{30}N_4S_4$) was assigned from elemental analysis data and mass spectra; ^1H and ^{13}C NMR spectra provide evidence for dimer **19** (Scheme 8).

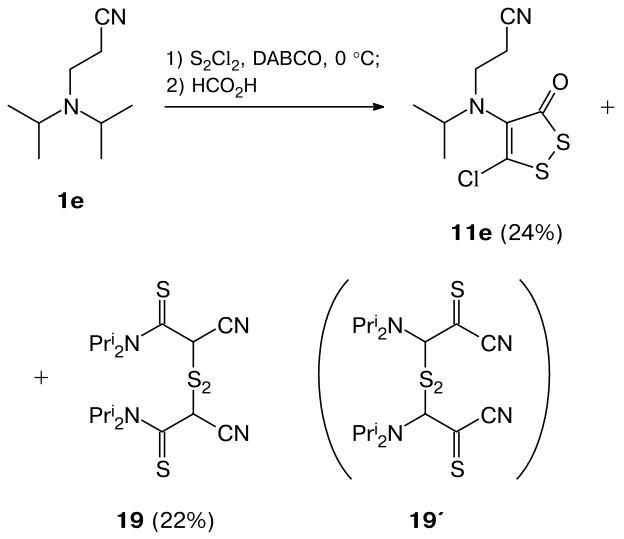
Alternative structure **19′** is possible for compound **19**; however, the calculated data of the ^{13}C NMR spectra are closer to the parameters of structure **19**. A plausible route

Scheme 7



i. 1) S_2Cl_2, DABCO, 0 °C; 2) HCO_2H.

Scheme 8

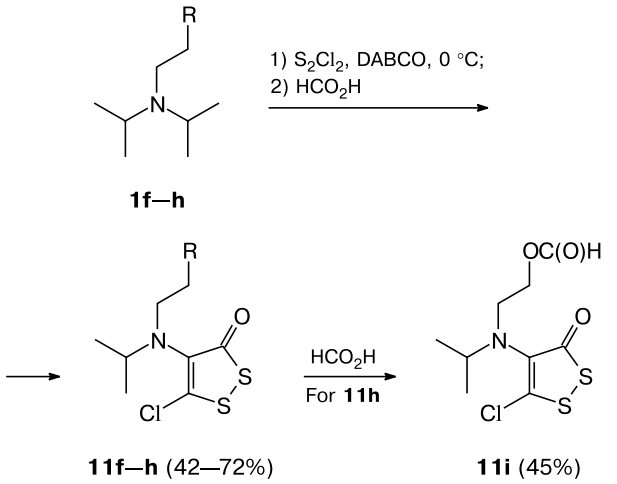


to product **19** involves an attack of S_2Cl_2 on the α-C atom with respect to the cyano group in compound **1e** (as shown in Scheme 7) followed by addition of another amine molecule and formation of a dimer *via* an S—S bridge. Then two thiocarbonyl groups will form according to the mechanism described for compound **16**.

Reactions of S_2Cl_2 with other substituted diisopropylamines containing ethoxycarbonylethyl (**1f**), phenylthioethyl (**1g**), and phenylsulfonylethyl groups (**1h**) gave under analogous conditions 1,2-dithiole derivatives in yields up to 70% (Scheme 9).

To obtain dithiolone **11h** from phenylsulfonyl derivative **1h**, a fivefold excess of formic acid is quite sufficient for the conversion of a dithiolium salt into dithiolone and quenching of the excess of S_2Cl_2. A greater excess of HCO_2H leads to nucleophilic displacement of the sulfonyl group to give formyloxy dithiolone **11i**.

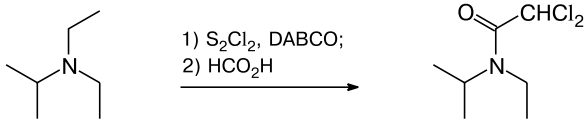
Scheme 9



R = CO_2Et (**f**), SPh (**g**), SO_2Ph (**h**)

In summary, we found that the reactions of *N*-(2-R-ethyl)-*N*,*N*-diisopropylamines with S_2Cl_2 and DABCO at 0 °C, in contrast to an analogous reaction of the Hünig base, not always yield dichloroacetamides; in some cases, the isopropyl group also undergoes a transformation leading to 1,2-dithiolones. That is why we tried to use in the reactions with S_2Cl_2 other tertiary diethylamines: *N*,*N*-diethyl-*N*-isopropylamine (**20**) and triethylamine. Under appropriate conditions, dichloroacetamide **21** was obtained from *N*,*N*-diethyl-*N*-isopropylamine in 34% yield. Moreover, even if the reaction was carried out at room temperature for three days, only the ethyl group was involved and the yield of acetamide **21** increased to 54% (Scheme 10).

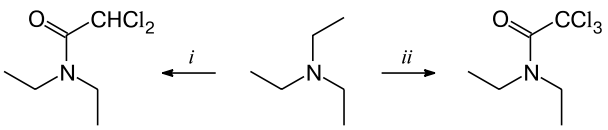
Scheme 10



Room temperature was also an optimum for a reaction of S_2Cl_2 and DABCO with triethylamine, which contains no isopropyl groups; the yield of dichloroacetamide **22** was 51%. However, with a decrease in the reaction temperature, the yield of amide **22** gradually declined to trace amounts. At –10 °C, the major product was trichloroacetyl derivative **23** (23%) (Scheme 11). The transformation of the *N*-ethyl group into the $N—C(O)CCl_3$ group has not been documented hitherto, as well. The formation of trichloroacetamide **23** in the chlorination of the ethyl group in triethylamine can be explained by dimin-

ished steric hindrances compared to the Hünig base and *N*,*N*-diethyl-*N*-isopropylamine.

Scheme 11



22 (51%) **23** (23%)

i. 1) S_2Cl_2, DABCO, ~20 °C; 2) HCO_2H.
ii. 1) S_2Cl_2, DABCO, −10 °C; 2) HCO_2H.

Experimental

^{1}H NMR spectra were recorded on Bruker WM-250 and Bruker AM-300 instruments (250 and 300 MHz, respectively) in $CDCl_3$. Chemical shifts are given on the δ scale with reference to Me_4Si. Melting points were determined on a Kofler instrument and are given uncorrected. Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument (EI).

The starting substituted diisopropylamines **1c**,[11] **1d**,[4] **1e**,[12] **1f**,[13] and **1g** [8] were prepared as described earlier.

***N*,*N*-Diisopropyl-*N*-[2-(phenylsulfonyl)ethyl]amine (1h)** was prepared from *N*-(2-chloroethyl)-*N*,*N*-diisopropylamine and sodium benzenesulfinate in THF at ~20 °C. The yield was 86%, a yellow oil. Found (%): C, 62.74; H, 8.72; N, 5.03. $C_{14}H_{23}NO_2S$. Calculated (%): C, 62.42; H, 8.61; N, 5.20. ^{1}H NMR ($CDCl_3$), δ: 0.93 (d, 12 H, 4 Me, J = 6.6 Hz); 2.63 (t, 2 H, CH_2, J = 5.9 Hz); 2.92 (sept, 2 H, 2 C<u>H</u>Me_2, J = 6.6 Hz); 3.56, 3.90 (both m, 1 H each, CH_2S); 7.54 (m, 3 H, Ph); 7.73 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 20.97 (4 Me); 35.21, 45.37 (2 CH_2); 49.17 (2 CH); 125.75 (CH_{Ph}); 128.86 (2 CH_{Ph}); 129.12 (2 CH_{Ph}); 139.94 (CS_{Ph}). MS (EI, 70 eV), m/z (I_{rel} (%)): 269 $[M]^+$ (3), 254 (23), 212 (17), 114 (100). IR (KBr), ν/cm^{-1}: 2970 (C—H).

Reactions of substituted diisopropylamines 1 with S_2Cl_2 and DABCO (general procedure). A solution of S_2Cl_2 (0.4 mL, 5 mmol) in chloroform (5 mL) was added dropwise at −40 to −45 °C to a solution of amine **1** (1 mmol) and DABCO (0.55 g, 5 mmol) in chloroform (20 mL). The mixture was left at 0 °C for 72 h and then HCO_2H (3.75 mL, 100 mmol) was added dropwise at 0 °C. The mixture was slowly warmed to ~20 °C, refluxed for 1 h, and filtered on cooling. The precipitate was washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was chromatographed on Merck 60 silica gel with CH_2Cl_2—light petroleum as an eluent.

The spectroscopic characteristics of substituted 3*H*-1,2-dithiol-3-ones **11b,d,e,f** are analogous to those cited earlier.[4,11]

The properties of dichloroacetamides **2**,[14] **21**,[15] and **22**,[16] trichloroacetamide **23**,[17] and compounds **13** [18] and **15** [19] are identical with the literature data.

2-{2-[*N*-(5-Chloro-3-oxo-3*H*-1,2-dithiol-4-yl)-*N*-isopropylamino]ethyl}-1*H*-isoindole-1,3(2*H*)-dione (11c). The yield was 33%, m.p. 104—106 °C. Found (%): C, 50.32; H, 4.06; N, 7.13. $C_{16}H_{15}ClN_2O_3S_2$. Calculated (%): C, 50.19; H, 3.95; N, 7.32. ^{1}H NMR ($CDCl_3$), δ: 1.11 (d, 6 H, ($C\underline{H}_3)_2$CH, J = 6.6 Hz); 3.35 (sept, 1 H, C<u>H</u>Me_2, J = 6.6 Hz); 3.35, 3.70 (both t, 2 H each, 2 CH_2, J = 6.6 Hz); 7.70, 7.83 (both m, 2 H each, Ar). ^{13}C NMR ($CDCl_3$), δ: 21.33 (2 Me); 37.54, 54.27 (2 CH_2); 42.54 (<u>C</u>HMe_2); 123.13, 133.89 (4 CH_{Ar}); 132.17, 137.28, 153.08, 168.17, 187.66 (5 C quaternary). MS (EI, 70 eV), m/z (I_{rel} (%)): 382 $[M]^+$ (11), 222 (91), 180 (100), 130 (46). IR (KBr), ν/cm^{-1}: 2908 (C—H); 1768, 1652 (C=O); 720 (C—Cl).

5-Chloro-4-{*N*-isopropyl-*N*-[2-(phenylthio)ethyl]amino}-3*H*-1,2-dithiol-3-one (11g). The yield was 72%, a yellow oil. Found (%): C, 48.23; H, 4.52; N, 4.32. $C_{14}H_{16}ClNOS_3$. Calculated (%): C, 48.61; H, 4.66; N, 4.05. ^{1}H NMR ($CDCl_3$), δ: 1.10 (d, 6 H, ($C\underline{H}_3)_2$CH, J = 6.6 Hz); 2.89, 3.34 (both t, 2 H each, 2 CH_2, J = 6.6 Hz); 3.39 (sept, 1 H, C<u>H</u>Me_2, J = 6.6 Hz); 7.20 (m, 3 H, Ph); 7.29 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 21.72 (2 Me); 33.45, 45.64 (2 CH_2); 53.69 (<u>C</u>HMe_2); 126.05 (CH_{Ph}); 128.99 (2 CH_{Ph}); 129.19 (2 CH_{Ph}); 130.99, 136.21, 154.19, 187.70 (4 C quaternary). MS (EI, 70 eV), m/z (I_{rel} (%)): 345 $[M]^+$ (15), 222 (100), 180 (98), 109 (50). IR (KBr), ν/cm^{-1}: 2968, 2924 (C—H); 1728, 1664 (C=O); 740 (C—Cl).

5-Chloro-4-{*N*-isopropyl-*N*-[2-(phenylsulfonyl)ethyl]amino}-3*H*-1,2-dithiol-3-one (11h). The yield was 67%, a yellow oil. Found (%): C, 44.26; H, 4.14; N, 3.98. $C_{14}H_{16}ClNO_3S_3$. Calculated (%): C, 44.49; H, 4.27; N, 3.71. ^{1}H NMR ($CDCl_3$), δ: 1.04 (d, 6 H, ($C\underline{H}_3)_2$CH, J = 6.6 Hz); 3.18, 3.39 (both t, 2 H each, 2 CH_2, J = 6.6 Hz); 3.49 (sept, 1 H, C<u>H</u>Me_2, J = 6.6 Hz); 7.63 (m, 3 H, Ph); 7.88 (d, 2 H, Ph, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.61 (2 Me); 45.78, 54.00 (2 CH_2); 63.58 (<u>C</u>HMe_2); 125.17 (2 CH_{Ph}); 129.02 (2 CH_{Ph}); 132.17 (CH_{Ph}); 133.84, 137.54, 154.28, 187.55 (4 C quaternary). MS (EI, 70 eV), m/z (I_{rel} (%)): 377 $[M]^+$ (4), 262 (3), 235 (13), 222 (47), 180 (74), 125 (49), 97 (30), 77 (100), 51 (64), 43 (100). IR (KBr), ν/cm^{-1}: 2968, 2928 (C—H); 1660 (C=O); 756 (C—Cl).

5-Chloro-4-{*N*-[2-(formyloxy)ethyl]-*N*-isopropylamino}-3*H*-1,2-dithiol-3-one (11i). The yield was 45%, a yellow oil. Found (%): C, 38.18; H, 4.25; N, 4.73. $C_9H_{12}ClNO_3S_2$. Calculated (%): C, 38.36; H, 4.29; N, 4.97. ^{1}H NMR ($CDCl_3$), δ: 1.11 (d, 6 H, ($C\underline{H}_3)_2$CH, J = 6.6 Hz); 3.37 (sept, 1 H, C<u>H</u>Me_2, J = 6.6 Hz); 3.39, 4.09 (both t, 2 H each, 2 CH_2, J = 5.9 Hz); 8.00 (s, 1 H, C(O)H). ^{13}C NMR ($CDCl_3$), δ: 21.65 (2 Me); 44.77, 54.13 (2 CH_2); 54.3 (<u>C</u>HMe_2); 137.56, 154.72 (2 C quaternary); 160.86 (C(O)H); 187.66 (C=O). MS (EI, 70 eV), m/z (I_{rel} (%)): 281 $[M]^+$ (18), 222 (18), 180 (41), 73 (100). IR (KBr), ν/cm^{-1}: 2986, 2928 (C—H); 1728, 1656 (C=O); 736 (C—Cl).

***N*,*N*-Diisopropyl-2-chloro-2-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)acetamide (12).** The yield was 22%, m.p. 160—162 °C. Found (%): C, 59.36; H, 5.72; N, 8.88. $C_{16}H_{19}ClN_2O_3$. Calculated (%): C, 59.54; H, 5.93; N, 8.68. ^{1}H NMR ($CDCl_3$), δ: 1.38, 1.41 (both d, 6 H each, 2 ($C\underline{H}_3)_2$CH, J = 5.9 Hz); 3.43, 3.98 (both sept, 1 H each, 2 C<u>H</u>Me_2, J = 5.9 Hz); 6.61 (s, 1 H, CHCl); 7.76, 7.90 (both m, 2 H each, Ar). ^{13}C NMR ($CDCl_3$), δ: 19.87, 19.93 (4 Me); 46.88, 49.40 (2 <u>C</u>HMe_2); 59.01 (CHCl); 124.08, 134.73 (2 CH_{Ar}); 131.52 (1 C quaternary); 160.59, 165.58 (2 C=O). MS (EI, 70 eV), m/z (I_{rel} (%)): 322 $[M]^+$ (1), 287 (2), 222 (2), 194 (20), 128 (82), 86 (95), 43 (100). IR (KBr), ν/cm^{-1}: 2930 (C—H); 1680 (C=O); 730 (C—Cl).

***N*,*N*-Diisopropyl-2-cyanothioacetamide (16).** The yield was 24%, yellow crystals, m.p. 75—78 °C. Found (%): C, 62.28; H, 9.23; N, 18.36. $C_8H_{14}N_2S$. Calculated (%): C, 62.31; H, 9.15;

N, 18.17. ^{1}H NMR ($CDCl_3$), δ: 1.35, 1.57 (both d, 6 H each, 4 Me, J = 6.2 Hz); 4.26 (br.s, 2 H, 2 CH). ^{13}C NMR ($CDCl_3$), δ: 18.53, 21.42 (2 Me); 51.86 (CH); 113.02 (CN); 163.74 (C=S). MS (EI, 70 eV), m/z (I_{rel} (%)): 170 $[M]^+$ (87), 127 (86), 113 (14), 101 (43). IR (KBr), ν/cm^{-1}: 2980 (C—H); 2150 (CN). High-resolution MS, found: m/z 170.0879 $[M]^+$. $C_8H_{14}N_2S$. Calculated: M = 170.0878.

[*N*-(5-Chloro-3-oxo-3*H*-1,2-dithiol-4-yl)-*N*-isopropylamino]acetonitrile (17). The yield was 20%, a yellow oil. Found (%): C, 38.39; H, 3.42; N, 11.48. $C_8H_9ClN_2OS_2$. Calculated (%): C, 38.63; H, 3.65; N, 11.26. ^{1}H NMR ($CDCl_3$), δ: 1.12 (d, 6 H, 2 Me, J = 6.6 Hz); 3.51 (q, 1 H, CH, J = 6.5 Hz); 4.01 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 21.17 (Me); 35.93 (CH_2); 53.59 (CH); 117.15 (CN); 136.12, 155.97, 187.17 (C=O, 2 C quaternary). MS (EI, 70 eV), m/z (I_{rel} (%)): 248 $[M]^+$ (74), 233 (47), 206 (61), 179 (33). IR (KBr), ν/cm^{-1}: 2980 (C—H); 2140 (CN); 1660 (C=O). High-resolution MS, found: m/z 247.9864 $[M]^+$. $C_8H_9ClN_2OS_2$. Calculated: M = 247.9845.

Bis(1-cyano-2-diisopropylamino-2-thioxoethyl) disulfide (19). The yield was 22%, yellow crystals, m.p. 124—126 °C. Found (%): C, 49.95; H, 7.00; N, 12.75; S, 29.96. $C_{18}H_{30}N_4S_4$. Calculated (%): C, 50.19; H, 7.02; N, 13.01; S, 29.78. ^{1}H NMR ($CDCl_3$), δ: 1.28 (d, 24 H, $(C\underline{H}_3)_2CH$, J = 6.6 Hz); 3.66, 4.79 (both br.s, 2 H each, $C\underline{H}Me_2$); 6.61 (s, 2 H, CHCN). ^{13}C NMR ($CDCl_3$), δ: 20.72, 23.40 (2 Me); 47.61, 49.67 (2 $\underline{C}HMe_2$); 64.85 ($\underline{C}HCN$); 120.57 (CN); 153.96 (C=S). MS (EI, 70 eV), m/z (I_{rel} (%)): 366 $[M - S_2]^+$ (22), 334 (20), 183 (100), 141 (100). IR (KBr), ν/cm^{-1}: 2930 (C—H); 2180 (CN); 1580; 1300.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32032).

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Received April 24, 2007;
in revised form June 8, 2007