Synthesis of 5-mercapto-1,2-dithiole-3-thiones and their transformation into 5-chloro-1,2-dithiol-3-ones

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A number of 4-dialkylamino-5-mercapto-1,2-dithiole-3-thiones were synthesized by reactions of alkyl(diisopropyl)amines with S_2Cl_2. Their reactions with S_2Cl_2—DABCO unexpectedly gave 5-chloro-4-dialkylamino-1,2-dithiol-3-ones.

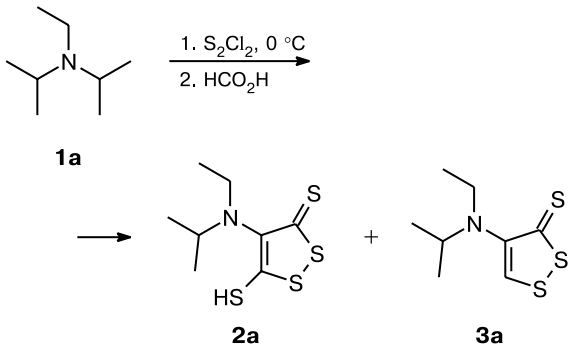
Key words: sulfur monochloride, 1,2-dithiole-3-thiones, 1,2-dithiol-3-ones, alkyl(diisopropyl)amines, DABCO.

Compounds containing 3*H*-1,2-dithiole-3-thione fragment have long been known[1] and are at present under intensive study because of a broad spectrum of their biological activity. Oltipraz (4-methyl-5-(2-pyrazinyl)-1,2-dithiole-3-thione), which is the most known preparation based on 1,2-dithioles, has been clinically tested in China as a chemotherapeutic agent against liver cancer,[2] while trithioanethol [5-(4-methoxyphenyl)-3*H*-1,2-dithiole-3-thione] has been used as a cholagogue.[3] 4-Aryl-5-chloro-3*H*-1,2-dithiole-3-thione derivatives exhibit insecticidal properties.[4]

Apart from biological activities, dithiolethiones are of interest as starting reagents for creation of novel materials, *e.g.*, for preparation of tetrathiafulvalene vinylogs with enhanced characteristics or nonlinear optical properties,[5] as π-donors for the synthesis of photoconductors which can be employed for recording holograms.[6]

Recently, we have shown that *N*-alkyldiisopropylamines can be easily converted by a single-step reaction with sulfur monochloride and 1,4-diazabicyclo[2.2.2]octane (DABCO) into complex thia- and azaheterocycles such as bis[1,2]dithiolo[1,4]thiazines,[7] bis[1,2]dithiolopyrroles,[8] [1,2]dithiolothiazines,[9] and bis[1,2]dithiolylamines.[10] The suggested mechanism of these reactions involve, as a key step, transformation of the isopropyl groups into 3-chlorodithiolium salts followed by nucleophilic substitution of oxygen or sulfur atoms (depending on the reagent used[7]) for the reactive Cl atom in position 3. Going further with investigations in this area, we demonstrated that the reaction can be stopped at the step of formation of monocyclic 1,2-dithioles (Scheme 1). The main conditions for the successful synthesis of monodithioles are a low reaction temperature (0 °C), use of an excess of the starting amine **1a**, and the absence of another base (DABCO).[11]

Scheme 1



Our synthesis of 1,2-dithiole-3-thiones under unusually mild conditions is exclusive among known relevant methods[1] and provides new wide possibilities for the study of this promising class of chemical compounds. Compounds **2a** and **3a** and their analogs obtained can be of interest as biologically active substances and serve as the starting reagents for the synthesis of tricyclic bis[1,2]dithiolo[1,4]thiazines with antitumor activities.[12]

Here we describe the synthesis of novel 4-dialkylamino-1,2-dithiole-3-thiones from *N*-substituted diisopropylamines and their subsequent reactions with S_2Cl_2.

We found that the reactions of *N*-alkyldiisopropylamines **1** with S_2Cl_2 give 4-alkyl(isopropyl)amino-5-mercapto-1,2-dithiole-3-thiones **2** as major products in nearly all the reactions; their yields substantially depend on the ratio **1** : S_2Cl_2 (Scheme 2). With compounds **1a**—**c** (R = Et (**1a**), CH_2Ph (**1b**), and $CH_2CH_2CO_2Et$ (**1c**)) as examples, we showed that the optimum ratio **1** : S_2Cl_2 is 2.2 : 1. With a decrease in the amine content (**1** : S_2Cl_2 = 1.8 : 1), the yield of dithiolethione **2** was lowered to 15% (**2a**), 5% (**2b**), and 2% (**2c**). With an increase in the

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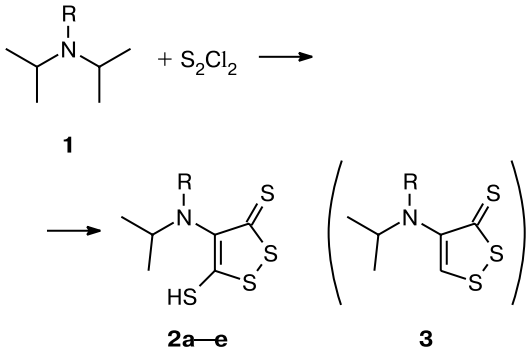
amine content (**1** : S_2Cl_2 = 2.5 : 1), the yield of product **2** did not decrease significantly; however, the formation of considerable amounts of dithiolethiones **3** hinders chromatographic isolation of the final products.

Scheme 2



Reagents and conditions: 1) 0 °C, 3 days; 2) HCO_2H, Δ, 1 h.

Compound	R	Yield (%)
2a	Et	22
2b	CH_2Ph	24
2c	$CH_2CH_2CO_2Et$	37
2d	CH_2CH_2CN	13
2e	$CH_2CH_2N_3$	11

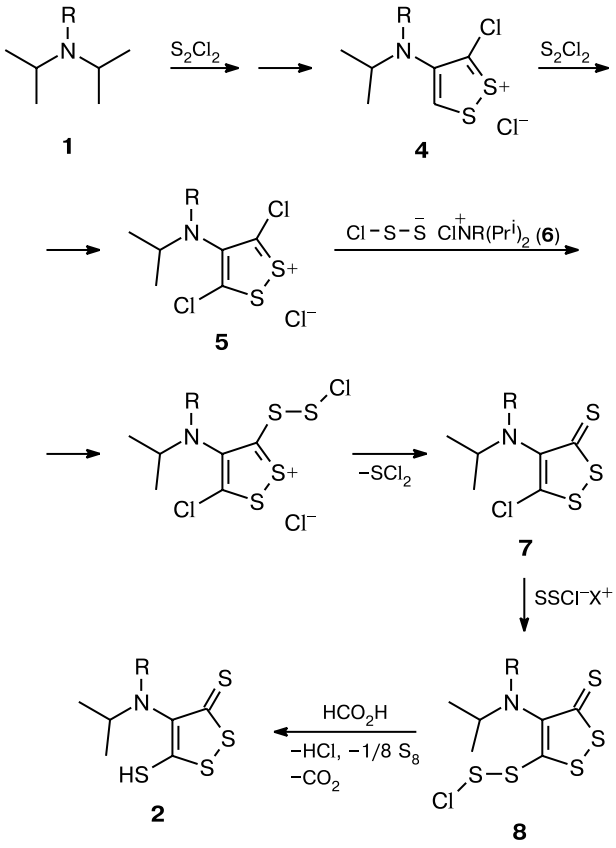
The formation of thiones in this reaction is rather unexpected since formic acid is known to transform dithiolium salts into 1,2-dithiol-3-ones.[7] This suggests that 3-chlorodithiolium salts **4** formed[7] in reactions of amines **1** with S_2Cl_2 are subsequently chlorinated with S_2Cl_2 to 3,5-dichlorodithiolium salts **5**, which then are sulfonated with nucleophilic species **6** (see Ref. 11) to successively give chloro thione **7** and intermediate **8**. Treatment of the latter with HCO_2H yields final mercaptodithiolethione **2** (Scheme 3).

Interesting results were obtained in the reactions of two other substituted diisopropylamines **1f**,**g** with S_2Cl_2. Instead of the expected mercaptodithiolethiones, we isolated dithiolothiazine **8** (Scheme 4). Presumably, the reaction intermediates are thiones **2f**,**g**, which then convert into bicyclic structure **9**, *via* elimination of HCl or phthalimide, respectively.

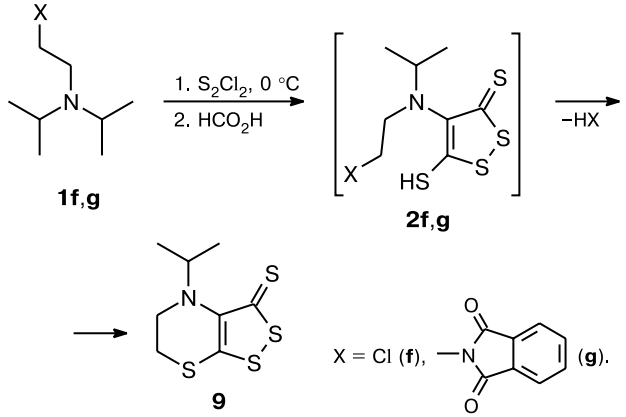
The structures of thiones **2** and dithiolothiazine **9** were proven by elemental analysis data, ^1H and ^{13}C NMR, IR, and mass spectra, and high-resolution mass spectra.

Mercaptodithiolethiones **2** were employed in reactions with a mixture of S_2Cl_2 and DABCO under the conditions for the formation of tricyclic bis(dithiolo)thiazines **10** from substituted diisopropylamines **1** (see Ref. 7). However, contrary to the expectations, 5-chlorodithiol-3-ones **11** were obtained in high yields from all compounds but **2a** (R = Et) (Scheme 5).

Scheme 3



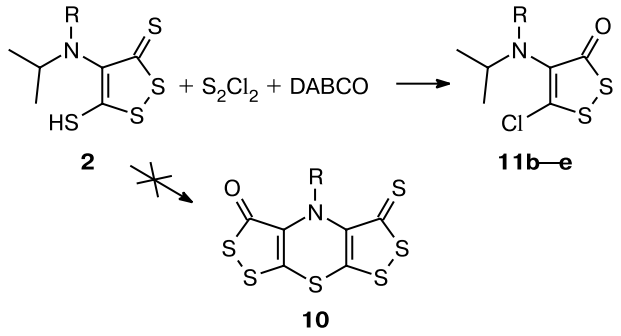
Scheme 4



The yield of compound **9** was 33 (from **1f**) and 21% (from **1g**).

It should be noted that the transformations of 5-mercapto-1,2-dithiole-3-thiones into 5-chloro-1,2-dithiol-3-ones have not been reported hitherto. Apparently, the most probable precursor of compounds **11** can be dichlorodithiolium salt **5**, which reacts with HCO_2H

Scheme 5



Reagents and conditions: 1) ~20 °C, 3 days; 2) HCO_2H, Δ, 1 h.

Compound	R	Yield (%)
11b	CH_2Ph	80
11c	$CH_2CH_2CO_2Et$	94
11d	CH_2CH_2CN	91
11e	$CH_2CH_2N_3$	77

to give chloro ketone **11** as has been described earlier.[11] The formation of this salt seems to involve a double electrophilic attack of mercaptodithiolethione **2** and derived chloro thione **7** by complex **12** (see Ref. 11; Scheme 6).

In the case of compound **2a** (R = Et), we failed to isolate the corresponding chloro ketone **11a**. TLC analysis of the reaction mixture detected a product with an R_f value close to those of ketones **11b—e**; however, this product decomposed on attempted isolation.

The chloro ketones **11** obtained are of interest as substances with potential biological (anticancer) activities since they are structurally similar to biologically active chloro ketones[13] and as synthons for their subsequent transformations, *e.g.*, by nucleophilic substitution for the Cl atom in position 5. We also found that mercaptodithiolethiones **2** cannot be intermediates in the synthesis of tricyclic bis(dithiolo)thiazines **10** from substituted diisopropylamines **1**.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker WM-250 and Bruker AM-300 instruments (250 and 300 (^1H) and 62.5 and 75 MHz (^{13}C), respectively) in $CDCl_3$. Chemical shifts are given on the δ scale relative to Me_4Si. Melting points were determined on a Kofler hot stage and are given uncorrected. Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument (EI).

The starting substituted diisopropylamines **1b**,[14] **1c**,[15] **1d**,[16] **1e**,[11] **1f**,[11] and **1g** (see Ref. 17) were prepared according to available procedures.

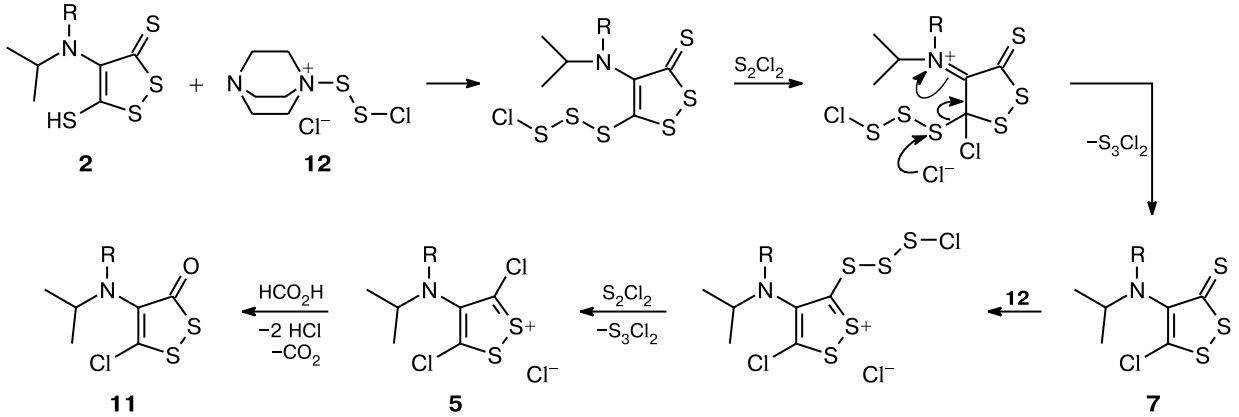
Reactions of substituted diisopropylamines 1 with S_2Cl_2 (general procedure). A solution of S_2Cl_2 (0.4 mL, 5 mmol) in chloroform (2 mL) was added dropwise at −15 to −20 °C to a solution of amine **1** in chloroform (12 mL). The mixture was left in a refrigerator at 0 °C for 72 h. Formic acid (1.9 mL, 50 mmol) was added dropwise at 0 °C and then the temperature was slowly raised to 20 °C. The reaction mixture was refluxed for 1 h and filtered and the precipitate was washed with CH_2Cl_2. The combined mother liquor was concentrated at reduced pressure and the residue was chromatographed on Merck 60 silica gel with CH_2Cl_2—light petroleum as the eluent.

4-[Ethyl(isopropyl)amino]-5-mercapto-3*H*-1,2-dithiole-3-thione (2a) was obtained as a yellow oil in 22% yield. Its spectroscopic characteristics are identical with the literature data.[11]

4-[Benzyl(isopropyl)amino]-5-mercapto-3*H*-1,2-dithiole-3-thione (2b). The yield was 24%, m.p. 160—163 °C. Found (%): C, 49.87; H, 5.14, N, 4.54. $C_{13}H_{15}NS_4$. Calculated (%): C, 49.80; H, 4.82; N, 4.47. ^1H NMR ($CDCl_3$), δ: 1.33, 1.73 (both d, 3 H each, CH_3, J = 6.4 Hz); 4.61 (m, 1 H, C<u>H</u>$_2$Ph); 5.11 (sept, 1 H, C<u>H</u>Me_2, J = 6.4 Hz); 5.88 (m, 1 H, C<u>H</u>$_2$Ph); 7.35 (m, 5 H, Ar); 9.10 (s, 1 H, SH). ^{13}C NMR ($CDCl_3$), δ: 19.1 and 20.6 (2 Me); 54.2 (<u>C</u>H_2Ph); 58.1 (<u>C</u>HMe_2); 128.7, 130.3, and 130.5 (3 C—H); 128.6, 134.2, 194.0, and 198.9 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 313 $[M]^+$ (95), 270 (15), 222 (100), 91 (18). Found: m/z 313.0085 $[M]^+$. $C_{13}H_{15}NS_4$. Calculated: 313.0087.

***N*-Isopropyl-*N*-(5-mercapto-3-thioxo-3*H*-1,2-dithiol-4-yl)-β-alanine ethyl ester (2c).** The yield was 37%, m.p. 40—42 °C. Found (%): C, 40.67; H, 5.51, N, 4.29. $C_{11}H_{17}NO_2S_4$. Calculated (%): C, 40.84; H, 5.30; N, 4.33. ^1H NMR ($CDCl_3$), δ: 1.26

Scheme 6



(d, 6 H, ($C\underline{H}_3$)$_2$CH), J = 6.6 Hz); 1.68 (d, 3 H, $C\underline{H}_3CH_2$, J = 6.6 Hz); 2.53 (t, 2 H, $C\underline{H}_2CH_2$, J = 3.9 Hz); 3.80 (m, 1 H, $C\underline{H}_2CH_2$); 4.17 (m, 2 H, $CH_2C\underline{H}_2$); 5.03 (sept, 1 H, $C\underline{H}Me_2$, J = 6.6 Hz); 5.07 (m, 1 H, $C\underline{H}_2CH_2$); 8.90 (s, 1 H, SH). ^{13}C NMR ($CDCl_3$), δ: 14.1, 18.8 and 19.9 (3 Me); 29.3, 45.3, and 61.8 (3 CH_2); 58.4 ($\underline{C}HMe_2$); 133.6, 171.0, 193.9, and 199.6 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 323 [M]$^+$ (100), 290 (37), 222 (25), 192 (45), 160 (40), 101 (42), 43 (88). Found: m/z 323.0131 [M]$^+$. $C_{11}H_{17}NO_2S_4$. Calculated: 323.0142.

3-[Isopropyl(5-mercapto-3-thioxo-3*H*-1,2-dithiol-4-yl)amino]propanenitrile (2d). The yield was 13%, m.p. 150—152 °C. Found (%): C, 39.12; H, 4.35, N, 10.17. $C_9H_{12}N_2S_4$. Calculated (%): C, 39.10; H, 4.37; N, 10.13. ^{1}H NMR ($CDCl_3$), δ: 1.22 (d, 6 H, ($C\underline{H}_3$)$_2$CH, J = 6.6 Hz); 2.53 (t, 2 H, CH_2, J = 6.6 Hz); 3.25 (m, 1 H, CH_2); 3.81 (sept, 1 H, $C\underline{H}Me_2$, J = 6.6 Hz); 4.18 (m, 1 H, CH_2); 8.95 (s, 1 H, SH). ^{13}C NMR ($CDCl_3$), δ: 19.2 (Me); 29.7 and 43.6 (2 CH_2); 53.3 ($\underline{C}HMe_2$); 118.7 (CN); 147.5, 174.3, and 208.0 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 276 [M]$^+$ (76), 240 (20), 192 (56), 160 (45), 100 (54), 43 (100). Found: m/z 275.9878 [M]$^+$. $C_9H_{12}N_2S_4$. Calculated: 275.9883.

4-[2-Azidoethyl(isopropyl)amino]-5-mercapto-3*H*-1,2-dithiole-3-thione (2e). The yield was 11% (yellow oil). Found (%): C, 32.72; H, 4.18, N, 19.33. $C_8H_{12}N_4S_4$. Calculated (%): C, 32.86; H, 4.14; N, 19.16. ^{1}H NMR ($CDCl_3$), δ: 1.16 (d, 6 H, ($C\underline{H}_3$)$_2$CH, J = 6.6 Hz); 3.25, 3.32 (both q, 2 H each, $C\underline{H}_2CH_2$, J = 5.9 Hz); 3.91 (sept, 1 H, $C\underline{H}Me_2$, J = 6.6 Hz); 7.92 (s, 1 H, SH). ^{13}C NMR ($CDCl_3$), δ: 18.7 and 20.0 (2 Me); 30.0 and 46.6 (2 CH_2); 59.0 ($C\underline{H}Me_2$); 134.2, 194.1, and 199.2 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 292 [M]$^+$ (100), 236 (21), 206 (54), 194 (75), 160 (28). Found: m/z 291.9934 [M]$^+$. $C_8H_{12}N_4S_4$. Calculated: 291.9944.

4-Isopropyl-5,6-dihydro-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazine-3-thione (9), a yellow oil. The yield was 33 (from **1f**) and 21% (from **1g**). Found (%): C, 38.75; H, 4.38, N, 5.51. $C_8H_{11}NS_4$. Calculated (%): C, 38.52; H, 4.45; N, 5.62. ^{1}H NMR ($CDCl_3$), δ: 1.16 (d, 6 H, Me_2C H, J = 6.7 Hz); 2.92, 3.40 (both t, 2 H each, CH_2, J = 4.9 Hz); 4.59 (sept, 1 H, $C\underline{H}Me_2$, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 22.0 (2 Me); 24.6 and 41.3 (2 CH_2); 50.0 ($\underline{C}HMe_2$); 145.0, 153.4 and 205.3 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 249 [M]$^+$ (65), 234 (28), 206 (90), 149 (58), 41 (100).

Reactions of dithiolethiones 2 with S_2Cl_2 and DABCO (general procedure). A solution of S_2Cl_2 (0.16 mL, 2 mmol) in chloroform (1 mL) was added dropwise at −40 to −45 °C to a solution of amine **1** (0.2 mmol) and DABCO (0.11 g, 1 mmol) in chloroform (7 mL). The mixture was left at room temperature for 72 h. Formic acid (0.375 mL, 10 mmol) was added dropwise at 0 °C and the temperature was slowly raised to 20 °C. Then the mixture was refluxed for 1 h and filtered and the precipitate was washed with CH_2Cl_2. The combined mother liquor was concentrated at reduced pressure and the residue was chromatographed on Merck 60 silica gel with CH_2Cl_2—light petroleum as the eluent.

4-[Benzyl(isopropyl)amino]-5-chloro-3*H*-1,2-dithiol-3-one (11b). The yield was 80%, m.p. 61—65 °C. Found (%): C, 52.23; H, 4.65, N, 4.57. $C_{13}H_{14}ClNOS_2$. Calculated (%): C, 52.08; H, 4.71; N, 4.67. ^{1}H NMR ($CDCl_3$), δ: 1.21 (d, 6 H, CH_3, J = 6.6 Hz); 3.46 (sept, 1 H, $C\underline{H}Me_2$, J = 6.6 Hz); 4.33 (s, 2 H, $C\underline{H}_2Ph$); 7.26 (m, 5 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 21.6 (2 Me); 50.1 ($\underline{C}HMe_2$); 54.2 ($\underline{C}H_2Ph$); 127.1, 128.2, and 128.6 (3 C—H); 137.9, 139.1, 153.9, and 187.8 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 299 [M]$^+$ (8), 256 (18), 91 (100). Found: m/z 299.0197 [M]$^+$. $C_{13}H_{14}ClNOS_2$. Calculated: 299.0205.

***N*-(5-Chloro-3-oxo-3*H*-1,2-dithiol-4-yl)-*N*-isopropyl-β-alanine ethyl ester (11c)**, a yellow oil. The yield was 94%. Found (%): C, 42.69; H, 5.42, N, 4.48. $C_{11}H_{16}ClNO_3S_2$. Calculated (%): C, 42.64; H, 5.21; N, 4.52. ^{1}H NMR ($CDCl_3$), δ: 1.12 (d, 6 H, ($C\underline{H}_3$)$_2$CH, J = 6.6 Hz); 1.26 (d, 3 H, $C\underline{H}_3CH_2$, J = 6.6 Hz); 2.34 (t, 2 H, CH_2, J = 6.6 Hz); 3.40 (sept, 1 H, $C\underline{H}Me_2$, J = 6.6 Hz); 3.45, 4.11 (both t, 2 H each, CH_2, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.3 and 21.6 (3 Me); 35.0, 41.8, and 60.5 (3 CH_2); 53.9 ($\underline{C}HMe_2$); 137.3, 154.6, 172.1, and 187.6 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 309 [M]$^+$ (72), 294 (95), 222 (100), 180 (97), 101 (56). Found: m/z 309.0256 [M]$^+$. $C_{11}H_{16}ClNO_3S_2$. Calculated: 309.0260.

3-[5-Chloro-3-oxo-3*H*-1,2-dithiol-4-yl(isopropyl)amino]propanenitrile (11d), a yellow oil. The yield was 91%. Found (%): C, 41.25; H, 4.41, N, 10.57. $C_9H_{11}ClN_2OS_2$. Calculated (%): C, 41.14; H, 4.22; N, 10.66. ^{1}H NMR ($CDCl_3$), δ: 1.15 (d, 6 H, ($C\underline{H}_3$)$_2$CH, J = 5.9 Hz); 2.36 (t, 2 H, CH_2, J = 6.6 Hz); 3.39 (sept, 1 H, $C\underline{H}Me_2$, J = 5.9 Hz); 3.43 (t, 2 H, CH_2, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.2 (Me); 29.7 and 42.2 (2 CH_2); 54.2 ($\underline{C}HMe_2$); 118.3 (CN); 136.7, 156.1, and 187.8 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 262 [M]$^+$ (36), 247 (48), 180 (76), 79 (79), 41 (100). Found: m/z 262.0003 [M]$^+$. $C_9H_{11}ClN_2OS_2$. Calculated: 262.0001.

4-[2-Azidoethyl(isopropyl)amino]-5-chloro-3*H*-1,2-dithiol-3-one (11e), a yellow oil. The yield was 77%. Found (%): C, 41.32; H, 4.05, N, 20.46. $C_8H_{11}ClN_4OS_2$. Calculated (%): C, 41.14; H, 3.98; N, 20.10. ^{1}H NMR ($CDCl_3$), δ: 1.12 (d, 6 H, ($C\underline{H}_3$)$_2$CH, J = 6.5 Hz); 3.17, 3.29 (both m, 2 H each, CH_2); 3.35 (sept, 1 H, $C\underline{H}Me_2$, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.5 (Me); 45.0 and 50.8 (2 CH_2); 54.3 ($\underline{C}HMe_2$); 137.0, 154.9, and 187.4 (sp^2 of the quaternary C atoms). MS (EI, 70 eV), m/z (I_{rel} (%)): 278 [M]$^+$ (10), 222 (69), 180 (100). Found: m/z 278.0060 [M]$^+$. $C_8H_{11}ClN_4OS_2$. Calculated: 278.0063.

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