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Synthesis of *N*,*N*'-Disubstituted Dithiooxamide Derivatives by the Modified Willgerodt–Kindler Reaction

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Abstract—The conditions of the reaction of trichloroethylene with sulfur and amines were optimized (the modified Willgerodt–Kindler reaction). The reaction of tetrachloroethylene with sulfur and some basic primary and secondary amines of the aliphatic series in DMF under mild conditions leads to *N*,*N*'-disubstituted dithiooxamides in 30–70% yields and with a 100% conversion of tetrachloroethylene.

Keywords: tetrachloroethylene, *N*,*N*'-disubstituted dithiooxamide, Willgerodt–Kindler reaction

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Dithiooxamide and its *N*- and *N*,*N*'-disubstituted derivatives are widely used in different fields of chemistry [1], in particular, as binucleophilic ligands for metal complexes and analytical reagents for detection and quantification of metals [2–4] and also as building blocks for heterocyclic synthesis [5, 6]. Some dithiooxamide derivatives showed antibacterial activity [7], while Sb(III) halide complexes of *N*,*N*'-dicyclohexyldithiooxamide were found to act as cytostatics [8]. The presence of two soft sulfur atoms along with hard nitrogen atoms in the thioamide moiety makes these molecules potent ligands in coordination chemistry [9].

The main methods for the synthesis of dithiooxamides include thionation of amides with phosphorus pentasulfide or Lawesson's reagent [10, 11], reaction of primary aliphatic amines with dithiooxamide [11, 12], Willgerodt–Kindler reaction with glyoxal, sulfur, and amines [13], as well as modified Willgerodt–Kindler reaction (prolonged boiling of a mixture of polychloroethylenes or polychloroethanes with sulfur and an amine in organic solvents, such hydrocarbons or alcohols) [14, 15]. Thionation of amides with phosphorus pentasulfide is two-step process, which requires preliminary synthesis of oxalamides and results in poor yields of final products. Transamidation of dithiooxamide is not a universal method, because it is only suitable for primary aliphatic amines, forms amidines as by-products, and involves evolution of hydrogen sulfide. The disadvantage of the modified Willgerodt–Kindler reaction is that it is carried out at high temperatures (> 100°C) for a long time (more than 20 h) using an excess of sulfur and amine.

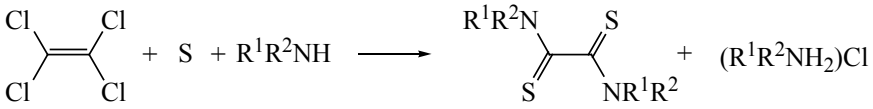
At the same time, there have been some efforts on the optimization of the classical Willgerodt–Kindler reaction with aromatic aldehydes and ketones [16, 17]. According to [18–21], the use of DMF favored much faster reaction. Even though the reaction mechanism is not clear, there are some suggestions concerning individual stages of the process still seem quite justified. At the first stage elemental sulfur S_8 reacts with amine R_2NH along several concurrent routes, including the reaction leading to an aminothiol, a potential *S*-nucleophile [22]:

$$R_2NH + S_8 = R_2N(S_7)SH.$$

The aim of the present work was to optimize the conditions of the reactions of tetrachloroethylene, sulfur, and amines of different structures in DMF (the modified Willgerodt–Kindler reaction) (Scheme 1).

The reaction conditions were optimized using the example of the reaction of tetrachloroethylene with sulfur and cyclohexylamine in DMF (for comparison of our results with published data). The reaction was performed by stirring a mixture of the reagents, a GLC standard (*n*-nonane or chlorobenzene), and a solvent

Scheme 1.



1–6

R^1 = H, R^2 = C_6H_{11} (**1**), $CH_3OCH_2CH_2$ (**2**), Ph (**6**); $R^1 + R^2$ = $(CH_2)_5$ (**3**), $CH_2CH_2OCH_2CH_2$ (**4**); $R^1 = R^2$ = *n*-Bu (**5**).

(DMF) under heating in a screw-capped tube. The tetrachloroethylene–sulfur–amine ratio was 1 : 3 : 8 (the excesses of sulfur and amine of 1.5 and 1.3 are usually in Willgerodt–Kindler reactions to avoid by-product formation [14, 15, 23, 24]). Furthermore, 4 mol of amine are need to bind 4 mol of HCl.

The conversion of tetrachloroethylene in the reaction for 1.5 h at 60°C was 36% (exp. no. 1), while the conversion in the reaction for 5.5 h at 100°C was 99% (exp. no. 2), i.e. tetrachloroethylene is consumed almost completely. The latter reaction conditions are milder compared to those reported in the literature (100–110°C, 30 h in toluene) [15].

To isolate the reaction product, the same reaction was performed on a preparative scale with 10 mmol of tetrachloroethylene. We obtained 1670 mg (89%) of a crude compound **1** and 1433 mg (77%) of the product recrystallized from propan-2-ol, mp 150–151°C (151–152°C [15]). The synthesized compound **1** was further analyzed by high-resolution mass spectrometry (ESI-HRMS), as well as ^{1}H and ^{13}C NMR spectroscopy.

The base peak in the negative mode was observed at *m*/z 283.1310, while that in the positive mode, at *m*/z 307.1272. These results provide evidence for the molecular formula of the reaction product (see Experimental). The ^{13}C NMR spectrum contains 5 signals assignable to 5 nonequivalent carbon atoms. The downfield signal at 182.97 ppm corresponds to the C=S carbon signal. The signal at 55.77 ppm belongs to the cyclohexane ring carbon attached to the electronegative nitrogen atom. Three upfield signals correspond to three nonequivalent cyclohexane ring carbons. The downfield singlet at 10.37 ppm (2H) in the ^{1}H NMR spectrum is assignable to the thioamide NH protons, and the multiplet at 4.26 ppm (2H), to the proton of the CH group attached to nitrogen. The five groups of upfield multiplets (20H) corresponding two protons of the two cyclohexane rings.

Thus, the reaction in the presence of DMF forms the target dithiooxamide **1** and occurs 5 times faster compared to the reaction in toluene described in [15].

Further on we turned to the reactions with a primary aliphatic amine (2-methoxyethylamine), secondary aliphatic amines (piperidine, morpholine, dibutylamine), and an aromatic amine (aniline). The resulting data are listed in Table 1.

It was found that piperidine was more active in the studied reactions than cyclohexylamine. A high conversion of tetrachloroethylene in the reaction with piperidine was attained in milder conditions than in the reaction with cyclohexylamine; the reaction time and temperature were also lower. In the case of cyclohexylamine, the tetrachloroethylene conversion of 99% was obtained within 5.5 h at 100°C (exp. no. 3), and in the case of piperidine, a 88% conversion was obtained within 1.5 h at 75°C (exp. no. 9).

It was found that reactivities of amines in the reactions of tetrachloroethylene with sulfur and amines correlate, on a qualitative level, with the basicities of the amines: the higher the basicity of the amine, the higher the conversion of the substrate under the same conditions. Thus, for example, the tetrachloroethylene conversion in most experiments with morpholine (pK_a 8.46) was lower than with piperidine (pK_a 11.22) (Table 1).

The structure of compounds **2–4** was established by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry (ESI-HRMS). The structure of compound **5** was confirmed by ESI-HRMS. In the ^{1}H and ^{13}C NMR spectra of compound **4**, all proton and carbon signals were of double integral intensity. The ^{13}C NMR spectrum showed C=S carbon signal at 192.35 ppm and three morpholine ring carbon signals at 66.15 (CH_2OCH_2) and 52.02 and 47.68 ppm (CH_2NCH_2; the two carbon atoms in this group are magnetically nonequivalent because of the partial double-bond character of the C–N bond). The chemical shifts of the signals of the morpholine CH_2NCH_2 carbon atoms located *cis* and *trans* with respect to the C=S group differ considerably due to anisotropy.

The ^{1}H NMR spectrum of compound **4** displays 5 groups of morpholine proton signals at (δ, ppm): 4.47 d.t (2H), 4.04 d.d.d (2H), 3.87 m (8H), 3.67 d.d.d

Table 1. Conversions of tetrachloroethylene in reactions with sulfur and amines in DMF at varied reaction temperature and time

Exp. no.	Amine	pK_a	Time, h	Temperature, °C	Conversion of C_2Cl_4, %
3	Cyclohexylamine	10.63	5.5	100	99
4	Cyclohexylamine	10.63	1.5	60	37
5	2-Methoxyethylamine	9.89	5.5	100	100
6	2-Methoxyethylamine	9.89	2.0	100	99
7	2-Methoxyethylamine	9.89	71	28	90
8	Dibutylamine	11.31	5.5	100	95
9	Piperidine	11.24	1.5	75	88
10	Piperidine	11.24	1.5	60	59
11	Piperidine	11.24	71	28	67
12	Morpholine	8.49	2.2	100	81
13	Morpholine	8.49	1.5	75	50
14	Morpholine	8.49	1.5	60	22
15	Aniline	4.60	5.5	100	0

(2H), and 3.57 d.d.d (2H). The signals were assigned on the basis of the HSQC spectrum, which contains the following cross-peaks (δ, ppm): C^2 66.15/3.87 ($4H^2$, $2H^6$), C^2 66.15/3.67 ($2H^6$), C^5 52.02/3.87 ($2H^5$), C^5 52.02/3.57 ($2H^5$), C^6 47.68/4.47 ($2H^3$), and C^6 47.68/4.04 ($2H^3$). The cross-peaks in the COSY spectrum allowed unambiguous assignment of all vicinal proton signals to the axial and equatorial protons (δ, ppm): 3.57 m (2H, H^5_{ax}), 3.67 m (2H, H^6_{ax}), 3.87 m [8H ($2H^2_{ax}$, $2H^2_{eq}$, $2H^5_{eq}$, $2H^6_{eq}$)], 4.04 m (2H, H^3_{ax}), 4.47 d.t (2H, H^3_{eq}) (Fig. 1). Considering the sets of coupling constants for all nonoverlapping signals, as well as their sums, we can conclude that the multiplet structure of the signals is the same (d.d.d), but the sum of the coupling constants for the most downfield signal is slightly smaller (by about 3–4 Hz) compared to the other three. Consequently, this signal belongs to a predominantly equatorial proton, but the others, to predominantly axial protons. The term "predomonantly" is used here to indicate the lifetime of a specific proton in the equatorial or axial position. Such terminology is conditional, because the morpholine rings undergo a fast (on the NMR time scale) *chair–chair* conformational transformation, and all vicinal coupling constants are averaged. The coupling constants of the four nonoverlapping signals cannot be estimated by simply measuring the distances between the components of these signals,

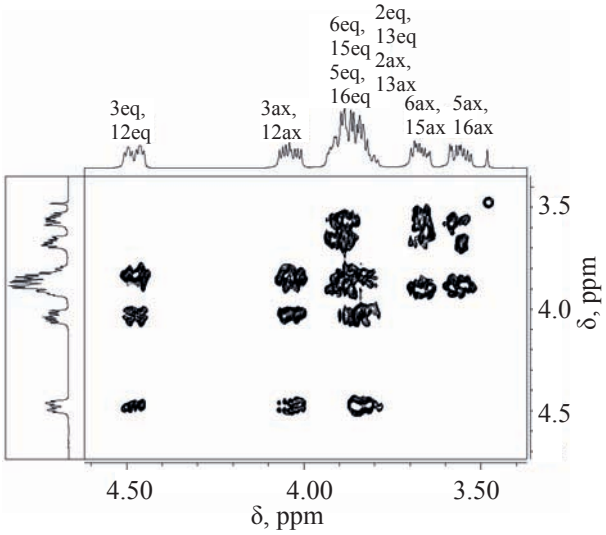


Fig. 1. Fragment COSY spectrum of compound **4**.

Table 2. Conversion of tetrachloroethylene in the reactions with amines and dissolved sulfur

Exp. no.	Cosolvent	Amine	Temperature, °C	Time, h	Conversion of C_2Cl_4, %
16	Cyclohexane	Piperidine	75	22.5	47
17	Cyclohexane	Morpholine	75	22.5	30
18	Dioxane	Piperidine	60	25	23
19	Dioxane	Cyclohexylamine	60	25	22
20	Benzene	Piperidine	75	23	58
21	Benzene	Cyclohexylamine	75	23	29
22	Benzene	Morpholine	75	23	23
23	Benzene	Morpholine	75	71	39
24	Benzene	2-Methoxyethylamine	75	71	34
25	Benzene	Dibutylamine	75	71	52

since the overlapping signals of eight protons at about 3.8 ppm form strongly coupled systems, which distort the multiplicity of all other non-overlapping signals (*ABX* spin system).

The conversion in the case of a weakly basic amine (aniline, pK_a 4.60) within 5.5 h at 100°C was less than 0.05%. According to the published data for the classical Willgerodt–Kindler reaction with carbonyl compounds, for example, benzaldehyde, aniline was also inactive in typical reaction conditions [19].

The reaction mixture of tetrachloroethylene with sulfur and an amine in the presence of DMF is generally heterogeneous. The solubility of sulfur in DMF at 25°C is not higher than 0.191 wt % [25]. As the reaction progresses, the quantity of sulfur in the mixture decreases, and the substituted dithiooxamide gradually precipitates. An especially low solubility is characteristic of the high-melting 1,2-dimorpholinoethane-1,2-dithione (**4**).

We tried to perform the reaction in homogeneous conditions, using a mixture of DMF with another organic solvent to dissolve sulfur. Taking into account that sulfur is poorly soluble in most organic solvents, for our experiments we chose cyclohexane, dioxane, and benzene. Saturated solutions of sulfur in these solvents were prepared. A calculated quantity of the reaction mixture of tetrachloroethylene (with internal standard), an amine, and DMF was added to a saturated (1–2 wt %) solution of sulfur in an organic solvent. The subsequent reaction and determination of the conversion of tetrachloroethylene were performed by a standard procedure. The resulting data are listed in Table 2.

The dilution of DMF with an inert organic solvent substantially decreased the reaction rate compared with that in a heterogeneous medium. For higher conversions of tetrachloroethylene, we had to prolong the reaction time several times.

It is well known that the classical Willgerodt–Kindler reaction characteristically gives a lot of by-products. Some of them are formed without involvement the carbonyl compound, from sulfur and amine exclusively, for example, $R_2N(S_n)NR_2$ (n = 1–6) [22]. When analyzing reaction mixtures by the GCMS method, in some cases we found trace amounts of some other by-products, for example, 4,4-dithiodimorpholine and cyclohexyl isothiocyanate.

The obtained dependence of the conversion of tetrachloroethylene in the Willgerodt–Kindler reaction on the nature of the strongly basic amine allows us to formulate some conclusions. Almost all studied amines proved to be able to form substituted dithiooxamides in moderate or high yields at appropriate reaction temperatures and times (4–7 h at 100°C).

The preparative reactions were performed by two procedures: *a* and *b*. The reactions by procedure *a* were performed at the tetrachloroethylene–sulfur–amine molar ratio of 1 : 3 : 8. The quantity of amine can be reduced compared to the stoichiometric quantity to 2.5–3.0 mol per mole of tetrachloroethylene, provided the reaction

in DMF is performed in the presence of a base (K_2CO_3) (procedure *b*). The yield of a crude product **1** in the reaction of tetrachloroethylene with sulfur and cyclohexylamine in DMF in the presence of potash (reagent ratio 1 : 3.0 : 3.0 : 2.2) at 100°C for 6 h was 95% (72% after recrystallization from methanol). The quantity of DMF was 0.5–1.5 mL per 1 mmol of tetrachloroethylene. Methyl cellosolve (bp 124°C) and propan-1-ol (bp 97°C) in a quantity of 0.5–1.5 mL per 1 mmol of tetrachloroethylene can be used as inert cosolvents. The use of inert cosolvents favors milder reaction conditions and facilitates stirring of the reaction mixture, especially in the presence of potash.

Thus, we optimized the conditions of the reaction of tetrachloroethylene with sulfur and primary and secondary aliphatic amines in DMF, forming substituted dithiooxamides. A qualitative correlation between the reactivity of the amines in this reaction and their basicity, i.e. the pK_a values, was established.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were registered on a Bruker Avance II+ spectrometer at 400.13 (^{1}H) and 100.61 (^{13}C) MHz at room temperature. The chemical shifts were measured against residual proton and carbon signals of the solvent: δ_H 7.27 ppm ($CHCl_3$), δ_C 77.0 ppm ($CDCl_3$). The ESI mass spectra were obtained on a Bruker micrOTOF instrument, scan range *m/z* 50–3000, electrospray voltage ±4500 V, and capillary exit voltage ±70–150 V. Samples for analysis were dissolved in MeOH. Gas chromatography–mass spectrometry analysis was performed on a Shimadzu GCMS QP-2010 SE instrument, electron ionization (70 eV), scan range *m/z* 50–500, detector temperature 220°C, column 1: Rtx-5MS (30 m × 0.32 mm × 0.25 μm), column 2: Optima-1 (25 m × 0.32 mm × 0.35 μm), carrier gas (argon) flow rate 0.8 mL/min. Commercial chemical and analytical grade inorganic compound and amines from Vekton, Acros, and Merck were used. Tetrachloroethylene from Vekton was preliminarily purified (see below).

Quantitative and qualitative GC–MS analysis. Chromatographic separations, both on column 1 and column 2, were performed in the programmed temperature mode, analysis time 15–20 min. A sample of the reaction mixture was diluted with distilled water 20–50 times, carefully neutralized with 1% HCl, and treated with diethyl ether. The organic extract with shaken with 5 volumes of distilled water. A 0.05–0.1-mL sample of the organic layer was diluted with 1.0–1.7 mL of hexane or a hexane–dichloromethane mixture (2 : 1 v/v), dried for 0.5–1.0 h over 50–100 mg of calcined Na_2SO_4, and 1 μL of the solution was taken for GC–MS analysis.

Purification of tetrachloroethylene. Tetrachloroethylene, 100 mL, and 10 mL of HCl were mixed in a separatory funnel, and C_2Cl_4 was separated, washed with water to remove HCl and once with 5% $NaHCO_3$, after which it was dried over 15 g of Na_2SO_4 and 1 g of Na_2CO_3 for a day and distilled in a vacuum (160 mm Hg), collecting the fraction boiling at 72–73°C. According to the GC–MS analysis, the preparation contained traces (< 0.2%) of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane.

1,2-Bis(cyclohexylamino)ethane-1,2-dithione (1). *a*. A mixture of 1742 mg (10.51 mmol) of tetrachloroethylene, 1011 mg (31.53 mmol) of finely ground sulfur, 5213 mg (52.56 mmol) of cyclohexylamine, 5.5 mL of DMF (DMF–C_2Cl_4 3 : 1 w/w), and 4 mL of methyl cellosolve was stirred at 100°C for 16 h. After completion of the reaction, the reaction mixture was poured into a beaker with 30–40 mL of distilled water and, after through mixing, neutralized with 2–3% HCl. The resulting product was filtered off, washed on the filter with distilled water, and left there to dry completely to obtain 1670 mg (89.4%) of a crude compound **1**, mp 143–144°C. The crude product was recrystallized from propan-2-ol to give 1433 mg (76.7%) of a pure compound **1**, mp 150–151°C (151–152°C [15], 149.0–149.5°C [11]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.35 m (2H, CH_2), 1.47 m (8H, $4CH_2$), 1.68 m (2H, CH_2), 1.79 m (4H, $2CH_2$), 2.07 m (4H, $2CH_2$), 4.26 m (2H, 2CH), 10.37 s (2H, 2NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.31 (CH_2), 25.42 (CH_2), 30.60 (CH_2), 55.77 (CHN), 182.97 (C=S). ESI–HRMS: *m/z* 283.1310 $[M-H]^-$. $C_{14}H_{23}N_2S_2$. Calculated: 283.1308 $[M-H]^-$; *m/z* 307.1272 $[M+Na]^+$. $C_{14}H_{24}N_2NaS_2$. Calculated 307.1274 $[M+Na]^+$.

b. A mixture of 1090 mg (6.57 mmol) of tetrachloroethylene, 632 mg (19.71 mmol) of finely ground sulfur, 1930 mg (19.55 mmol) of cyclohexylamine, 2010 mg (14.54 mmol) of potash, 3.5 mL of DMF, and 6.5 mL of methyl cellosolve was stirred at 100°C for 7 h. The subsequent work-up was performed by the above procedure. The yield of a crude product was 1765 mg (94.4%). Recrystallization from methanol gave 1343 mg (71.8%) of compound **1**, mp 150–151°C.

1,2-Bis(2-methoxyethylamino)ethane-1,2-dithione (2). *a*. A mixture of 936 mg (5.64 mmol) of tetrachlo-

roethylene, 542 mg (16.92 mmol) of sulfur, 3389 mg (45.12 mmol) of 2-methoxyethylamine, and 5.6 mL of DMF was stirred at 95°C for 8 h. The subsequent work-up was performed by the above procedure. The yield of a crude product was 816 mg. Recrystallization from ethanol gave 683 mg (51.0%) of compound **2**, mp 101–102°C (99–99.5°C [26]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.42 s (6H, OCH_3), 3.67 m (4H, $2OCH_2$), 3.86 m (4H, NCH_2), 10.48 s (2H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 47.16 (OCH_3), 59.02 (OCH_2), 184.98 (C=S). ESI-HRMS: *m*/*z* 259.0545 [*M* + Na]$^+$. $C_8H_{16}N_2NaS_2$. Calculated 259.0551.

b. A mixture of 1210 mg (7.30 mmol) of tetrachloroethylene, 702 mg (21.9 mmol) of sulfur, 1420 mg (18.91 mmol) of 2-methoxyethylamine, 1690 mg (12.23 mmol) of potash, and 5.6 mL of DMF was stirred at 95°C for 8 h. The subsequent work-up was performed by the above procedure. The yield of a crude product was 1124 mg (65.0%), mp 98–99°C. Recrystallization from ethanol gave 929 mg (53.9%) of compound **2**, mp 100–101°C.

1,2-Dipiperidinoethane-1,2-dithione (3). *a*. A mixture of 1046 mg (6.31 mmol) of tetrachloroethylene, 607 mg (18.93 mmol) of finely ground sulfur, 4298 mg (50.48 mmol) of piperidine, 8.5 mL of DMF, and 10 mL of propan-1-ol was heated at 95°C for 9 h. The subsequent work-up was performed by the above procedure. The yield of a crude product was 940 mg (58%), mp 90–92°C. Consecutive recrystallization from chloroform–hexane (1 : 2 v/v) and methanol gave 440 mg (27.2%) of compound **3**, mp 169–170°C (126°C [27]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.54 m (2H, CH_2), 1.72 m (8H, $4CH_2$), 1.95 m (2H, CH_2), 3.50 m (2H, CH_2), 3.70 m (2H, CH_2), 4.02 m (2H, CH_2), 4.33 m (2H, CH_2N). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 23.99 (CH_2), 25.13 (CH_2), 26.07 (CH_2), 48.46 (CH_2N), 52.72 (CH_2N), 191.90 (C=S). Mass spectrum (ESI-MS): *m/z* 279.0966 [*M* + Na]$^+$. $C_{12}H_{20}N_2NaS_2$. Calculated 279.0969 [*M* + Na]$^+$.

b. A mixture of 1050 mg of tetrachloroethylene (6.33 mmol), 690 mg (21.52 mmol) of finely ground sulfur, 1600 mg (18.79 mmol) of piperidine, 2030 mg (14.69 mmol) of K_2CO_3, 3.5 mL of DMF, and 7 mL methyl cellosolve was stirred at 100°C for 8 h. The subsequent work-up was performed by the above procedure. The yield of a crude product was 833 mg (51.3%), mp 90–92°C. Consecutive recrystallization from chloroform–hexane (1 : 2 v/v) and methanol gave 408 mg (25.1%) of compound **3**, mp 169–170°C (126°C [27]).

1,2-Dimorpholinoethane-1,2-dithione (4). *a*. A mixture of 860 mg of tetrachloroethylene (5.19 mmol), 499 mg (15.57 mmol) of finely ground sulfur, 3617 mg (41.52mmol) of morpholine, and 6 mL DMF was stirred at 100°C for 7 h. The subsequent work-up was performed by the above procedure. The yield of a crude product was 852 mg (63.0%), mp 248–249°C. Recrystallization from ethanol gave 704 mg (52.1%) of compound **4**, mp 284–285°C (255°C [14]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.57 m (2H, H^5_{ax}), 3.67 m (2H, H^6_{ax}), 3.87 m [8H ($2H^2_{ax}$, $2H^2_{eq}$, $2H^5_{eq}$, $2H^6_{eq}$)], 4.04 m (2H, H^3_{ax}), 4.47 d.t (2H, H^3_{eq}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 47.68 and 52.02 (CNC), 66.15 (CH_2, COC), 192.35 (C=S). Mass spectrum (ESI): *m*/*z* 283.0549 [*M* + Na]$^+$. $C_{19}H_{16}N_2NaS_2$. Calculated 283.0545.

1,2-Bis(dibutylamino)ethane-1,2-dithione (5). A mixture of 65 mg (0.51 mmol) of tetrachloroethylene, 49 mg (1.53 mmol) of finely ground sulfur, 527 mg (4.08 mmol) of dibutylamine, and 1 mL of DMF was stirred at 100°C for 5.5 h. The subsequent work-up was performed by the above procedure. The structure was confirmed by high-resolution mass spectrometry. ESI-HRMS: 367.2205 [*M* + Na]$^+$. $C_{18}H_{36}N_2NaS_2$. Calculated 367.2213. Compound **5** was described in the patent [28].

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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