Russian Journal of Organic Chemistry, Vol. 41, No. 3, 2005, pp. 370–375. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 3, 2005, pp. 381–386.

Synthesis of Sulfides by Reactions of 1,1-Dichloro-2-chloromethylcyclopropane with S-Nucleophiles

E. I. Mikhed'kina[1], P. V. Nedel'ko[1], and V. V. Prezhdo[2]

[1] *"Khar'kovskii politekhnicheskii institut" National Technical University, ul. Frunze 21, Khar'kov, 61002 Ukraine*
e-mail: nedelko@kpi.kharkov.ua

[2] *Institute of Chemistry, J. Kochanowski Higher Pedagogical School, Kielce, Poland*

Received October 15, 2003

Abstract—1,1-Dichloro-2-chloromethylcyclopropane reacts with thiolates to give 2,2-dichlorocyclopropylmethyl sulfides via replacement of the side-chain chlorine atom. The resulting sulfides are readily oxidized to the corresponding sulfones.

As shown in [1–4], 1,1-dichloro-2-chloro(bromo)methylcyclopropanes react with O- and C-nucleophiles to give both products of substitution of the halogen atom in the side chain and 1,1- or 1,2-disubstituted methylenecyclopropanes according to the elimination–addition pattern. As concerns S-nucleophiles, only the reaction of such compounds with benzenethiol has been reported [1, 2].

In the present work we examined reactions of 1,1-dichloro-2-chloromethylcyclopropane with various S-nucleophiles with the goal of synthesizing sulfides which may be useful from the viewpoint of searching for new biologically active compounds. It is known [5] that the 2,2-dichlorocyclopropyl group is a structural fragment of the drug Ciprofibrate and that a number of sulfides possessing the above group exhibit herbicide and fungicide activity [6].

The reactions of 1,1-dichloro-2-chloromethylcyclopropane (**I**) with benzenethiol, *p*-methylbenzenethiol, and 1*H*-1,2,4-triazole-5-thiol in anhydrous ethanol in the presence of sodium ethoxide afforded sulfides **IIa**–**IIc** (Scheme 1). These results are consistent with the data of Jonczyk and Kmiotek-Skarzynska [2] who studied the reaction of chloride **I** with benzenethiol, depending on the basicity of the medium and solvent nature. In all cases the authors isolated 2,2-dichlorocyclopropylmethyl phenyl sulfide (**IIa**) as the only product. The poor solubility of 1*H*-1,2,4-triazole-5-thiol in anhydrous ethanol makes it difficult to obtain sulfide **IIc** in a preparative yield. We have found that the reaction of 1*H*-1,2,4-triazole-5-thiole with chloride **I** successfully occurs in DMF in the presence of anhydrous potassium carbonate.

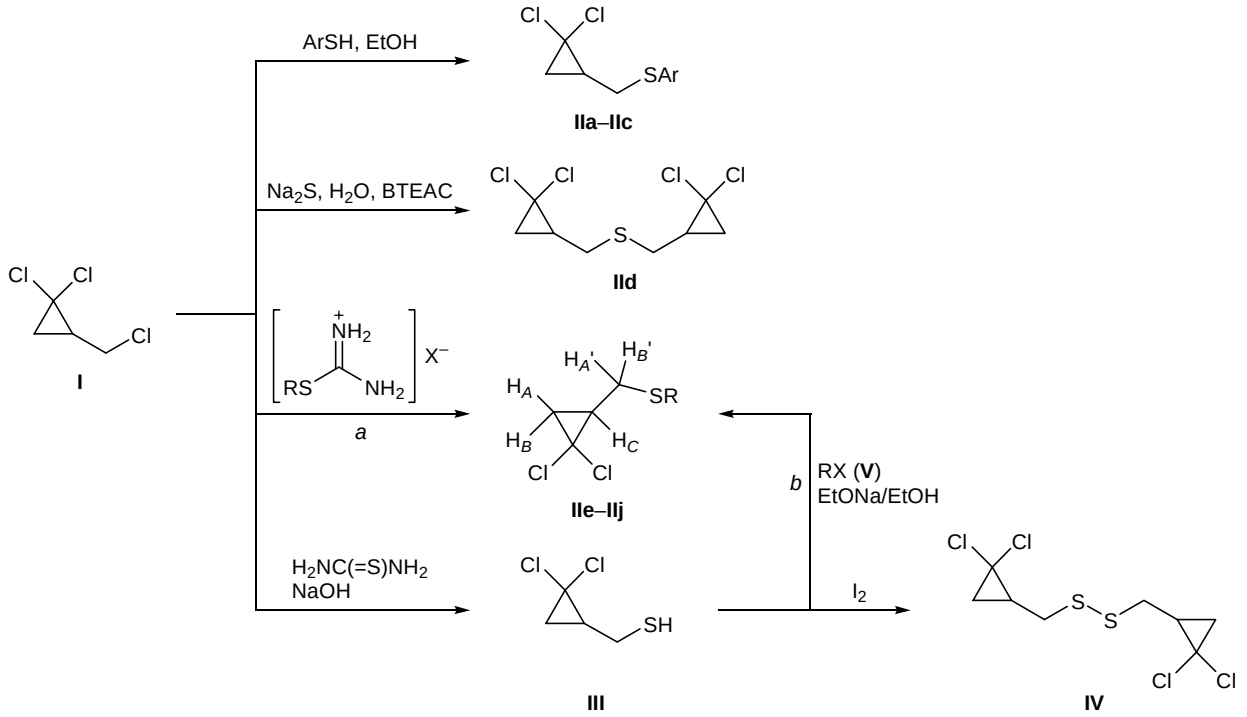
In the reaction of **I** with thiourea, followed by treatment of the reaction mixture with aqueous sodium hydroxide, we isolated two products. One of these was identified as 2,2-dichlorocyclopropylmethanethiol (**III**), and the other, as symmetric sulfide **IId**. The latter was identical to the product described in [7] and to that obtained from 2-bromomethyl-1,1-dichlorocyclopropane by heating in boiling ethanol. Sulfide **IId** can also be prepared by phase-transfer reaction using an aqueous solution of sodium sulfide and benzyltriethylammonium chloride (BTEAC) as catalyst. Under these conditions, the yield of **IId** was greater (~80%) than that reported in [7] (70%). According to the ^{1}H NMR data, sulfide **IId** is formed as a 1:1 mixture of two possible diastereoisomers.

Treatment of chloride **I** with sodium thiosulfate in aqueous ethanol gave 85% of thiol **III** which was identical to a sample obtained from compound **I** and thiourea. The structure of **III** was confirmed by the spectral data. Its ^{1}H NMR spectrum (DMSO-d_6) contained a multiplet at δ 2.61 ppm from the SH proton. In the IR spectrum of **III**, an absorption band corresponding to stretching vibrations of the S–H bond was observed at 2576 cm^{-1}. Thiol **III** is readily oxidized to disulfide **IV** by the action of iodine in alkaline solution.

Unsymmetrical dialkyl sulfides **IIe**–**IIj** containing a dichlorocyclopropyl fragment were synthesized from chloride **I** or thiol **III** in two ways. In the first case, chloride **I** was brought into reaction with the corresponding *S*-alkylisothiuronium salt under conditions of phase-transfer catalysis using benzene as organic phase and tetrabutylammonium bromide as catalyst

1070-4280/05/4103-0370

Scheme 1.

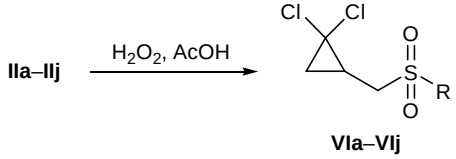


II, Ar = Ph (**a**), 4-$CH_3C_6H_4$ (**b**), 1*H*-1,2,4-triazol-5-yl (**c**); R = Me (**e**), Et (**f**), Pr (**g**), Bu (**h**), C_5H_{11} (**i**), $PhCH_2$ (**j**); **V**, X = I (**e**, **f**, **g**), Br (**h**, **i**), Cl (**j**).

(method *a*). According to method *b*, 2,2-dichlorocyclopropylmethanethiol was treated with the corresponding alkyl halide **V** in anhydrous ethanol in the presence of sodium ethoxide. Method *b* ensured greater yields of sulfides **IIe**–**IIj**, regardless of the order of reactant mixing. In the ^{1}H NMR spectra of sulfides **IIa**–**IIj**, signals from the exocyclic methylene protons H'_A and H'_B are displaced upfield (δ 2.52–3.37 ppm) relative to the corresponding signals of initial chloride **I** (δ 3.58–3.64 ppm).

Most sulfides **IIa**–**IIj** are liquids. By treatment with hydrogen peroxide in acetic acid they were oxidized to the corresponding sulfones **VIa**–**VIj** (Scheme 2). Sulfones **VIa**–**VIj** characteristically showed in the IR spectra absorption bands at 1140–1160 and 1300–1320 cm^{-1} due to symmetric and antisymmetric stretching vibrations of the SO_2 group. Signals from the exocyclic methylene protons H'_A and H'_B appeared in the ^{1}H NMR spectra of **VIa**–**VIj** in a weaker field as compared to the initial sulfides, while the positions of the H_C, H_A, and H_B signals remained essentially unchanged in going from sulfides **II** to sulfones **VI**. The ^{1}H NMR spectrum of symmetric sulfone **VId** contained a double set of signals, indicating formation of a mixture of two diastereoisomers. We succeeded in separating these isomers by fractional recrystallization of sulfone **VId** from diethyl ether–hexane.

Scheme 2.



VI, R = Ph (**a**), 4-MeC_6H_4 (**b**), 1*H*-1,2,4-triazol-5-yl (**c**), 2,2-dichlorocyclopropylmethyl (**d**), Me (**e**), Et (**f**), Pr (**g**), Bu (**h**), C_5H_{11} (**i**), $PhCH_2$ (**j**).

Thus we have found that 1,1-dichloro-2-chloromethylcyclopropane reacts with S-nucleophiles via replacement of the side-chain chlorine atom, the dichlorocyclopropane fragment remaining intact. The corresponding sulfides are formed in good yields, and they can readily be converted into the respective sulfones.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-82 spectrometer from samples prepared as thin films (liquids) or KBr pellets. The ^{1}H NMR spectra were obtained on a Varian Mercury VX-200 spectrometer (200 MHz) from solutions in DMSO-d_6 or $CDCl_3$

using tetramethylsilane as internal reference. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates using hexane–chloroform (5:1) as eluent; the chromatograms were developed by treatment with iodine vapor in a moist chamber.

1,1-Dichloro-2-chloromethylcyclopropane (**I**) was synthesized by the procedure described in [8].

General procedure for the preparation of isothiuronium salts. A mixture of 0.1 mol of appropriate alkyl halide, 0.1 mol of thiourea, and 35 ml of 96% ethanol was heated for 4 h under reflux with stirring. The mixture was cooled, and the precipitate was filtered off, washed with alcohol, and dried in air.

Sulfides IIa–IIj (*general procedure***).** *a*. A mixture of 80 mmol of isothiuronium salt, 12.76 g (80 mmol) of chloride **I**, 0.25 g of tetrabutylammonium bromide, 150 ml of benzene, and 150 g of 30% aqueous sodium hydroxide was stirred for 4 h at 20°C under nitrogen. The organic phase was separated, the aqueous phase was extracted with benzene (2×20 ml), the extracts were combined with the organic phase, washed with 100 ml of water, dried over $MgSO_4$, and evaporated, and the residue was distilled under reduced pressure.

b. A solution of sodium ethoxide, prepared from 1.84 g of metallic sodium and 27 ml of anhydrous ethanol, was cooled to 0°C, 80 mmol of appropriate thiol was added with stirring under nitrogen, and (5 min later), 88 mmol of the corresponding alkyl halide **V** was added. After 30 min, the cooling bath was removed, and the mixture was allowed to warm up to 20°C and was stirred at that temperature, the progress of the reaction being monitored by TLC. When the reaction was complete, the solvent was partially distilled off, and water was added to the residue in an amount sufficient to dissolve the inorganic precipitate. The organic phase was separated, the aqueous phase was extracted with diethyl ether (2×10 ml), the extracts were combined with the organic phase, washed with a 1 M solution of NaOH and with water, dried over $MgSO_4$, and evaporated, and the residue was distilled under reduced pressure. In the synthesis of compound **IIc**, 1.84 g of sodium and 50 ml of ethanol were used, and the residue obtained by removal of the solvent was recrystallized from methanol.

2,2-Dichlorocyclopropylmethyl phenyl sulfide (IIa). Following method *b*, from 8.81 g of benzenethiol and 14.03 g of chloride **I** we obtained 16.79 g (90%) of sulfide **IIa** as a colorless liquid. bp 123–125°C (3 mm); published data [1]: bp 96–99°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 t (1H, H_A, J = 7.4 Hz), 1.62–1.70 d.d (1H, H_B, J = 7.2, 10.3 Hz), 1.79–1.95 m (1H, H_C), 2.89–3.29 m (2H, H'_A, H'_B, J = 6.8, 7.3, 13.7 Hz), 7.20–7.46 m (5H, H_{arom}). Found, %: C 51.25; H 4.16; Cl 30.08. $C_{10}H_{10}Cl_2S$. Calculated, %: C 51.52; H 4.32; Cl 30.41.

2,2-Dichlorocyclopropylmethyl 4-methylphenyl sulfide (IIb). Following method *b*, from 9.94 g of *p*-methylbenzenethiol and 14.03 g of chloride **I** we obtained 16.81 g (85%) of sulfide **IIb** as a colorless liquid. bp 175–176°C (13 mm). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.39 t (1H, H_A, J = 6.8 Hz), 1.72–1.81 d.d (1H, H_B, J = 6.8, 10.5 Hz), 1.80–1.96 m (1H, H_C), 2.29 s (3H, CH_3), 3.10 d (2H, H'_A, H'_B, J = 6.8 Hz), 7.15–7.36 m (4H, H_{arom}). Found, %: C 53.12; H 4.75; Cl 28.38. $C_{11}H_{12}Cl_2S$. Calculated, %: C 53.45; H 4.89; Cl 28.69.

2,2-Dichlorocyclopropylmethyl 1*H*-1,2,4-triazol-5-yl sulfide (IIc). A mixture of 10.1 g (0.1 mol) of 1*H*-1,2,4-triazole-5-thiol, 17.54 g (0.11 mol) of chloride **I**, 15.2 g (0.11 mol) of K_2CO_3, and 100 ml of DMF was stirred for 6 h at room temperature and poured into 100 ml of water. The aqueous phase was separated by decanting, and the residue was recrystallized from methanol. Yield 12.77 g (57%), mp 74–76°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (1H, H_A, J = 7.5 Hz), 1.66–1.75 d.d (1H, H_B, J = 7.3, 10.4 Hz), 2.04–2.20 m (1H, H_C), 3.37 d (2H, H'_A, H'_B, J = 7.4 Hz), 8.33 s (1H, CH), 9.78 s (1H, NH). Found, %: C 31.83; H 3.01; Cl 31.35. $C_6H_7Cl_2N_3S$. Calculated, %: C 32.16; H 3.15; Cl 31.64.

Following method *b*, from 8.09 g of 1*H*-1,2,4-triazole-5-thiol and 14.03 g of chloride **I** we obtained 11.65 g (65%) of sulfide **IIc** as a viscous liquid. The product was purified by recrystallization from methanol, mp 74–76°C; no depression of the melting point was observed on mixing with a sample prepared as described above.

Bis(2,2-dichlorocyclopropylmethyl) sulfide (IId). A mixture of 15.95 g (0.1 mol) of chloride **I**, 14.41 g (0.06 mol) of $Na_2S·9H_2O$, 3 g of benzyltriethylammonium chloride, and 30 ml of water was stirred for 7 h at 90°C. The mixture was poured into 150 ml of water, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (2×20 ml). The extracts were combined with the organic phase, washed with water, dried over $MgSO_4$, and evaporated, and the residue was distilled under reduced pressure. Yield 11.20 g (80%), yellowish liquid,

bp 166°C (13 mm); published data [7]: bp 117–118°C (1–1.5 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 t (1H, H_A, J = 7.0 Hz), 1.68–1.77 d.d (1H, H_B, J = 7.0, 10.4 Hz), 1.80–2.00 m (1H, H_C), 2.65–3.00 m (2H, H'_A, H'_B, J = 6.6, 7.2, 13.5 Hz). Found, %: C 34.05; H 3.46; Cl 50.23. $C_8H_{10}Cl_4S$. Calculated, %: C 34.31; H 3.60; Cl 50.64.

2,2-Dichlorocyclopropylmethyl methyl sulfide (IIe). Following method *b*, from 12.56 g of thiol **III** and 12.49 g of methyl iodide we obtained 8.62 g (63%) of sulfide **IIe** as a colorless liquid, bp 90°C (20 mm). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.37 t (1H, H_A, J = 7.3 Hz), 1.75–1.83 d.d (1H, H_B, J = 7.0, 10.6 Hz), 1.88–2.04 m (1H, H_C), 2.16 s (3H, CH_3), 2.58–2.78 m (2H, H'_A, H'_B, J = 6.5, 7.5, 13.8 Hz). Found, %: C 34.85; H 4.66; Cl 41.28. $C_5H_8Cl_2S$. Calculated, %: C 35.10; H 4.71; Cl 41.45.

2,2-Dichlorocyclopropylmethyl ethyl sulfide (IIf). Following method *b*, from 12.56 g of thiol **III** and 13.73 g of ethyl iodide we obtained 10.37 g (70%) of sulfide **IIf** as a colorless liquid, bp 85–87°C (13 mm). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.22 t (3H, CH_3), 1.36 t (1H, H_A, J = 7.2 Hz), 1.74–1.83 d.d (1H, H_B, J = 7.0, 10.4 Hz), 1.86–2.02 m (1H, H_C), 2.57–2.68 m (2H, CH_2), 2.64–2.80 m (2H, H'_A, H'_B, J = 7.4, 14.0 Hz). Found, %: C 38.65; H 5.28; Cl 37.98. $C_6H_{10}Cl_2S$. Calculated, %: C 38.93; H 5.44; Cl 38.30.

2,2-Dichlorocyclopropylmethyl propyl sulfide (IIg). Following method *b*, from 12.56 g of thiol **III** and 14.96 g of propyl iodide we obtained 11.63 g (73%) of sulfide **IIg** as a colorless liquid, bp 105°C (12 mm). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.96 t (3H, CH_3), 1.36 t (1H, H_A, J = 7.2 Hz), 1.49–1.67 m (2H, CH_2), 1.74–1.83 d.d (1H, H_B, J = 7.0, 10.5 Hz), 1.86–2.02 m (1H, H_C), 2.55–2.63 m (2H, CH_2), 2.67–2.78 m (2H, H'_A, H'_B, J = 7.5, 14.0 Hz). Found, %: C 41.85; H 5.88; Cl 35.28. $C_7H_{12}Cl_2S$. Calculated, %: C 42.22; H 6.07; Cl 35.61.

Butyl 2,2-dichlorocyclopropylmethyl sulfide (IIh). Following method *a*, from 17.05 g of *S*-butylisothiuronium bromide and 12.76 g of chloride **I** we obtained 8.53 g (50%) of sulfide **IIh** as a colorless liquid, bp 110–112°C (12 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (3H, CH_3), 1.20 t (1H, H_A, J = 7.2 Hz), 1.36–1.62 m [4H, $(CH_2)_2$], 1.63–1.72 d.d (1H, H_B, J = 7.1, 10.4 Hz), 1.76–1.92 m (1H, H_C), 2.52–2.89 m (2H, H'_A, H'_B, J = 6.8, 13.7 Hz), 2.57–2.71 q (2H, CH_2). Found, %: C 44.84; H 6.47; Cl 32.94. $C_8H_{14}Cl_2S$. Calculated, %: C 45.08; H 6.62; Cl 33.26.

Following method *b*, from 12.56 g of thiol **III** and 12.06 g of butyl bromide we obtained 12.62 g (74%) of sulfide **IIh** as a colorless liquid. The product was identical to a sample prepared according to method *a*.

2,2-Dichlorocyclopropylmethyl pentyl sulfide (IIi). Following method *a*, from 18.17 g of *S*-pentylisothiuronium bromide and 12.76 g of chloride **I** we obtained 8.54 g (47%) of sulfide **IIi** as a colorless liquid, bp 110–112°C (12 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (3H, CH_3), 1.20 t (1H, H_A, J = 7.1 Hz), 1.26–1.72 m [6H, $(CH_2)_3$], 1.64–1.70 d.d (1H, H_B, J = 7.1, 10.4 Hz), 1.77–1.92 m (1H, H_C), 2.52–2.89 m (2H, H'_A, H'_B, J = 6.8, 13.6 Hz), 2.56–2.71 q (2H, CH_2). Found, %: C 47.25; H 6.96; Cl 30.88. $C_9H_{16}Cl_2S$. Calculated, %: C 47.58; H 7.10; Cl 31.21.

Following method *b*, from 12.56 g of thiol **III** and 13.29 g of *n*-pentyl bromide we obtained 13.45 g (74%) of sulfide **IIi** as a colorless liquid. The product was identical to a sample prepared according to method *a*.

Benzyl 2,2-dichlorocyclopropylmethyl sulfide (IIj). Following method *a*, from 16.22 g of *S*-benzylisothiuronium chloride and 12.76 g of chloride **I** we obtained 12.85 g (65%) of sulfide **IIj** as a colorless liquid, bp 110–112°C (12 mm). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.32 t (1H, H_A, J = 7.3 Hz), 1.69–1.78 d.d (1H, H_B, J = 7.1, 10.5 Hz), 1.83–1.99 m (1H, H_C), 2.56–2.73 m (2H, H'_A, H'_B, J = 7.4, 13.9 Hz), 3.86 s (2H, CH_2), 7.20–7.46 m (5H, H_{arom}). Found, %: C 53.14; H 4.77; Cl 28.38. $C_{11}H_{12}Cl_2S$. Calculated, %: C 53.45; H 4.89; Cl 28.69.

Following method *b*, from 12.56 g of thiol **III** and 11.14 g of benzyl chloride we obtained 17.40 g (88%) of sulfide **IIj** as a colorless liquid. The product was identical to a sample prepared according to method *a*.

2,2-Dichlorocyclopropylmethanethiol (III). *a*. Chloride **I**, 12.76 g (80 mmol), was added in one portion to a solution of 6.09 g (80 mmol) of thiourea in 26 ml of 96% ethanol, and the mixture was refluxed for 6 h under vigorous stirring. The mixture was diluted under nitrogen with 50 ml of 10% aqueous sodium hydroxide, stirred for 2 h, cooled to room temperature, and 10 ml of 20% sulfuric acid was added. The organic phase was separated, and the aqueous phase was extracted with benzene (2×20 ml). The extracts were combined with the organic phase, washed with water, and dried over $MgSO_4$. The solvent was removed, and the residue was distilled under reduced pressure in a stream of nitrogen. We isolated

3.77 g (30%) of sulfide **III** as a colorless liquid, bp 74–75°C (19 mm), and 1.35 g (12%) of sulfide **IId** as a yellowish liquid, bp 177–180°C (19 mm). According to the TLC data (R_f 0.38), product **IId** was identical to a sample prepared as described above. IR spectrum of **III**, ν, cm^{-1}: 760, 1232, 1432, 2576, 2936. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.39 t (1H, H_A, J = 7.3 Hz), 1.71–1.80 d.d (1H, H_B, J = 7.3, 10.4 Hz), 1.87–2.03 m (1H, H_C), 2.54–2.74 m (2H, H'_A, H'_B, J = 7.0, 14.0 Hz), 2.61 m (1H, SH). Found, %: C 30.42; H 3.69; Cl 44.83. $C_4H_6Cl_2S$. Calculated, %: C 30.59; H 3.85; Cl 45.15.

b. A solution of 11.16 g (70 mmol) of chloride **I** in 19 ml of ethanol was added to a solution of 17.37 g (70 mmol) of $Na_2S_2O_3 \cdot 5H_2O$ in 18 ml of water. The mixture was heated for 6 h at the boiling point under vigorous stirring, 31 ml of 50% sulfuric acid was added under nitrogen, and the mixture was heated for an additional 2 h. It was then cooled, and the product was isolated as described above in *a*. Yield of thiol **III** 9.34 g (85%). The product was identical to a sample prepared as described in *a* in the TLC (R_f 0.51) and IR data (νSH 2576 cm^{-1}).

Bis(2,2-dichlorocyclopropylmethyl) disulfide (IV). Thiol **III**, 7.54 g (48 mmol), was added to a solution of 1.92 g of sodium hydroxide and 0.12 g of potassium iodide in 12 ml of water. The mixture was stirred for 40 min, and 6.09 g (24 mmol) of iodine was added until the mixture turned slightly colored. The mixture was decolorized by adding a 20% solution of Na_2SO_3, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (2× 20 ml). The extracts were combined with the organic phase, dried over $MgSO_4$, and evaporated, and the residue was distilled under reduced pressure. Yield 5.02 g (67%), yellowish viscous liquid, bp 145°C (2 mm). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.50 t (1H, H_A, J = 7.3 Hz), 1.81–1.91 d.d (1H, H_B, J = 7.3, 10.4 Hz), 2.02–2.19 m (1H, H_C), 3.02 d (2H, H'_A, H'_B, J = 7.0 Hz). Found, %: C 30.52; H 3.07; Cl 45.11. $C_8H_{10}Cl_4S_2$. Calculated, %: C 30.79; H 3.23; Cl 45.44.

Sulfones VIa–VIj (*general procedure*). Sulfide **IIa**–**IIj**, 5 mmol, was dissolved in 5 ml of acetic acid, 15 mmol of 30% hydrogen peroxide was added, and the mixture was heated for 4–5 h at 85°C. It was then poured into 50 ml of water, and the precipitate was filtered off, dried over NaOH, and recrystallized from appropriate solvent. In the synthesis of sulfone **Vf**, the oily material was separated, and the aqueous phase was extracted with two portions of diethyl ether. The extracts were combined with the oily material, dried over $MgSO_4$, and evaporated, and the residue was distilled under reduced pressure.

2,2-Dichlorocyclopropylmethyl phenyl sulfone (VIa). Yield 1.13 g (85%), colorless crystals, mp 87–88°C (from AcOH). IR spectrum, ν, cm^{-1}: 752, 1088, 1152, 1268, 1308, 2952. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.21 t (1H, H_A, J = 7.6 Hz), 1.67–1.76 d.d (1H, H_B, J = 7.6, 10.5 Hz), 1.91–2.07 m (1H, H_C), 3.09–3.59 m (2H, H'_A, H'_B, J = 6.6, 7.5, 14.6 Hz), 7.56–7.98 m (5H, H_{arom}). Found, %: C 45.05; H 3.65; Cl 26.59. $C_{10}H_{10}Cl_2O_2S$. Calculated, %: C 45.30; H 3.80; Cl 26.74.

2,2-Dichlorocyclopropylmethyl 4-methylphenyl sulfone (VIb). Yield 1.30 g (93%), colorless crystals, mp 73–74°C (from AcOH). IR spectrum, ν, cm^{-1}: 752, 1104, 1160, 1308, 1320, 1408, 2916. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.32 t (1H, H_A, J = 5.5 Hz), 1.77–1.84 d.d (1H, H_B, J = 6.0, 10.6 Hz), 1.83–1.96 m (1H, H_C), 2.43 s (3H, CH_3), 3.35–3.71 m (2H, H'_A, H'_B, J = 6.4, 14.8 Hz), 7.47–7.84 m (4H, H_{arom}). Found, %: C 47.05; H 4.00; Cl 25.05. $C_{11}H_{12}Cl_2O_2S$. Calculated, %: C 47.32; H 4.33; Cl 25.40.

2,2-Dichlorocyclopropylmethyl 1*H*-1,2,4-triazol-5-yl sulfone (VIc). Yield 0.82 g (64%), colorless crystals, mp 174–175°C (from AcOH). IR spectrum, ν, cm^{-1}: 760, 1000, 1152, 1192, 1340, 1468, 1776, 2572, 2916. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.43 t (1H, H_A, J = 7.4 Hz), 1.81–1.90 d.d (1H, H_B, J = 7.4, 10.7 Hz), 1.96–2.12 m (1H, H_C), 3.55–3.87 m (2H, H'_A, H'_B, J = 6.7, 13.7 Hz), 8.92 s (1H, CH), 15.13 s (1H, NH). Found, %: C 27.85; H 2.61; Cl 27.45. $C_6H_7Cl_2N_3O_2S$. Calculated, %: C 28.14; H 2.75; Cl 27.69.

Bis(2,2-dichlorocyclopropylmethyl) sulfone (Vd). Yield 1.42 g (91%), colorless crystals. Fractional recrystallization from diethyl ether–hexane (1:1) gave 0.57 g of isomer **A**, mp 82–84°C, and 0.51 g of isomer **B**, mp 118–120°C, both as colorless crystals. Isomer **A**: IR spectrum, ν, cm^{-1}: 760, 1116, 1142, 1316, 1405, 2927. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.53 t (1H, H_A, J = 7.6 Hz), 1.89–1.98 d.d (1H, H_B, J = 7.6, 10.4 Hz), 2.07–2.24 m (1H, H_C), 3.06–3.61 m (2H, H'_A, H'_B, J = 6.3, 7.6, 14.3 Hz). Found, %: C 30.48; H 3.07; Cl 45.14. $C_8H_{10}Cl_4O_2S$. Calculated, %: C 30.79; H 3.23; Cl 45.45. The IR spectrum of isomer **B** was identical to that of isomer **A**. Found, %: C 30.49; H 3.08; Cl 45.15. $C_8H_{10}Cl_4O_2S$. Calculated, %: C 30.79; H 3.23; Cl 45.45.

2,2-Dichlorocyclopropylmethyl methyl sulfone (Ve). Yield 0.98 g (97%), colorless crystals, mp 52–53°C (from MeOH). IR spectrum, ν, cm^{-1}: 760, 1108, 1136, 1152, 1264, 1308, 2928. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.61 t (1H, H_A, J = 7.3 Hz), 1.90–1.99 d.d (1H, H_B, J = 7.3, 10.5 Hz), 2.02–2.18 m (1H, H_C), 3.13–3.66 m (2H, H'_A, H'_B, J = 5.6, 7.4, 14.5 Hz), 3.06 s (3H, CH_3). Found, %: C 29.21; H 3.82; Cl 34.60. $C_5H_8Cl_2O_2S$. Calculated, %: C 29.57; H 3.97; Cl 34.91.

2,2-Dichlorocyclopropylmethyl ethyl sulfone (Vf). The oily product was purified by vacuum distillation. Yield 0.78 g (72%), colorless viscous liquid, bp 144°C (2 mm). IR spectrum, ν, cm^{-1}: 756, 1108, 1148, 1288, 1316, 2932. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.25 t (3H, CH_3), 1.59 t (1H, H_A, J = 7.1 Hz), 1.90–1.99 d.d (1H, H_B, J = 7.0, 10.7 Hz), 2.00–2.16 m (1H, H_C), 3.11–3.63 m (2H, H'_A, H'_B, J = 6.0, 7.4, 14.4 Hz), 3.13–3.24 m (2H, CH_2). Found, %: C 32.85; H 4.48; Cl 32.35. $C_6H_{10}Cl_2O_2S$. Calculated, %: C 33.19; H 4.64; Cl 32.66.

2,2-Dichlorocyclopropylmethyl propyl sulfone (Vg). Yield 1.03 g (89%), colorless crystals, mp 34–35°C (from diethyl ether–hexane, 1:1). IR spectrum, ν, cm^{-1}: 756, 1108, 1144, 1292, 1316, 2964. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.01 t (3H, CH_3), 1.59 t (1H, H_A, J = 7.3 Hz), 1.65–1.84 m (2H, CH_2), 1.90–1.99 d.d (1H, H_B, J = 7.0, 10.4 Hz), 2.01–2.16 m (1H, H_C), 3.10–3.63 m (2H, H'_A, H'_B, J = 6.0, 7.6, 13.7 Hz), 3.13–3.24 m (2H, CH_2). Found, %: C 36.05; H 4.94; Cl 30.32. $C_7H_{12}Cl_2O_2S$. Calculated, %: C 36.38; H 5.23; Cl 30.68.

Butyl 2,2-dichlorocyclopropylmethyl sulfone (Vh). Yield 1.13 g (92%), colorless crystals, mp 59–60°C (from AcOH). IR spectrum, ν, cm^{-1}: 752, 1116, 1148, 1268, 1316, 2964. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.91 t (3H, CH_3), 1.34–1.52 m (2H, CH_2), 1.59 t (1H, H_A, J = 7.3 Hz), 1.66–1.78 m (2H, CH_2), 1.90–1.99 d.d (1H, H_B, J = 7.1, 10.5 Hz), 2.01–2.17 m (1H, H_C), 3.11–3.22 m (2H, CH_2), 3.11–3.62 m (2H, H'_A, H'_B, J = 6.0, 7.5, 14.5 Hz). Found, %: C 38.98; H 5.61; Cl 28.76. $C_8H_{14}Cl_2O_2S$. Calculated, %: C 39.19; H 5.76; Cl 28.92.

2,2-Dichlorocyclopropylmethyl pentyl sulfone (Vi). Yield 1.06 g (82%), colorless crystals, mp 44–45°C (from AcOH). IR spectrum, ν, cm^{-1}: 743, 1091, 1136, 1258, 1290, 1315, 2926. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (3H, CH_3), 1.32–1.58 m [4H, $(CH_2)_2$], 1.47 t (1H, H_A, J = 7.6 Hz), 1.81–1.97 m (2H, CH_2), 1.85–1.94 d.d (1H, H_B, J = 7.5, 10.5 Hz), 2.04–2.20 m (1H, H_C), 2.95–3.49 m (2H, H'_A, H'_B, J = 6.5, 7.2, 14.5 Hz), 3.01–3.08 m (2H, CH_2). Found, %: C 41.42; H 6.03; Cl 27.03. $C_9H_{16}Cl_2O_2S$. Calculated, %: C 41.71; H 6.22; Cl 27.36.

Benzyl 2,2-dichlorocyclopropylmethyl sulfone (Vj). Yield 1.24 g (89%), colorless crystals, mp 85–86°C (from AcOH). IR spectrum, ν, cm^{-1}: 776, 1080, 1136, 1316, 1360, 2968. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.58 t (1H, H_A, J = 7.3 Hz), 1.87–1.96 d.d (1H, H_B, J = 7.3, 10.5 Hz), 2.00–2.15 m (1H, H_C), 3.12–3.62 m (2H, H'_A, H'_B, J = 5.9, 7.7, 14.9 Hz), 4.58 s (2H, CH_2), 7.31–7.51 m (5H, H_{arom}). Found, %: C 47.03; H 4.20; Cl 25.14. $C_{11}H_{12}Cl_2O_2S$. Calculated, %: C 47.32; H 4.33; Cl 25.40.

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