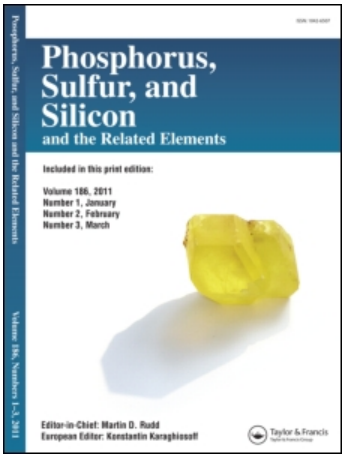


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# THE NOVEL MACROCYCLIC AND LINEAR-CHAIN THIOETHERS FROM PERCHLOROBUTADIENE AND DITHIOLES

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# THE NOVEL MACROCYCLIC AND LINEAR-CHAIN THIOETHERS FROM PERCHLOROBUTADIENE AND DITHIOLES

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*Compounds **3a–c**, **4a,b**, **5a–c**, and **6a,c** were obtained from the reactions of perchlorobutadiene (**1**) with 1,4-butanedithiol (**2a**), 1,5-pentanethiol (**2b**), and 2.2′-(ethlene-dioxyl)diethanethiol (**2c**) in ethanol in the presence of sodium hydroxide. Compounds **7a,b** were obtained from the reactions of thioethers **3a,b** with m-chlorperbenzoic acid in $CHCl_3$.*

*Keywords:* Cyclic thioethers; disulphids; dithiols; hexachlorobutadiene; sulphone; thioethers



Previously, the reactions of hexachlorobutadienes with some thiols were reported.[1–6] The same thioehers were obtained in the reactions of hexachlorobutadiene with methanethiol. It was reported in the US Patent that these compounds exhibit biological activity.[7] We reported previously the synthesis of cyclic and straight-chain thioethers from the reactions of hexachlorobutadiene with some thiols.[8–12]

The aim of this work was to synthesis novel compounds from the reactions of perchlorobutadiene with some dithiols and also establish the structure of these novel compounds.

Macrocyclic thio-crown ethers are of particular interest, among other reasons, as potential heavy-metal receptors and could be useful for treatment of heavy-metal poisoning.[13]

Previously, mono(thio)- and bis(thio)substituted diene compounds have been produced from the ractions of nitrodienes with thiols in the presence of NaOH in ethanol.[14–21]

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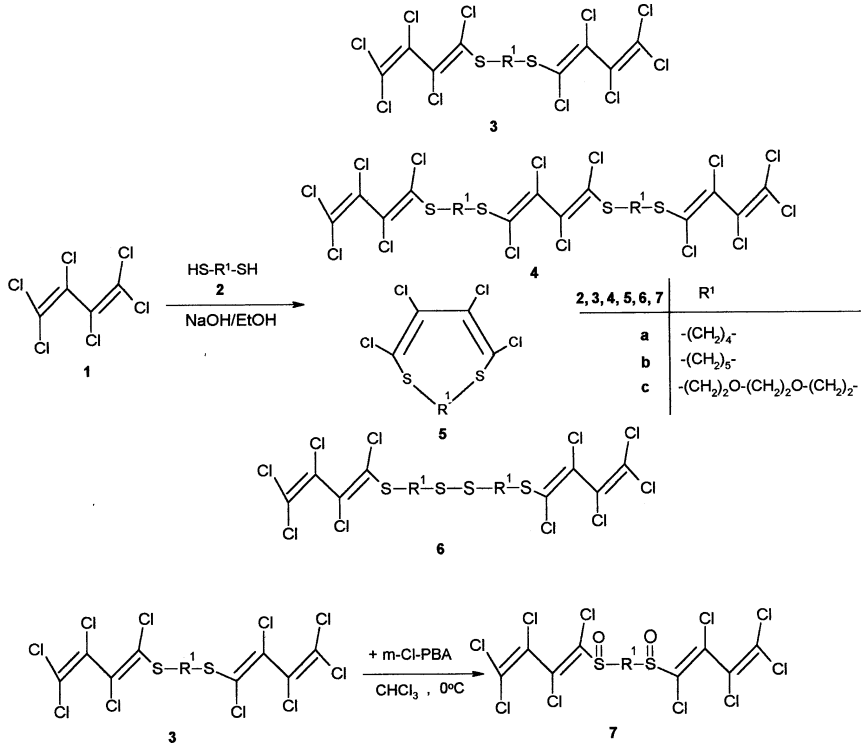
Compounds **3a–c**, **4a**,**b**, **5a–c**, and **6a**,**c** were obtained from the reactions of compounds **1** with dithiols (Scheme 1).




**SCHEME 1**

Compounds **3a**, **5a**, and **6a** were known.[22] Compounds **4a**,**b**, **3b**,**c**, **5b**,**c** and **6c** are novel and stable. Compounds **5b** and **5c** have an interesting cyclic thioether structure. Compound **6c** has a disulfide structure and is stable. The IR spectra of compound **6c** shows a characteristic band for S–S at 500 $cm^{-1}$.

The structures of these compounds were determined by microanalysis and spectroscopic data. Probably the reactions occurred according to the addition–elimination mechanism.

It was known that R–SO–SR and R–$SO_2$–SR have been obtained from the oxidation reactions of cyclic and straight-chain disulfides.[23] In addition, it was also known that the sulfoxides R–SO–R and sulfones R–$SO_2$–R have been obtained from the cyclic and straight-chain thioethers.[24,25]

The oxidation reactions of organosulfur compounds are important in the biochemistry and in industrial processes.[26]

Compounds **7a** and **7b** sulfoxide were obtained from the reactions of 1 mole **3a**,**b** and 4 mole m-Cl-PBA in $CHCl_3$. The IR spectra of **7a** and **7b** show a characteristic band for the >S=O group at 1100 $cm^{-1}$.

## EXPERIMENTAL SECTION

$^1H$ NMR: Varian (Inova) 500 MHz. IR: Shimadzu FTIR-8101. Microanalyses: Carlo-Erba 1106 Elemental Analyzer. Melting points: Büchi SMP 20. Products were isolated by column chromatography on $SiO_2$ (Fluka Kieselgel 60, particle size 0.063–0.2 mm). Thin layer chromatography (TLC) plates silica 60 $F_{254}$ (Merck, Darmstadt), detection with UV light (254 nm).



### Preperation of S-Substituted Polyhalodienes General Procedure I

Equimolar amounts of hexachlorobutadiene (**1**) in 10 ml of ethanol and dithioles in 10 ml of ethanol were mixed, and NaOH (in 8 ml of water) was added at room temperature. The mixture was stirred for 24 h until completion of the reaction (TLC). Chloroform was added to the reaction mixture. The organic layer was separated and washed with water (4 × 30 ml), and dried with anhydrous $Na_2SO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel.

### *General Procedure II*

Compounds **3a** or **3b** (1 mol) in 30 ml of chloroform was mixed with m-chloroperbenzoic acid (4 moles) in 30 ml of chloroform at 0°C for 24 h; 2N NaOH was added to the mixture, and then chloroform was added to the reaction mixture. The organic layer was separated and washed with water (4 × 30 ml) and dried with anhydrous $Na_2SO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel.

### 6,6′-Dithia-tetrachlorobutadiene-1,3-bis(11-thia-12,13,14, 15,15-pentachloro-decadienyl-7,8) (4a)

Compound **4a** was synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (**1**) (2 g, 7.66 mmol) and butanedithiol (**2a**) (0.935 g, 7.66 mmol) according to general procedure I, yield, 1.5 g (22%); oil. $R_f = 0.3333$ (Petroleumether/$CCl_4$ 1:1). IR (film): $\nu = 2950$, 2900 $cm^{-1}$

(C—H), 1600 (C=C). $^1$H NMR ($CDCl_3$): $\delta$ = 1.6–2.0 ppm (m, 8H, $4CH_2$), 2.6–3.2 (m, 8H, $4CH_2$-S). $C_{20}H_{16}Cl_4S_4$ (880.95) calcd.: C, 27.27; H, 1.83; S, 14.56. Found: C, 27.98; H, 1.81; S, 14.54.

## 5,5′-Pentadithio-bis(1,1,2,3,4-pentachloro-1,3-butadine) (3b), 6,6′-Dithia-tetrachlorobutadiene-1,3-bis(12-thia-13,14,15,16,16-pentachloro-undecadienyl-8,10) (4b), 2,3,4,5-tetra-chloro-1,6-dithia-cycloundeca-2,4-dien (5b)

Compounds **3b**, **4b**, and **5b** were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (**1**) (5 g 19.15 mmol) and pentadithiol (**2b**) (2.61 g, 19.15 mmol) according to general procedure I.

**3b**: yield, 0.926 g (11%); oil. $R_f$ = 0.4167 (Petroleumether). IR (film): $\nu$ = 2950, 2900 cm$^{-1}$ (C—H), 1600 (C—C). $^1$H NMR ($CDCl_3$): $\delta$ = 12–2.2 ppm (m, 6H, $3CH_2$), 2.4–3.3 (m, 4H $2CH_2$-S). $C_{13}H_{10}Cl_{10}S_2$ (584.88) calcd.: C, 26.7; H, 1.72; S, 10.96. Found: C, 26.89; H, 1.32; S, 10.50.

**4b**: yield, 1.236 g (9%); oil. $R_f$ = 0.7917 (Petroleumether/$CCl_4$ 1:1) IR (film): $\nu$ = 2950, 2900 cm$^{-1}$ (C—H), 1600 (C=C). $^1$H NMR ($CDCl_3$): $\delta$ = 1.2–2.0 ppm (m, 12H, $6CH_2$), 2.4–3.3 (m, 8H, $4CH_2$-S). $C_{22}H_{20}Cl_{14}S_4$ (909.0) calcd.: C, 29.07; H, 2.22; S, 14.11. Found: C, 29.59; H, 2.45; S, 14.29.

**5b**: yield, 0.92 g (19%); oil. $R_f$ = 0.7083 (Petroleumether/$CCl_4$ 1:1) IR (film): $\nu$ = 2950, 2900 cm$^{-1}$ (C—H), 1600 (C=C). $^1$H NMR ($CDCl_3$): $\delta$ = 1.2–2.0 ppm (m, 6H, $3CH_2$), 2.4–3.2 (m, 4H, $2CH_2$—S). $C_9H_{10}Cl_4S_4$ (324.12) calcd.: C, 33.35; H, 3.10; S, 19.78. Found: C, 33.08; H, 3.05; S, 19.52.



## 1,1,2,3,4,15,16,17,18,18-Decachloro-5,14-dithia-8,11-dioxa-octadecan-1,3,15,17-tetraen (3c); 1,1,2,3,4,25,26,27,28,28-Decachloro-5,14,15,24-tetrathia-8,11,18,21-tetraoxa-octaeiko-san-1,3,25,27-tetraen (5c); and 1,6-dithia-9,12-dioxa-2,3,4,5-tetrachloro-tetradeca-2,4-dien (6c)

Compounds **3c**, **5c**, and **6c** were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (**1**) (5 g, 19.15 mmol) and 2,2′-(ethylenedioxy)-diethanethiol (**2c**) (3.49 g, 19.15 mmol) according to general procedure I.

**3c**: yield, 2 g (16%); oil. $R_f$ = 0.3913 ($CH_2Cl_2$/$CCl_4$ 1:2). IR (film): $\nu$ = 2900 cm$^{-1}$ (C—H), 1600, 1550 (C=C), 1100, 1300 (C—O—C). $^1$H NMR ($CDCl_3$): $\delta$ = 3.1–3.2 ppm (m, 4H, $2CH_2$-S), 3.5–3.7 (m, 8H, $4CH_2$-O). $C_{14}H_{12}Cl_{10}S_2O_2$ (631.284) calcd.: C, 26.65; H, 1.92; S, 10.16. Found: C, 26.38; H, 1.89; S, 10.53.

**5c**: yield, 3.4 g (11%); oil. $R_f = 0.7200$ ($CH_2Cl_2/CCl_4$ 1:1). IR (film): $\nu = 2900\ cm^{-1}$ (C—H), 1600, 1550 (C=C), 1110, 1300 (C—O—C). $^1H$ NMR ($CDCl_3$): $\delta = 3.6$–$3.8$ ppm (m, 16H, $8CH_2$), 3.2–3.3 (m, 4H, $2CH_2$—S—S), 2.6–2.8 (m, 4H, $2CH_2$). $C_{20}H_{24}Cl_{10}S_4O_4$ (811.568) calcd; C, 29.61; H, 2.98; S, 15.81. Found: C, 29.82; H, 2.73; S, 15.99.

**6c**: yield, 1.8 g (13%); oil. $R_f = 0.5071$ ($CHCl_3$). IR (film): $\nu = 2950\ cm^{-1}$ (C—H), 1610 (C=C), 1100, 1305 (C—O—C). $^1H$ NMR ($CDCl_3$): $\delta = 3.6$–$3.8$ ppm (m, 8H, $4CH_2$-S), 2.8–3.2 (m, 4H, $2CH_2$-O). $C_{10}H_{12}Cl_4S_2O_2$ (370.284) calcd.: C, 32.45; H, 3.27; S, 17.27. Found: C, 32.68; H, 3.18; S, 17.23.

## 5,5′-Butanyldisulfinyl-bis(1,1,2,3,4-pentachloro-1,3-butadiene (7a)

Compound **7a** was synthesized from 4,4′-butanedithio-bis (1,1,2,3,4-pentachloro-1,3-butadiene (**3a**) (0.5 g, 0.875 mmol) and m-chloroperbenzoic acid (0.151 g, 0.875 mmol) according to the general procedure II, yield, 0.3 g (57%); oil. $R_f = 0.4545$ ($CCl_4/CH_2Cl_2$ 2:1). IR (film): $\nu = 2950$, 2900 $cm^{-1}$ (C—H), 1605 (C=C), 1100 (S=O). $C_{16}H_8Cl_{10}S_2O_2$ (603.228) calcd.: C, 23.91; H, 1.34; S, 10.64. Found: C, 23.74; H, 1.32; S, 10.50.

## 6,6′-Pentanyldisulfinyl-bis(1,1,2,3,4-pentachloro-1,3-butadien (7b)

Compound **7b** was synthesized from 5,5′-pentanedithio-bis (1,1,2,3,4-pentachloro-1,3-butadiene (**3b**) (0.5 g 0.875 mmol) and m-chloroperbenzoic acid (0.151 g, 0.875 mmol) according to the general procedure II, yield, 0.005 g (25%); oil. $R_f = 0.3333$ ($CCl_4/CH_2Cl_2$ 1:1). IR (film): $\nu = 2950$, 2990 $cm^{-1}$ (C—H), 1600, 1550 (C=C), 1080 (S=O). $C_{13}H_{10}Cl_{10}S_2O_2$ (616.883) calcd.: C, 25.3; H, 1.63; S, 10.40. Found: C, 25.4; H, 1.6; S, 10.5.

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