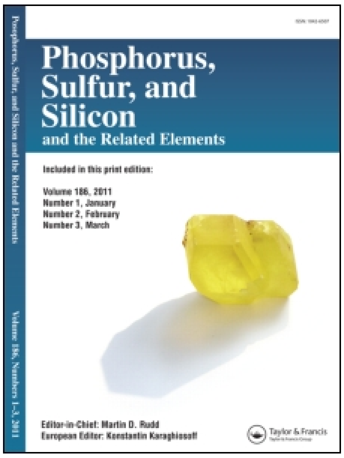

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New Perchlorobutadienyl Sulfanes

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New Perchlorobutadienyl Sulfanes

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Hexachlorobutadiene ***1*** *reacts with 3-mercapto-1-hexanol in water-ethanol mixture in the presence of sodium hydroxide to give the new monosubstituted thioether 3-(perchlorobuta-1,3-dienyl-thio)-hexan-1-ol* ***3a*** *and the disubstituted thioether 3,3′-(perchlorobuta-1,3-diene-1,4-diyl) bis(sulfane-diyl)-dihexan-1-ol* ***4a****. 1-Chlorohexan-3-yl-pentachlorobutadienyl-sulfide* ***5a****, 2-chloroethyl-pentachlorobutadienyl-sulfide* ***5b****, 2-chloropropyl-pentachlorobutadienyl-sulfide* ***5c*** *and 1,2,3,4-tetra-chlorobuta-1,4-bis(2-chloroethylsulfanyl)-buta-1,3-diene* ***6b*** *were obtained from the reaction of* ***3a–c*** *and* ***4b*** *with* $SOCl_2$ *in pyridine. The derivatives* ***8b–k*** *and* ***9a*** *were synthesized from the reaction of componds* ***5b*** *and* ***5c*** *in water-ethanol mixture in the presence of sodium hydroxide with the corresponding thiol, respectively.*

Keywords Hexachloro-1,3-butadiene; (perchlorobuta-1,3-dienyl)sulfanes; thioalcohols; thioethers

INTRODUCTION

Thioethers are involved in the synthesis of specific classes of compounds including agricultural chemicals,[1–3] pharmacological drugs,[4–5] chemical-resistant polymers,[6–7] and rubber antioxidants.[8–9] Alkyl and heterocyclic sulfides exhibit pharmacological activity, e.g., germicidal properties;[10] some unsymmetrical sulfides exhibit antioxidant activity (AOA).[11]

The occurance of sulfur as a donor atom for transition metals is well-known. Sulfur acts as a very good ligating atom in the form of the sulfide ion (S^{-2}) or as a mercaptide ion (RS^{-}), while complexes of thioethers (R-S-R) are much less common.[12]

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The reaction of hexachloro-1,3-butadiene **1** with some thiols in DMF, DMSO and EtOH has been reported.[13–21] Some thioethers were obtained from the reaction of hexachloro-1,3-butadiene with methanethiol in EtOH. In a US Patent, it is reported that these compounds exhibit biological activity.[22]

Previously, we described the synthesis of cyclic and open-chain thioethers from the reactions of hexachlorobutadiene with some thiols.[23] The aim of this work was to synthesize new unsaturated sulfanes and to determine their structures.

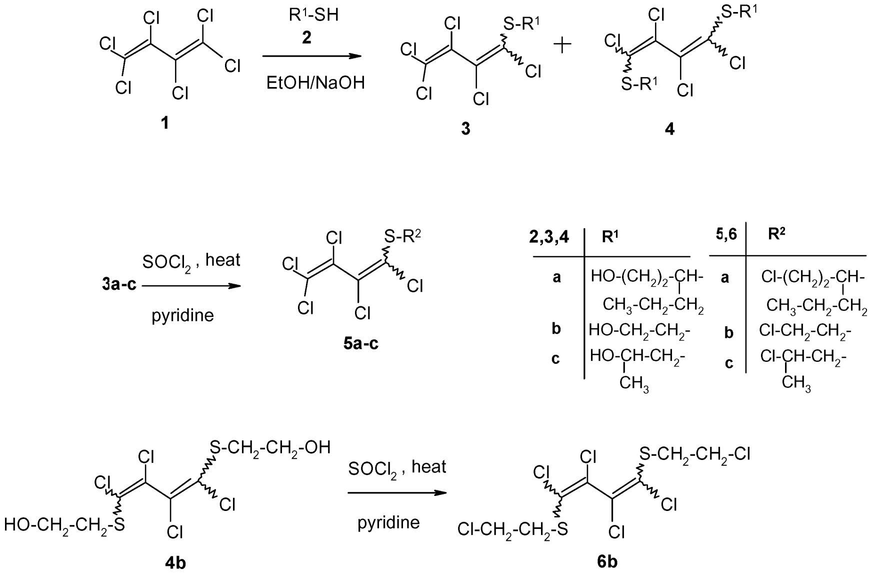
RESULTS AND DISCUSSION

Hexachlorobutadiene reacted with 3-mercapto-1-hexanol in water-ethanol mixture in the presence of sodium hydroxide to give the new mono(thio)substituted thioether 3-(pentachlorobuta-1,3-dienyl-thio)-hexan-1-ol **3a** and di(thio)substituted thioether 3,3′-(perchlorobuta-1,3-diene-1,4-diyl-bis(sulfanediyl)-dihexan-1-ol **4a**, respectively. The IR spectrum of **3a** and **4a** showed a band characteristic for the OH groups. The ^{13}C NMR spectrum of compounds **3a** and **4a** showed signals for the hydroxy carbon atoms at $\delta = 59.4$ ppm. The ^{13}C NMR spectrum of compound **4a** showed signals for diene carbon atoms at $\delta = 136.1$ (C-1 and C-4) and 120.1 (C-2 and C-3) ppm.

The hydroxy derivatives **3a**, **3b**[20], **3c**,[21] and **4b**[20] were converted to chlorides **5a–5c** with $SOCl_2$ in pyridine.[24] The OH band was not observed in the IR spectra of compounds **5a–c** and **6b**. (Scheme 1).

We synthesized compounds **8b–k** from the reaction of compound **5b** with some aliphatic and aromatic thiols in water-ethanol mixture in the presence of sodium hydroxide. 1-(2-pentachlorobuta-1,3-dienylsulfanyl-propylsulfanyl)-decane **9a** was synthesized from the reaction of compound **5c** with decanethiol. The IR spectrum of **8b** showed a band characteristic for OH group. The mass spectrum of compound **8b** confirms its molecular mass (362.55) MS: m/z = 362.57. The ^{1}H NMR spectra of compounds **8c–h**, **8j**, and **8k** showed signals at $\delta = 6.57-7.81$ ppm characteristic for the protons of the aromatic group. The ^{1}H NMR spectrum of compound **8i** showed signals for the protons of the vinyl group at $\delta = 5.09-5.58$ ($C\mathbf{H}_2$=CH–) and 6.01 (CH_2=C**H**–) ppm (Scheme 2).

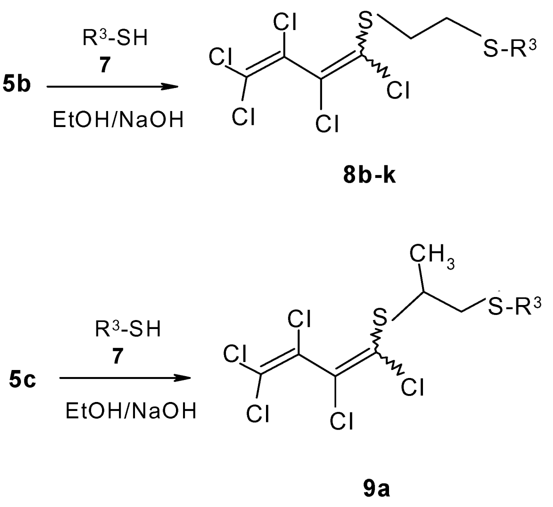
Compounds **8b–k**, **9a** are new aliphatic and aromatic perchloro-buta-1,3-dienylsulfanes. They are stable colorless oils. All compounds were isolated in good yield and fully characterized. Their structures result from the spectroscopic data and are supported by microanalysis.

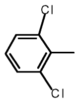


2,3,4	R¹
a	HO-(CH₂)₂-CH- CH₃-CH₂-CH₂
b	HO-CH₂-CH₂-
c	HO-CH-CH₂- CH₃

5,6	R²
a	Cl-(CH₂)₂-CH- CH₃-CH₂-CH₂
b	Cl-CH₂-CH₂-
c	Cl-CH-CH₂- CH₃

SCHEME 1



7,8, 9	R³
a	CH_3-$(CH_2)_9$-
b	HO-CH_2-CH_2-
c	*p*-Cl-C_6H_4-
d	C_6H_5-
e	*p*-CH_3-C_6H_4-
f	
g	*p*- F-C_6H_4-
h	*p*- Br-C_6H_4-
i	CH_2=CH-CH_2-
j	*o*-CH_3-C_6H_4-
k	*p*- CH_3O-C_6H_4-

SCHEME 2

TABLE I Analytical and IR Spectroscopic Data of the New Perchlorobuta-1,3-dienylsulfanes

	Molecular formula (Yield %)	Elemental Analysis Calcd. (Found) C	H	S	IR (cm^{-1})	MS (m/z)	R_f (Solvent)
3a	$C_{10}H_{13}Cl_5SO$ (45)	33.50 (34.15)	3.65 (3.67)	8.94 (8.97)	3480 (OH), 1550, 1600 (C=C), 2980, 2970 (C—H)	358.58	0.20 ($CHCl_3$)
4a	$C_{16}H_{26}Cl_4S_2O_2$ (12)	42.11 (42.77)	5.74 (6.02)	14.05 (14.89)	3480 (OH), 1565, 1615 (C=C), 2995, 2980 (C—H)	454.81	0.57 Et.Ac./petrol.eth. (1:1)
5a	$C_{10}H_{12}Cl_6S$ (82)	31.86 (32.12)	3.20 (3.79)	8.50 (8.65)	3050 (C—H), 1540, 1590 (C=C)	—	0.56 Hexane
5b	$C_6H_4Cl_6S$ (68)	22.46 (22.79)	1.26 (1.58)	9.99 (10.22)	3050 (C—H), 1540, 1600 (C=C)	—	0.60 Hexane
5c	$C_7H_6Cl_6S$ (63)	25.10 (25.64)	1.80 (1.72)	9.57 (10.02)	3040 (C—H), 1570, 1600 (C=C)	—	0.47 Hexane
6b	$C_8H_8Cl_6S_2$ (38)	25.22 (25.74)	2.12 (2.49)	16.83 (16.98)	2990 (C—H), 1530, 1580 (C=C)	380.27	0.50 Hexane/CCl_4(1:1)
8b	$C_8H_9Cl_5S_2O$ (64)	26.50 (26.64)	2.50 (2.78)	17.68 (17.72)	3480 (OH), 1550, 1620 (C=C), 2990 (C—H)	362.57	0.80 Hexane
8c	$C_{12}H_8S_2Cl_6$ (87)	33.59 (33.79)	1.87 (1.97)	14.95 (14.84)	2970, 2995 (C—H), 1550, 1595 (C=C)	—	0.76 Hexane
8d	$C_{12}H_9Cl_5S_2$ (46)	36.53 (36.27)	2.29 (2.58)	16.25 (16.54)	3005 (C—H), 1550, 1590 (C=C)	—	0.66 Hexane

8e	$C_{13}H_{11}Cl_5S_2$	38.21	2.71	15.69	2990 (C—H), 1550, 1590, 1620 (C=C)	410.49	0.81 Hexane.
	(35)	(38.43)	(2.78)	(15.72)			
8f	$C_{12}H_7Cl_7S_2$	31.09	1.52	13.84	2995 (C—H), 1550, 1580, 1600 (C=C)	—	0.55 Hexane
	(23)	(30.94)	(1.46)	(13.52)			
8g	$C_{12}H_8Cl_5FS_2$	34.93	1.95	15.54	3000 (C—H), 1550, 1610 (C=C)	—	0.75 Hexane
	(64)	(34.78)	(1.85)	(15.47)			
8h	$C_{12}H_8Cl_5BrS_2$	30.44	1.70	13.54	2980 (C—H), 1550, 1620 (C=C)	—	0.73 Hexane
	(75)	(30.21)	(1.78)	(13.22)			
8i	$C_9H_9Cl_5S_2$	30.14	2.53	17.88	2990 (C—H), 1580, 1600 (C=C)	358.53	0.74 Hexane
	(69)	(30.33)	(2.78)	(17.72)			
8j	$C_{13}H_{11}Cl_5S_2$	38.21	2.71	15.69	2980 (C—H), 1570, 1600, 1610 (C=C)	—	0.71 Hexane
	(50)	(38.17)	(2.74)	(15.76)			
8k	$C_{13}H_{11}Cl_5S_2O$	36.77	2.61	15.10	2990 (C—H), 1550, 1620 (C=C)	424.57	0.77 Hexane
	(45)	(36.64)	(2.78)	(15.27)			
9a	$C_{17}H_{27}S_2Cl_5$	43.19	5.76	13.56	2995, 2970 (C—H), 1545, 1590 (C=C)	473.45	0.76 Hexane
	(48)	(43.35)	(5.97)	(14.02)			

TABLE I ^1H NMR and ^{13}C NMR Spectroscopic Data of the New Perchlorbuta-1,3-dienylsulfanes

	$^1H/^{13}C$- NMR ($CDCl_3$)	δ(ppm)
3a	^1H	4.38 (s, 1H, OH), 1.48−3.8 (m, 8H, CH_2), 0.90 (s, 3H, CH_3), 2.52 (s, 1H, CH)
	^{13}C	13.7, 31.4, 32.3, 35.4, 39.6, 59.4, 119.0, 124.3, 126.6, 136.1
4a	^1H	4.38 (s, 2H, OH), 1.90–3.80 (m, 16H, CH_2), 0.90 (s, 6H, CH_3), 2.52 (s, 2H, CH)
	^{13}C	13.7, 31.5, 32.2, 35.4, 39.6, 59.4, 120.1, 136.1
5a	^1H	1.57−3.74 (m, 8H, CH_2), 0.90 (s, 3H, CH_3), 2.52 (s, 1H, CH)
	^{13}C	13.7, 31.4, 33.3, 34.6, 39.4, 41.5, 120.1, 124.3, 126.6, 136.0
5b	^1H	3.15−4.05 (m, 4H, CH_2)
	^{13}C	30.4, 42.5, 120.1, 124.2, 126.7, 136.0
5c	^1H	2.98−3.23 (m, 2H, CH_2), 1.60 (s, 3H, CH_3), 3.92 (s, 1H, CH)
	^{13}C	24.4, 39.4, 52.0, 120.1, 124.2, 126.7, 136.0
6b	^1H	3.15−4.05 (m, 8H, CH_2)
	^{13}C	30.4, 42.5, 120.1, 136.0
8b	^1H	4.78 (s, 1H, OH), 2.56−3.33 (m, 8H, CH_2)
	^{13}C	28.6, 33.4, 34.0, 61.5, 120.1, 124.2, 126.7, 136.0
8c	^1H	7.26−7.39 (m, 4H, arom-H), 3.11−4.06 (m, 4H, CH_2)
	^{13}C	25.2, 34.6, 120.9, 124.7, 126.4, 129.5, 130.9, 131.7, 133.2, 135.7
8d	^1H	7.20−7.51 (m, 5H, arom-H), 3.09−4.05 (m, 4H, CH_2)
	^{13}C	32.2, 39.3, 119.8, 124.8, 125.4, 126.1, 128.2, 129.7, 130.7, 136.1
8e	^1H	6.57−7.26 (m, 4H, arom-H), 2.11−2.76 (m, 3H, CH_3), 3.23−3.99 (m, 4H, CH_2)
	^{13}C	21.3, 28.2, 36.2, 120.9, 124.8, 126.5, 128.6, 129.4, 133.4, 136.0, 137.5
8f	^1H	6.57−7.26 (m, 3H, arom-H), 3.33−4.07 (m, 4H, CH_2)
	^{13}C	28.2, 36.8, 120.9, 124.2, 126.5, 128.6, 131.3, 135.2, 136.0, 141.4

(*Continued on next page*)

TABLE II ^{1}H NMR and ^{13}C NMR Spectroscopic Data of the New Perchlorbuta-1,3-dienylsulfanes *(Continued)*

	^{1}H/^{13}C- NMR ($CDCl_3$)	δ(ppm)
8g	^{1}H	6.58–7.26 (m, 4H, arom-H), 3.25–4.35 (m, 4H, CH_2)
	^{13}C	28.2, 36.8, 115.7, 120.9, 124.7, 126.4, 129.4, 131.7, 136.0, 158.5
8h	^{1}H	7.43–7.81 (m, 4H, arom-H), 3.25–3.89 (m, 4H, CH_2)
	^{13}C	28.2, 36.8, 119.5, 120.9, 124.8, 126.5, 129.8, 131.7, 133.6, 136.0
8i	^{1}H	6.01 (s, 1H, CH_2 =CH-), 5.09–5.58 (m, 2H, CH_2 =CH—), 3.11–3.29 (m, 6H, CH_2)
	^{13}C	29.7, 34.0, 35.2, 118.3, 120.8, 124.7, 126.5, 133.6, 135.9
8j	^{1}H	7.27–7.55 (m, 4H, arom-H), 2.34 (s, 3H, CH_3), 3.25–3.90 (m, 4H, CH_2)
	^{13}C	21.5, 28.2, 38.1, 120.8, 124.7, 125.5, 125.9, 126.0, 126.4, 130.9, 131.7, 135.8, 136.1
8k	^{1}H	7.16–7.26 (m, 4H, arom-H), 3.83 (s, 3H, OCH_3), 3.21–3.89 (m, 4H, CH_2)
	^{13}C	28.2, 36.8, 55.8, 114.5, 120.9, 125.3, 126.5, 128.2, 129.4, 137.9, 152.4
9a	^{1}H	1.29–3.33 (m, 20H, CH_2), 0.88–1.26 (s, 6H, CH_3), 2.98 (s, 1H, CH)
	^{13}C	14.1, 21.1, 22.7, 28.5, 28.9, 29.3, 29.6, 30.9, 31.8, 35.4, 36.5, 40.1, 120.1, 124.2, 126.7, 136.0

EXPERIMENTAL

All chemicals and solvents were obtained commercially and used without purification. TLC was performed on precoated aluminum plates (Silicagel 60 $F_{254,}$ Merck). Elemental analyses were performed by Carlo Erba 1106 Elemental analyzer. IR spectra were recorded in KBr pellets or in Nujol mulls with a Shimadzu FTIR-8101 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a Varian^{UNITY} INOVA instrument, operating at 500 MHz (^{1}H) and at 125 MHz (^{13}C). Mass spectra were obtained using a Finnigan LCQ Advantage Max. LC/MS instrument.

Preparation of S- and S,S-Substituted Polyhalodienes—General Procedure

2 g (7.66 mmol) of 1,1,2,3,4,4-hexachloro-1,3-butadiene **1** in 25 mL of ethanol and 2.06 g (15.32 mmol) of 3-mercapto-1-hexanol **2a** in 25 mL of ethanol were mixed and 0.62 g NaOH in 8 mL of water was added at room temperature. The mixture was stirred for 24 h. Then chloroform (20 mL) was added to the reaction mixture. The organic layer was separated, washed with water (4 × 30 mL) and dried with $MgSO_4$. The solvent was eveporated and the residue was purified by column chromatography on silica gel with $CHCl_3$ as eluent. Compounds **3a**,**4a**, **8b–k**, and **9a** were synthesized in the same way.

Chlorination of Hydroxysulfides—General Procedure

To a solution of the compounds **3a–c** and **4b** (1 equiv.) in pyridine (1 equiv.) was added dropwise thionyl chloride (2 equiv.). The reaction mixture was strirred at room temperature for 1 h and then refluxed for an additional 1 h. After, cooling water (50 mL) was added. The reaction mixture was then extracted with $CHCl_3$ (100 mL). The organic layer was washed with 35 mL of aqueous NaOH (5%), with water (4 × 30 mL), and then dried over $MgSO_4$. The solvent was eveporated and the residue was purified by column chromatography on silica gel with hexane as eluent. Compounds **5a–c** and **6b** were synthesized in the same way.

The characteristics of compounds **3a**, **4a**, **5a–c**,**6b**, **8b–k**, and **9a** are given in Tables I and II.

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