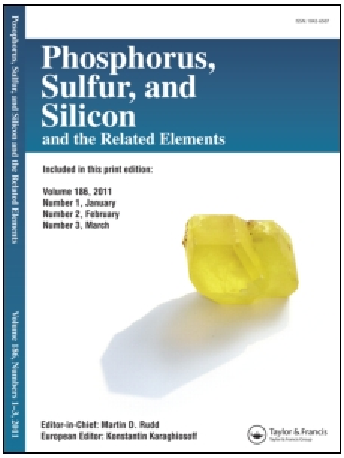

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N,S-, S-, S,S-, <SO-, and < SO_2-Substituted Dienes from Halo-1,3-Butadienes

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N,S-, S-, S,S-, >S=O-, and >SO_2-Substituted Dienes from Halo-1,3-Butadienes

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Mono(thio)substituted dienes ***1*** *gave* ***3a–g****,* ***5****, and* ***7*** *with piperazine derivatives in dichloromethane. Hexachlorobutadiene* ***14*** *in a water-ethanol mixture in the presence of sodium hydroxide reacted with thiol* ***15*** *to give the mono(thio)substituted thioether* ***16*** *and di(thio)substituted thioether* ***17****.* ***18*** *was obtained from the reaction of* ***16*** *with m-CPBA in chloroform.* ***9*** *was obtained from the reaction of l,2,3,4,4-pentachloro-(1-2-hydroxyethylthio)-1,3- butadiene* ***8*** *with 47% HI, and* ***11*** *was synthesized from the reaction of* ***8*** *with concentrated* H_2SO_4 *and KBr. Compounds* ***9*** *and* ***11*** *gave in the reaction with m-CPBA in chloroform* ***10****,* ***12****, and* ***13****, respectively.*

Keywords Hexachloro-1,3-butadiene; thioether, N,S-thiosubstituted nitrodiene; piperazine; sulfone; sulfoxide; thiol

The reaction of nitrodiene compounds with some thiols and amines are known.[1–9] Previously, we have obtained N,S-substituted dienes from the reaction of mono(thio)substituted dienes with some amines.[9–13]

The reaction of hexachloro-l,3-butadiene **14** with thiols in DMF, DMSO, and EtOH have been reported.[14,15] Hexachloro-1,3-butadiene in presence of DMSO at r.t. reacted with Na-tert-buthanethiolates to give tetrakis(thio)butatrien,[16] and monothiosubstituted and dithiosubstituted dienes were obtained from the reaction of **14** with morpholine.[17]

The aim of this work is to synthesize new N,S-, S-, S,S-, >S=O-, and >SO_2-substituted 1,3-diene compounds and to determine their structures.

The piperazine compounds are imported for clinical chemistry, also, some piperazine compounds were used in gen-transfer reactions.[18,19] The piperidinyl derivatives show an excellent biological activity.[20]

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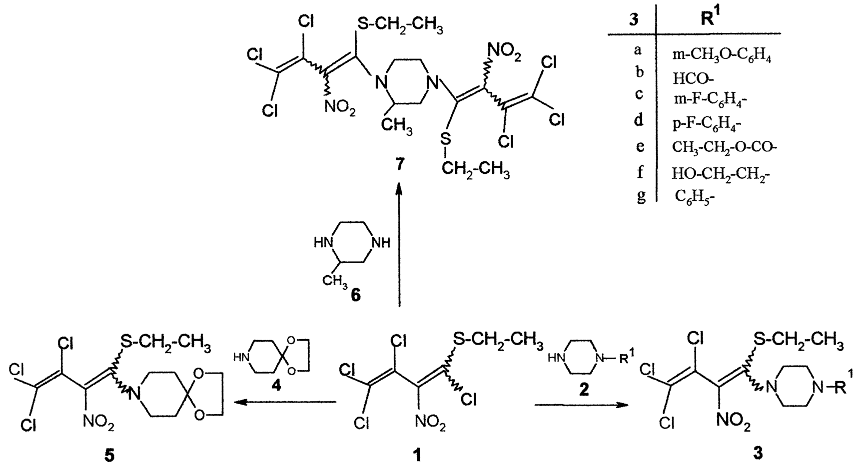
Compound **1**[21] treated with **2** gave **3a–g**. **5** and **7** were obtained from the reaction of **1** with **6** and **4**. **3a–g**, **5**, and **7** are novel and stable compounds. The structure of these compounds was determined by microanalysis and spectroscopic data. The IR spectrum of **3b** and **3e** showed a band characteristic for the >C=O groups, and compound **3f** showed a band characteristic for the HO-group (Scheme 1).



3	R^1
a	m-CH$_3$O-C$_6$H$_4$
b	HCO-
c	m-F-C$_6$H$_4$-
d	p-F-C$_6$H$_4$-
e	CH$_3$-CH$_2$-O-CO-
f	HO-CH$_2$-CH$_2$-
g	C$_6$H$_5$-

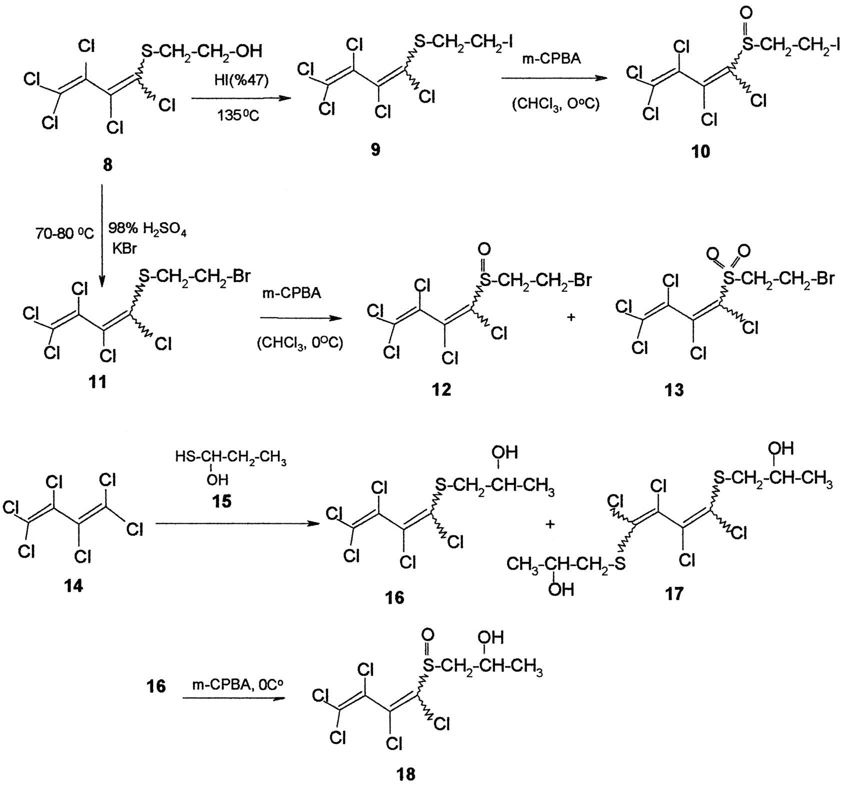
SCHEME 1

It is known that the sulfones and sulfoxides compounds were obtained from the reaction of mono(thio)-, bis(thio)-, tris(thio)-, and tetrakis(thio)substituted-1,3-butadienes with m-CPBA.[14,15,22–25]

8[9] gave **9** with HI (47%). The sulfoxide **10** was obtained from the reaction of **9** with m-CPBA. The sulfoxide **12** and the sulfone **13** were obtained from the reaction of **11** with m-CPBA.

Mono(thio)- and 1,4-bis(thio)substituted-l,3-diene were obtained from the reaction of thioalcohol **15** with **14**. **16** gave the sulfoxide **18** with m-CPBA. The IR spectrum of **10**, **12**, and **18** showed a band at $\nu = 1070\ \mathrm{cm}^{-1}$ characteristic for the >S=O- group, and the IR spectrum of **13** showed a band at $\nu = 1300\ \mathrm{cm}^{-1}$ characteristic for the >SO$_2$-group (Scheme 2).

The obtained compounds **9**, **10**, **11**, **12**, **13**, **16**, **17**, and **18** are stable oils. The IR spectrum of **16**, and **18** showed a band at $\nu = 3480\ \mathrm{cm}^{-1}$ characteristic for the HO-group.



SCHEME 2

EXPERIMENTAL SECTION

^{1}H NMR Spectra: Varian (INOVA) 500 mHz. IR Spectra: Shimadzu FTIR-8101. Microanalyses: Carlo-Erba 1106 Elemental Analyzer. Melting Points: Büchi SMP 20 capillary apparatus. Products were isolated by column chromatography on SiO_2 (Fluka Kieselgel 60, particle size 0.063–0.2 mm). TLC plates silica 60 F_{254} (Merck, Darmstadt).

The Preparation of N,S-Substituted Polyhalonitrodienes: General Procedure

Appropriate amounts of 1,3,4,4-tetrachloro-ethyl(thio)-2-nitro-1,3-butadiene **1** and amine derivatives in dry ether were stirred until completion of the reaction. Then chloroform 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 evaporated, and the residue was purified by crystallization in methanol. **3b** to **3g**, **5**, and **7** were synthesized in the same way. The characteristics of these compounds are given in Table I.

1,2,3,4,4-Pentachloro-1-(β-ıodoethylthio)-1,3-butadiene (9)

In a 100-mL round-bottom flask, 3.02 g of 1,2,3,4,4-pentachloro-1-(2-hydroxyethylthio)-1,3-butadiene **8** and 5 volumes (4.6 mL) of 47% HI were placed. The reaction was maintained at a temperature of about 135°C for 1.5 h and was continually stirred. At the end of the reaction, chloroform and a solution of sodiumsulfide were 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 petroleum ether as an eluent to give **9**.

1,2,3,4,4-Pentachloro-1-(β-bromoethyhio)-1,3-butadiene (11)

In a 100-mL round-bottom flask, 2 g of 1,2,3,4,4-pentachloro-1-(2-hydroxyethylthio)-1,3-butadiene **8** and 2 mL of concentrated H_2SO_4 were placed, and the mixture was cooled. To the mixture was addded 2 g of ice-cold water and 1.68 g of anhydrous KBr. The reaction was maintained at a temperature of about 70–80°C for 1.5 h and was continually stirred. At the end of the reaction, chloroform and a solution of sodiumsulfide were added to the reaction mixture. The organic layer was separated, washed with water (4 × 30 mL), and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel with petroleum ether as eluent to give **11**.

The Preparation of Sulfinyl and Sulfonyl Polyhalodienes: General Procedure

To 0.39 g (0.095 mmol) of l,2,3,4,4-pentachloro-1-(B-ıodoethylthio)-1,3-butadiene **9** in 30 mL of chloroform were added 0.1631 g (0.095 mmol) 3-chloroperbenzoic acid in 15 mL of chloroform. The mixture was kept in the cold at 0°C for 24 h. After the completion of the reaction, chloroform was added to the mixture, washed with 2N $NaHCO_3$ and water (4 × 30 mL), and dried with $MgSO_4$. The solvent was evaporated, and the organic layer was purified by column chromatography on silica gel. Compounds **10**, **12**, **13**, and **18** were synthesized in the same way.

The 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 **14** in 10 mL of ethanol and 0.706 g (7.66 mmol) of 2-hydroxyl-1-propanethiol **15** in

TABLE I Characteristics of the Polyhalonitrodienes

Compound no.	Molecular formula (yield %)	M.P (°C)	Elemental analysis Calcd. (found)				IR (cm^{-1})	^{1}H-NMR (ppm)
			C	H	N	S		
3a	$C_{17}H_{20}N_3Cl_3SO_3$ (88)	Oil	45.09 (45.28)	4.45 (4.40)	9.28 (9.91)	7.08 (7.73)	2970, 3020 (C—H), 1580, 1620 (C=C), 3500 (NH) 1295, 1530 (C—NO$_2$)	6.9–7.1 (m, 4H, Ar-H), 3.4–4.0 (m, 8H, 4 CH$_2$), 1.2–1.4 (m, 6H, S—CH$_2$-CH$_3$), —O—CH$_3$), 3.1 (m, 2H, S—CH$_2$-)
3b	$C_{11}H_{14}N_3Cl_3SO_3$ (45)	120	35.26 (35.47)	3.77 (3.53)	11.22 (11.93)	8.56 (8.71)	2985, 3010 (C—H), 1590, 1610 (C=C), 1720 (C=O) 1270, 1510 (C—NO$_2$)	3.2–3.5 (m, 8H, 4 CH$_2$) 2.8 (m, 2H, S—CH$_2$-)1.2 (m, 3H, S—CH$_2$-CH$_3$)
3c	$C_{16}H_{17}N_3Cl_3SFO_2$ (87)	123	43.60 (43.70)	3.89 (3.92)	9.53 (9.79)	7.27 (7.71)	2980, 3010 (C—H), 1570, 1600 (C=C) 1285, 1500 (C—NO$_2$)	7.0–7.8 (m, 4H, Ar-H), 3.2–3.8 (m, 8H, 4 CH$_2$) 3.0 (m, 2H, S—CH$_2$-) 1.4 (m, 3H, S—CH$_2$-CH$_3$),
3d	$C_{16}H_{17}N_3Cl_3SO_2F$ (67)	135	43.60 (43.40)	3.89 (3.85)	9.53 (9.99)	7.27 (7.38)	3100 (C—H), 1620 (C=C) 1290, 1525 (C—NO$_2$),	7.0–7.2 (m, 4H, Ar-H), 3.3–3.8 (m, 8H, 4 CH$_2$), 1.2 (m, 3H, S—CH$_2$-CH$_3$), 3.1 (m, 2H, S—CH$_2$-)
3e	$C_{13}H_{18}N_3Cl_3SO_4$ (37)	118	37.29 (37.81)	4.33 (4.46)	10.03 (10.83)	7.65 (7.94)	2980 (C—H), 1720 (C=O) 1580 (C=), 1270 (C—NO$_2$)	3.3–3.8 (m, 10H, 5 CH$_2$), 1.2–1.4 (m, 6H, S—CH$_2$-CH$_3$, -O-CH$_3$), 3.0 (m, 2H, S—CH$_2$-)
3f	$C_{12}H_{18}N_3Cl_3SO_3$ (69)	115	36.89 (37.44)	4.64 (4.57)	10.75 (10.11)	8.20 (8.33)	3010, 3020 (C—H), 1600 (C=C), 3480 (OH) (1290), 1525 (C—NO$_2$)	2.6–2.8 (m, 1H, HO-), 3.1 (m, 2H, S—CH$_2$-) 1600 (C=), 3480 (OH) 3.2–3.8 (m, 8H, 4CH$_2$), 1290, 1525 (C—NO$_2$) 1.2–1.4 (m, 6H, S—CH$_2$-CH$_3$),
3g	$C_{16}H_{18}N_3Cl_3SO_2$ 27	136	45.36 (45.46)	2.68 (2.79)	6.62 (6.63)	7.12 (7.58)	3100 (C—H), 1580, 1600 (C=C), 1280, 1520 (C—NO$_2$)	6.8–7.3 m, 5H Ar—H, 3.1 (m, 2H, S—CH$_2$) 3.2–3.8 (m, 8H, 4 CH$_2$), 1.2 (m, 3H, S—CH$_2$-CH$_3$),
5	$C_{13}H_{17}N_2Cl_3SO_4$ 73	Oil	38.68 (38.69)	4.24 (4.89)	6.94 (6.85)	7.94 (8.08)	2970, 3010, (C—H), 1570, 1600 (C=C), 3500 (NH) 1290, 1520 (C—NO$_2$)	3.3–3.8 (m, 8H, 4 CH$_2$), 3.0 (m, 2H, S—CH$_2$) 1.3 (m, 3H, S—CH$_2$-CH$_3$) 4.0–4.5 (m, 4H, O-(CH$_2$)$_2$-O)
7	$C_{17}H_{20}N_4Cl_6S_2O_4$ 29	Oil	32.87 (32.93)	3.24 (3.58)	9.02 (9.61)	10.83 (10.97)	2980, 3010 (C—H), 1590 1600 (C=C), 1300, 1540 (C—NO$_2$)	2.4 (m, 3H, CH$_3$), 3.0–3.4 (m, 10H, 2 S—CH$_2$-, 3 -N-CH$_2$) 1.3–1.5 (m, 6H, 2 S—CH$_2$-CH$_3$)

TABLE II Characteristics of the S-, S,S-, >S=O-, and >SO_2 dienes

Compound no.	Molecular formula (yield %)	Elemental analysis Calcd. (found) C	H	S	IR (cm^{-1})	^{1}H-NMR (ppm)
9	$C_6H_4ICl_5S$ (42)	17.48 17.29	0.97 1.10	7.77 7.48	2980, 3000 (C—H), 1550, 1600 (C—C)	3.1–3.4 (m, 4H, S—CH_2, —CH_2-I)
10	$C_6H_4ICl_5SO$ (14)	16.82 16.01	0.94 0.99	7.49 8.16	2980, 3010 (C—H), 1570, 1620 (C=C), 1070 (S=O)	3.1–3.5 (m, 4H, S—CH_2-, —CH_2-I)
11	$C_6H_4BrCl_5S$ (14)	19.73 19.80	0.97 1.05	7.77 7.98	2980, 3000 (C—H), 1550, 1600 (C=C)	3.2–3.6 (m, 4H, S—CH_2-, —CH_2-Br)
12	$C_6H_4BrCl_5SO$ (30)	18.89 18.76	1.05 1.04	8.40 8.78	2980, 3010 (C—H), 1590, 1600 (C=C), 1070 (S=O)	3.1–3.5 (m, 4H, S—CH_2-, —CH_2-Br)
13	$C_6H_4BrCl_5SO$ (43)	18.13 18.10	1.01 1.03	8.07 8.13	2980, 3010 (C—H), 1550, 1620 (C=C), 1300 (–SO_2)	3.1–3.5 (m, 4H, S—CH_2-, —CH_2-Br)
16	$C_7H_7Cl_5SO$ (27)	26.57 26.62	2.23 2.21	10.13 10.59	2980, (C—H), 1540, (C=C), 3940 (OH)	3.8–4.8 (m, 1H, 2 OH—CH) 2.6–3.2 (m, 2H, S—CH_2-) 1.9–2.1 (s, 1H, OH), 1.1–1.4 (m, 6H, 2 CH_3)
17	$C_{10}H_{14}Cl_4S_2O_2$ (17)	32.27 32.26	3.79 4.09	17.23 17.58	2990, 3000, (C—H), 1580, (C=C), 3480 (OH)	3.8–4.0 (m, 2H, 2 OH—CH) 2.8–3.2 (m, 4H, 2 S—CH_2-) 1.9–2.1 (s, 2H, 2 OH), 1.1–1.4 (m, 6H, 2 CH_3)
18	$C_7H_7Cl_5SO_2$ (13)	25.29 25.90	2.12 2.29	10.64 9.43	2980, (C—H), 1610, (C=C), 1070 (S=O) 3490 (HO)	3.7–4.0 (m, 1H, OH—CH) 2.8–3.2 (m, 2H, S—CH_2-) 1.9–2.1 (s, 1H, 2 OH), 1.0–1.4 (m, 3H, CH_3)

10 mL ethanol were mixed, and 0.31 g of NaOH (in 8 mL of water) was added at r.t. The mixture was stirred for 24 h. Then chloroform 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 evaporated, and the residue was purified by column chromatography on silica gel with $CHCl_3$ as an eluent. Compounds **16** and **17** were synthesized in the same way.

The characteristics of compounds **9**, **10**, **11**, **12**, **13**, **16**, **17**, and **18** are given in Table II.

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