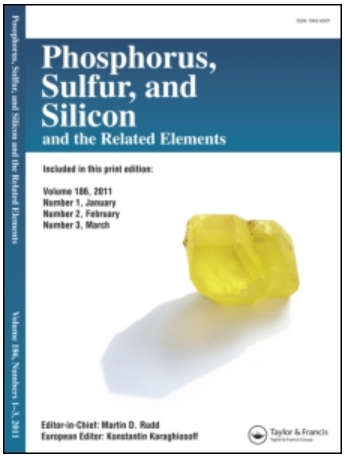

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The Sulphides, Sulfoxides, and Sulfones of New Dienyl Groups

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THE SULPHIDES, SULFOXIDES, AND SULFONES OF NEW DIENYL GROUPS

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*Mono(thio)substituted dienes **1a–c** gave compounds **3a–i** with piperazine **2** in dichloromethane. Compounds **5a–c** were synthesized from the reaction of mono(thio)substituted **1a–c** with 4-piperidinol **4**. Compounds **7a–b** were obtained from the reaction of mono(thio)substituted dienes **1a–b** with 2-aminoethylmorpholino **6**. N,N-Bis(mono(thio)substituted)-2-nitro-1,3-butadienyl **9a–b** were synthesized from the reactions of mono(thio)substituted dienes **1a–b** with 2,5-dimethyl-piperazine **8**. Compound **10a** was obtained from the reaction of perchlorobutadiene with 2-napthylthiol in ethanol in the presence of sodium hydroxide. Compounds **11a–b** were obtained from the reactions of mono(thio)substituted dienes **10a–b** with m-chloroperbenzoic acid in $CHCl_3$. Di(thio)substituted diene **12b** gave compound mono(sulfnyl)dienes **13b** with m-chloroperbenzoic acid in $CHCl_3$. Compound **15** was synthesized from the reaction of tris(thio)substituted nitrodiene **14** with m-chloroperbenzoic acid in $CHCl_3$.*

Keywords: Thiol; thioether; hexachlorobutadiene; sulfoxide; sulfone; mono(thio)- and di(thio)-substituted halodienes; N,S-thiosubstituted nitrodiene; piperazine; piperidine

It is known that mono(thio)- and polythiosubstituted dienes were obtained from the reaction of 2H-pentachlorobutadiene, hexachlorobutene, perchlorbutenin, perchlorobutadiene and 2-nitrodienes with thiolats.[1–9] In the past, we published that N,S-substituted dienes were obtained from the reaction of some mono(thio)substituted nitrodienes with amine.[10–22]

The aim of this study is to synthesize new S,N-substituted dienes and to oxidize some thioethers and determine their structure.

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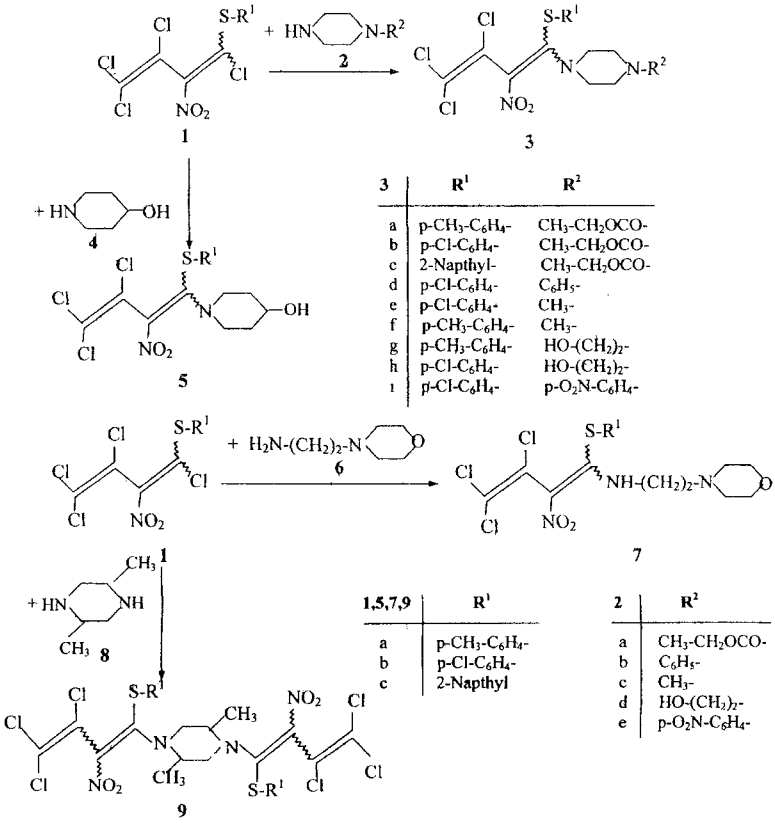
Piperazine compounds are important chemicals of clinical chemistry.[23] Also, piperazine compounds were used in gen-transfer.[24] The piperidinyl derivatives are known to show biological activity.[25]

R,S-substitute nitrodiene compound **1** gave N,S-substituted diene compounds **3a–i** with piperazine compounds. The IR-spectra of compounds **3a–c** showed a peak at $\nu = 1700\ cm^{-1}$ which is characteristic for carbonyl groups. The IR spectra of compounds **3g–h** showed a peak at $\nu = 3500\ cm^{-1}$ for the HO-group. Compound **1** gave compounds **5a–c** after reacting with 4-hydroxypiperidinyl. The IR-spectra of compounds **5a–c** showed a peak at $\nu = 3500\ cm^{-1}$ attributed to the HO-group. Compounds **7a** and **7b** were obtained from the reaction of compound **1a–b** with the amine compound **6**. The ^{1}H-NMR spectra of compounds **7a–b** showed multiplet signals at $\delta = 11$ ppm for the protons of the NH-groups. Compounds **9a–b** were obtained from the reaction of compounds **1a–b** with the piperazine compound **8**. The >NH-band was not observed in the ^{1}H-NMR spectra of compounds **9a–b** (Scheme 1). The structures



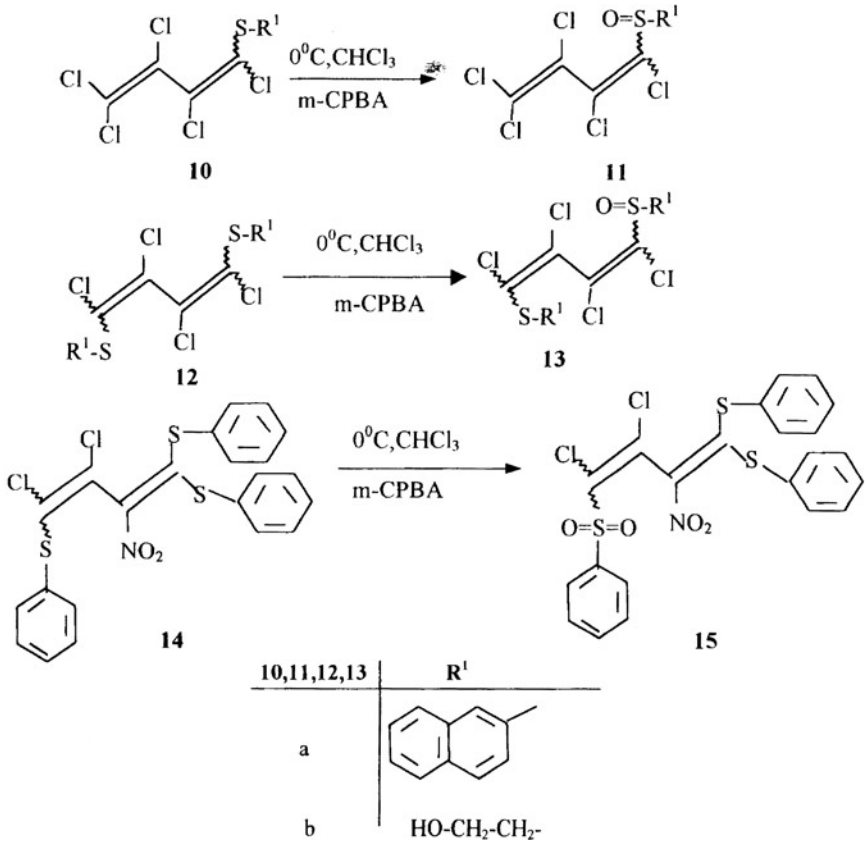
SCHEME 1

of the stable yellow compounds were determined by microanalysis and spectroscopic data.

The oxidation reaction of organo sulphur compounds is interesting for chemists because these compounds are important in the biochemistry and in industrial processes.[26] Previously, it has been stated that sulfone and sulfoxide compounds are formed in the oxidation reaction of some thioethers with diene groups.[27–30]

Compound **10a** was obtained from the reaction of hexachlorobutadiene with 2-napthylthiol in ethanol in the presence of NaOH. Compound **10a** is a new thioether.

11a and **11b** sulfoxide compounds were obtained from the reaction of compounds **10a** and **10b**[31] with m-chloroperbenzoic acid. Also, the sulfoxide compound **13b** was obtained from the oxidation reaction of compound **12b** (Scheme 2). The IR spectra of compounds **11a**, **11b**, and



SCHEME 2

13b showed a peak at $\nu = 1050\ cm^{-1}$ which is characteristic of the >SO- group. The sulfone compound was not formed when more m-CPBA was used for the oxidation. The reason is probably the steric and inductive effect of the R groups.

It was observed that the S atoms connecting to nitrovinyl group of mono(thio)-[-$C(NO_2)$=$CCl(SR)$] and di(thio)substituted dienes [-$C(NO_2)$=$C(SR)_2$] were not effected with m-chloroperbenzoic acid in $CHCl_3$.

The sulfone compound **15** was obtained from the reaction of the tris(thio)substituted diene compound **14** with m-CPBA. The IR-spectra of compound **15** showed peaks at $\nu = 1310$ and $1150\ cm^{-1}$ characteristic for the $>SO_2$ group. The sulphur atom connected to the fourth carbon atom was oxidized to the sulfone in the oxidation of compound **14**, whereas the sulphur atom connected to the nitrovinyl groups of compound **14** was not oxidized.

EXPERIMENTAL SECTION

- ^1H NMR: Bruker AC 200 L.
- IR: Shimadzu FTIR-8101.
- Microanalyses: Carlo Erba 1106 Elemental Analyser
- Melting Points: Büchi SMP 20.
- Products were isolated by column chromatography on SiO_2 (Fluka Kieselgel 60, particle size 63–200 μm).
- TLC plates silica 60 F_{254} (Merck, Darmstadt), detection with ultraviolet light (254 nm).

Preperation of N,S-Substituted Polyhalonitrodienes

General Procedure I

A mixture of 1,3,4,4-tetrachloro-mono(thio)-2-nitro-1,3-butadienes (**1a**, **1b**, **1c**) and amine derivatives in dry ether were stirred until completion of the reaction then chloroform was added. The organic layer was seperated washed with water (4 × 30 ml), and dried with $MgSO_4$. The solvent was evaporated and the residue was either crystallized or purified by column chromatography on silica gel.

Preperation of Sulfinyl and Sulfonyl Polyhalonitrodienes

General Procedure II

To 1.5 g (3.9 mmol) of 1,2,3,4,4-pentachloro-1-(2-napthylthio)-1,3-butadiene **10a** in 30 ml of chloroform were added 3-chloroperbenzoic acid in 15 ml of chloroform. The mixture was kept in the cold at 0°C for

24 h. After completion of the reaction chloroform was added to the mixture and washed with 2N $NaHCO_3$ and water (4×30 ml). The organic layer was separated and dried with Na_2SO_4. The solvent was eveporated and the residue was purified by column chromatography on silica gel. The same procedure was used for the oxidation of **10b**, **12b**, and **14**.

*3,4,4-Trichloro-1-(4-ethoxycarbonylpiperazino)-1-(p-methylphenylthio)-2-nitro-1,3-buta-diene (**3a**).* Compound **3a** was synthesized from **1a** (0.1 g, 0.279 mmol) and 1-ethoxycarbonylpiperazine (0.044 g, 0.279 mmol) according to the general procedure I. The mixture was purified by crystallization in methanol. **3b** to **3i** were synthesized in the same way.

3a: Yield: 0.098 g (%74). m.p. 169–170°C. $R_f = 0.375$ ($CHCl_3$/Petroleumether 2:1). -IR(KBr): $\nu = 2970, 3000\ cm^{-1}$ (C—H), 1600 (C=C), 1270, 1520 (C—NO_2). 1700 (C=O). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta =$ 7.2–7.4 ppm (m, 4H, Ar—H), 2.4 (s, 3H, S—CH_3), 3.1–4.1 (m, 10H, $5CH_2$), 1.2–1.6 (m, 3H, Alkyl—CH_3). $C_{18}H_{20}N_3Cl_3SO_4$ (480.801). calcd. C 44.96; H 4.19; N 8.74; S 6.67; found C 45.01; H 4.23; N 8.66; S 5.91.

3b: Yield: 0.117 g (%66). m.p. 151–152°C. $R_f = 0.7857$ (*$CHCl_3$/Petroleumether 2:1*). —IR(KBr): $\nu = 2970, 3000\ cm^{-1}$ (C—H), 1600 (C=C), 1290, 1510 (C—NO_2), 1700 (C=O). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta =$ 7.3–7.5 ppm (m, 4H, Ar—H), 1.2–1.6 (m, 3H, CH_3), 3.2–4.1 (m, 10H, $5CH_2$). $C_{17}H_{17}N_3Cl_4SO_4$ (501.219) calcd. C 40.73; H 3.42; N 8.38; S 6.39; found C 39.66; H 3.45; N 8.41; S 6.92.

3c: Yield: 0.060 g (%46). m.p. 153–154°C. $R_f = 0.733$ ($CHCl_3$/Petroleumether 2:1). —IR(KBr): $\upsilon = 2980, 3010\ cm^{-1}$ (C—H), 1570, 1600 (C=C), 1290, 1510 (C—NO_2), 1700 (C=O). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 7.3$–8.0 ppm (m, 7H, Ar—H), 1.2–1.5 (m, 3H, CH_3), 3.3–4.1 (m, 10H, $5CH_2$). $C_{21}H_{20}N_3Cl_4SO_4$ (516.834) calcd. C 48.80; H 3.90; N 8.13; S 6.20; found C 48.84; H 4.07; N 8.02; S 6.76.

3d: Yield: 0.095 g (%72). m.p. 146–147°C. $R_f = 0.5789$ ($CHCl_3$/Petroleumether 2:1). —IR(KBr): $\upsilon =$ 2990, 3005 cm^{-1} (C—H), 1590 (C=C), 1280, 1525 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 6.8$–7.5 ppm (m, 9H, Ar—H), 3.0–3.8 (m, 8H, $4CH_2$). $C_{20}H_{17}N_3Cl_4SO_2$ (505.253) calcd. C 47.54; H 3.39; N 8.31; S 6.35; found C 47.44; H 3.80; N 8.10; S 6.30.

3e: Yield: 0.085 g (%74). m.p. 179–180°C. $R_f = 0.25.64$ ($CHCl_3$/Petroleumether 2:1). —IR(KBr): $\upsilon =$ 2990, 3010 cm^{-1} (C—H), 1600 (C=C), 1290, 1540 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta =$ 7.3–7.5 ppm (m, 4H, Ar—H), 2.3 (s, 3H, CH_3), 3.5–3.7 (m, 8H, $4CH_2$). $C_{15}H_{15}N_3Cl_4SO_2$ (443.162) calcd. C 40.65; H 3.41; N 9.48; S 7.23; found C 40.57; H 3.36; N 9.28; S 7.18.

3f: Yield 0.065 g (%55). m.p. 164–165°C. $-R_f = 0.5625$ ($CHCl_3$/Petroleumether 2:1). −IR(KBr): $\upsilon =$ 2970, 3000 cm^{-1} (C−H), 1600 (C=C), 1295, 1530 (C−NO_2). $-^1$H-NMR ($CDCl_3$, TMS int.): $\delta =$ 7.2–7.4 ppm (m, 4H, Ar−H), 2.1–2.4 (m, 6H, $2CH_3$), 3.6 (m, 8H, $4CH_2$). $C_{16}H_{18}N_3Cl_3SO_2$ (422.763) calcd. C 45.45; H 4.29; N 9.93; S 7.58; found C 45.34; H 4.37; N 9.57; S 7.25.

3g: Yield: 0.216 g (%87). m.p. 149–150°C $R_f = 0.533$ (Ethylacetate). −IR(KBr): $\upsilon = 2980$, 3010 cm^{-1} (C−H), 1590 (C=C), 1290, 1525 (C−NO_2), 3500 (OH). $-^1$H-NMR ($CDCl_3$, TMS int.): $\delta = 7.2$–7.4 ppm (m, 4H, Ar−H), 2.4 (m, 3H, CH_3), 3.4–3.6 (m, 12H, $6CH_2$). $C_{17}H_{20}N_3Cl_3SO_3$ (452.79) calcd. C 45.09; H 4.45; N 9.28; S 7.08; found C 45.12; H 4.18; N 9.78; S 7.88.

3h: Yield: 0.096 g (%39). m.p. 126–127°C $R_f = 0.42$ (Ethylacetate). −IR(KBr): $\upsilon =$ 2970, 3005 cm^{-1} (C−H), 1570 (C=C), 1290, 1520 (C−NO_2), 3450 (OH). $-^1$H-NMR ($CDCl_3$, TMS int.): $\delta =$ 7.3 ppm (m, 4H, Ar−H), 3.4–3.6 (m, 8H, $4CH_2$), 2.3–2.5 (m, 4H, 2O−CH_2). $C_{16}H_{17}N_3Cl_4SO_3$ (473.207) calcd. C 40.61; H 3.62; N 8.87; S 6.67; found C 40.48; H 3.12; N 8.85; S 6.80.

3i: Yield: 0.09 g (%62). m.p. 194–196°C. $-R_f = 0.30$ (Ethylacetate). −IR(KBr): $\upsilon =$ 2970, 3005 cm^{-1} (C−H), 1600 (C=C), 1290, 1510 (C−NO_2). $-^1$H-NMR ($CDCl_3$, TMS int.): $\delta = 6.8$–8.2 ppm (m, 8H, Ar−H), 3.3–3.8 (m, 8H, $4CH_2$). $C_{20}H_{16}N_4Cl_4SO_4$ (550.252) calcd. C 43.65; H 2.93; N 10.18; S 5.82; found C 43.42; H 2.62; N 9.98; S 5.79.

*3,4,4-Trichloro-1-(4-hydroxypiperidino)-1-(p-methylphenylthio)-2-nitro-1,3-butadiene (**5a**).* Compound **5a** was synthesized from **1a** (0.1 g, 0.2792 mmol) and 4-piperidinol (0.028 g, 0.279 mmol) according to the general procedure I. The mixture was purified by crystallization in methanol. **5b** and **5c** were synthesized in the same way.

5a: Yield: 0.04 g (%34). m.p. 156–157°C. $R_f = 0.2916$ ($CHCl_3$). −IR(KBr): $\upsilon =$ 2970, 3000 cm^{-1} (C−H), 1600 (C=C), 1290, 1520 (C−NO_2), 3500 (OH). $-^1$H-NMR ($CDCl_3$, TMS int.): $\delta =$ 7.2–7.4 ppm (m, 4H, Ar−H), 2.4 (s, 3H, CH_3), 3.5–3.9 (m, 8H, $4CH_2$), 1.3–1.7 (m, 1H, OH). $C_{16}H_{17}N_2Cl_3SO_3$ (423.747) calcd. C 45.35; H 4.04; N 6.61; S 7.56; found C 45.35; H 3.98; N 6.85; S 7.46.

5b: Yield: 0.06 g (%53). m.p. 188–189°C. $R_f = 0.3333$ (CH_3CI_3). −IR(KBr): $\upsilon =$ 2990, 3000 cm^{-1} (C−H), 1595 (C=C), 1290, 1520 (C−NO_2), 3500 (OH). ^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 7.0$–8.0 ppm (m, 4H, Ar−H), 3.0–4.5 (m, 8H, $4CH_2$), 1.8–2.8 (m, 1H, OH). $C_{15}H_{14}N_2SO_3CI_4$ (444.166) calcd. C 40.56; H 3.17; N 6.30; S 7.21; found C 40.52; H 3.28; N 6.26; S 7.55.

5c: Yield: 0.082 g (%71). m.p. 177–178°C. $R_f = 0.28.57$ (Ethylacetate/Pet.ether 1:1). −IR(KBr): $\upsilon =$ 2970, 3000 cm^{-1} (C−H), 1600 (C=C),

1290, 1540 (C—NO_2), 3490 (OH). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 7.3$–7.8 ppm (m, 7H, Ar—H), 3.4–4.0 (m, 8H, $4CH_2$), 1.3–1.8 (m, 1H, OH). $C_{19}H_{17}N_2Cl_3SO_3$ (459.781) calcd. C 49.63; H 3.72; N 6.09; S 6.97; found C 48.97; H 3.98; N 5.85; S 6.98.

*3,4,4-Trichloro-1-(4-(2-aminoethyl)morpholino)-1-(p-methylphenylthio)-2-Nitro-1,3-butadiene (**7a**).* Compound **7a** was synthesized from **1a** (0.1 g, 0.2792 mmol) and 4-(2-aminoethyl)morpholin (0.1 g, 0.2792 mmol) according to the general procedure I. The mixture was purified by crystallization in methal. **7b** was synthesized in the same way.

7a: Yield: 0.06 g (%48). m.p. 126–128°C $R_f = 0.59$ ($CHCl_3$). —IR(KBr): $\upsilon = 2970$, 3005 cm^{-1} (C—H), 1575, 1600 (C—C), 1230, 1500 (C—NO_2), 3500 (NH). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 7.2$ ppm (m, 4H, Ar—H), 2.4 (m, 3H, CH_3), 3.3–3.7 (m, 8H, $4CH_2$), 1.3–1.6 (m, 4H, $2CH_2$), 11 (s, 1H, NH). $C_{17}H_{20}N_3Cl_3SO_3$ (452.79) calcd. C 45.09; H 4.45; N 5.28; S 7.08; found C 45.20; H 4.09; N 5.93; S 6.98.

7b: Yield: 0.021 g (%17). m.p. 151–152°C $R_f = 0.591$ ($CHCl_3$). —IR(KBr): $\upsilon = 3000$ cm^{-1} (C—H), 1600 (C=C), 1290, 1520 (C—NO_2), 3490 (NH). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 6.0$–7.5 ppm (m, 4H, Ar—H), 3.0–4.3 (m, 12H, $6CH_2$), 11 (m, 1H, NH). $C_{16}H_{17}N_3Cl_4SO_3$ (473.207) calcd. C 40.61; H 3.62; N 8.87; S 6.77; found C 41. 13; H 3.65; N 8.55; S 6.55.

*N,N-Bis(3,4,4-trichloro-1-(p-methylphenylthio)-2-nitro-1,3-butadienyl)-2,5-dimethylpiperazine (**9a**).* Compound **9a** was synthesized from **1a** (0.1 g, 0.2792 mmol) and 2,5-dimethylpiperazine (0.030 g, 0.2792 mmol) according to the general procedure I. The mixture was purified by crystallization in methanol. **9b** was synthesized in the same way.

9a: Yield: 0.05 g (%41). m.p. 230–231°C. $R_f = 0.66$ (Ethylacetate). —IR(KBr): $\upsilon = 2990$, 3010 cm^{-1} (C—H), 1590, 1610 (C=C), 1290, 1520 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 7.3$ ppm (m, 8H, Ar—H), 1.3–1.6 (m, 12H, $4CH_3$), 2.5 (m, 4H, $2CH_2$). $C_{27}H_{26}N_4Cl_6S_2O_4$ (747.38) calcd. C 43.39; H 3.50: N 7.49; found C 43.10; H 3.45; N 7.32.

9b: Yield: 0.03 g (%25). m.p. 138–139°C. $R_f = 0.72$ (Ethylacetate). —IR(KBr): $\upsilon = 3000$ cm^{-1} (C—H), 1570, 1620 (C=C), 1295, 1510 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 6.9$–7.2 ppm (m, 8H, Ar—H), 0.8–1.8 (m, 6H, $2CH_3$), 2.5–3.8 (m, 4H, $2CH_2$), 4.5–4.8 (m, 2H, 2CH). $C_{26}H_{20}N_4Cl_8S_2O_4$ (800.226) calcd. C 42.21; H 3.74; N 7.01; found C 42.10; H 3.09; N 7.59.

*1,2,3,4,4-pentachloro-1-(2-napthylthio)-1,3-butadiene (**10a**).* 2 g (7.66 mmol) of 1,1,2,3,4,4-hexachloro-1,3-butadiene in 10 ml of ethanol and 2.457 g (7.66 mmol) of 2-napthylthiol in 10 ml of ethanol were

mixed and NaOH (in 8 ml of water) was added at room temperature. The mixture was strirred for 24 h. Chloroform was added to the reaction mixture. The organic layer was separated and washed with water (4×30) and dried with $MgSO_4$. The solvent was eveporated and the residue was purified by column chromatography with petroleum ether as eluent.

10a: Yield: 0.867 g (% 30). Oil. $R_f = 0.565$ (Petroleumether). —IR(film): $\upsilon = cm^{-1}$ (C—H), 1540, 1600 (C=C). UV(chloroform) $\lambda_{maks} = 257$ nm. $C_{14}H_7Cl_5S$ (384.541) calcd. C 43.72; H 1.83; found C 43.35; H 1.72. —MS: 384.0.

*1,2,3,4,4-pentachloro-1-(2-napthylsulfinyl)-1,3-butadiene (**11a**).* Compound **11a** synthesized from 1,2,3,4,4-pentachloro-1-(2-napthylthio)-1,3-butadiene **10a** (1.5 g, 3.9 mmol) and 3-chloroperbenzoic acid (1.345 g, 3.9 mmol) according to the general Procedure II. The mixture was purified by column chromatography with $CHCl_3$/Petroleumether 1:1 as eluent. **11b** and **13b** were synthesized in the same way.

11a: Yield 0.848 g (%54). Oil. $R_f = 0.558$ $CHCl_3$/Petroleumether 1:1 —IR(film): 3010 cm^{-1}(C—H), 1500, 1600 (C=C), 1050, 1100 (S=O). UV (chloroform) $\lambda_{maks} = 249$ nm. $C_{14}H_7Cl_5SO$ (400.54) calcd. C 41.98; H 1.76; found C 41.70; H 1.94.

11b: 0.698 g (%44). Oil. $R_f = 0.62$ Ethylacetate. IR (film): 2990 cm^{-1} (C—H), 1560, 1610 (C=C), 3490 cm^{-1} (HO—), 1050, 1150 (S=O). $C_6H_5Cl_5SO_2$ (318.435) calcd. C 22.63; H 1.58; found C 23.02; H 1.91.

13b: 0.4 g (%38). Oil. $R_f = 0.529$ Ethylacetate. IR (film): 2990 cm^{-1} (C—H), 1560, 1610 (C=C), 3490 cm^{-1} (HO—), 1050, 1150 (S=O). $C_2H_5Cl_5SO_2$ (360.107) calcd. C 26.68; H 2.79; found C 27.07; H 3.04. -MS: 359.

*3,4-Dichloro-4-(phenylsulfonyl)-bis(phenylthio)-2-nitro-1,3-butadiene (**15**).* Compound **15** synthesized from tris(phenylthio)butadiene **14** (0.2 g, 0.40 mmol) and 3-chloroperbenzoic acid (0.009 g, 0.80 mmol) according to the general procedure II. The mixture was purified by column chromatography with $CCl_4/CHCl_3$ 2:1 as eluent.

15: Yield: 0.13 g (%62). m.p.: 144–145°C. $R_f = 0.530$ CH_2Cl_2/Hexane 1:1. —IR(KBr): $\upsilon = 3065$ cm^{-1} (Ar—H), 1590, 1620 (C=C), 1290, 1525 (C—NO_2), 1310, 1150 (—SO_2). $C_{22}H_{15}Cl_2S_3O_4N$ (524.468) calc. C 50.38; H 2.86; N 2.67; found C 50.21; H 2.92; N 2.56.

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