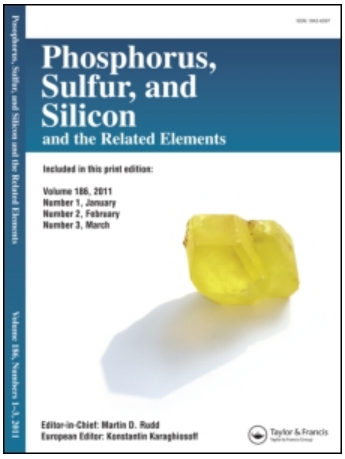

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New N,S-Substituted Dienes from the Reactions of Some Aliphatic Mono(thio)substituted Nitrodienes with Aromatic Primary Amines and Cyclic Amines

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NEW N,S-SUBSTITUTED DIENES FROM THE REACTIONS OF SOME ALIPHATIC MONO(THIO)-SUBSTITUTED NITRODIENES WITH AROMATIC PRIMARY AMINES AND CYCLIC AMINES

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Reaction of 2-nitropentachlorobutadiene with thiols and amines gave new N,S- and S,S-substituted nitrodiene compounds is discussed.

Keywords: 2-Nitropentachlorobutadiene; amine; morpholine; N,S-substituted dienes; p-diaminobenzene; piperazine; piperidine; thioether; thiols

It has been reported previously that some mono-, bis-, tris-, tetrakis, and pentakis(thio)substituted diene compounds were prepared from pentachloro- and hexachloro-1,3-dienes.[1–6] Moreover, it is known that the synthesis of some mono-, bis-, tris- and tetrakis(thio)substituted nitrodiene compounds and N,N-, N,S-substituted nitrodiene compounds have been reported previously.[7–14]

Some alkyl(thio)substituted derivatives of hexachlorobutadienes and the derivatives containing a phosphorus atom of hexachlorobutadienes exhibit biological activity.[15–17] The aim of this work was to synthesize the novel S- and S,N-substituted diene compounds developing our previous studies and to characterize the structures of these compounds.

RESULTS AND DISCUSSION

It is known that arylsubstituted piperazine compounds are important for clinical chemistry and some piperazine compounds were used in

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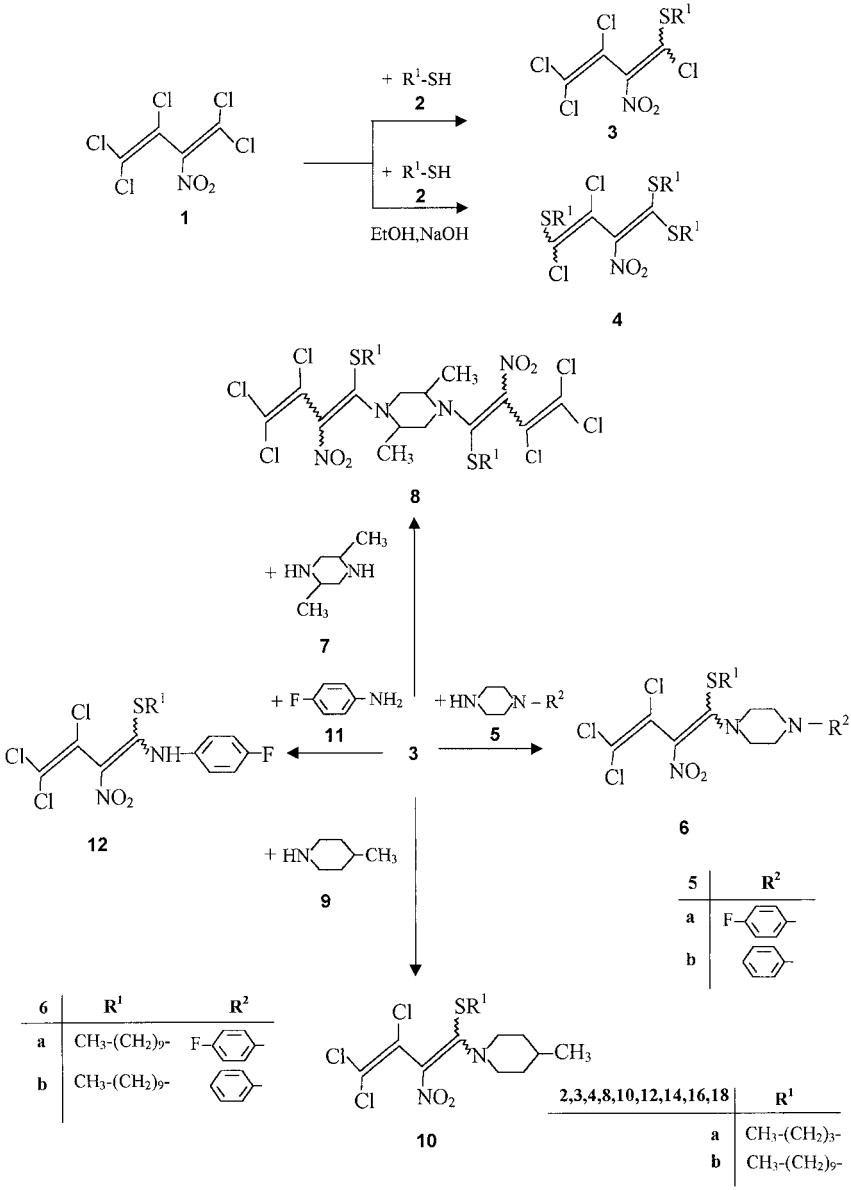
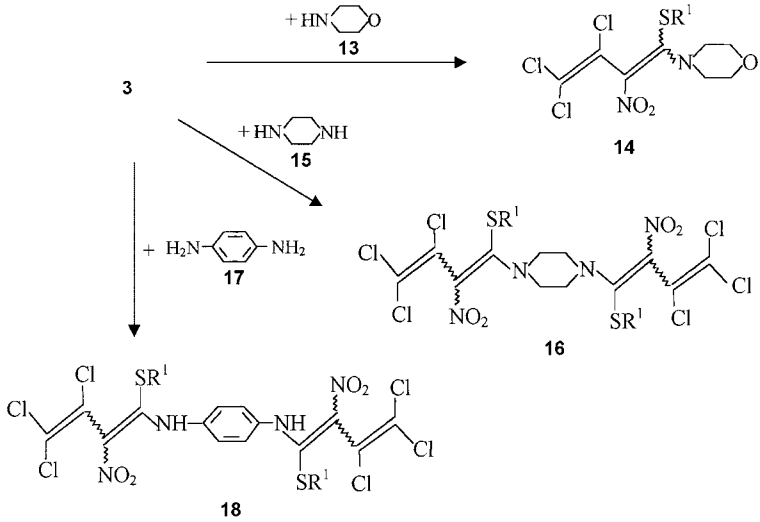
gen transfer reactions. The piperidinyl derivatives show an excellent biological activity.[17–19]

Compound **3** was obtained when compound **1** was stirred for a long time with CH_3-$(CH_2)_9$-SH **2b** (Scheme 1).



SCHEME 1

Compound **1** gave tris(thio)substituted diene **4** with CH_3- $(CH_2)_9$-SH in EtOH in the presence of NaOH. Compound **3b** has been known[20] and compound **4b** is an unknown compound. The compounds **6a** and **6b** were obtained from the reaction of compound **3b** with the derivatives of piperazine. Compound **3b** gave the dibutadienyl piperazine compound with compound **7**. S,N-substituted diene compound **12** was obtained from the reaction of compound **3b** with an aromatic amine **11**. Compound **10** was obtained from the reaction of compound **3b** with the piperidine compound **9**. Compounds **3a** and **3b** gave **14a** and **14b** with morpholine **13**. Compound **3a** gave dibutadienyl piperazine **16a** with piperazine **15**. N,N′-dibutadienyl substituted compound **18a** was obtained from the reaction of compound **3a** with an aromatic diamine **17** (Scheme 2).



SCHEME 2

^{1}H-NMR spectra of compounds **12** and **18** gave a characteristic singlet at $\delta \cong 12$ ppm for the protons of the NH-group. Compounds **3** and **4** are probably formed by the addition-elimination reaction. Also N,S-substituted dienes obtained by compound **3** are formed by the same reaction mechanism.

These new compounds are N,S-substituted- and S,S-substituted nitrodiene compounds obtained with good yields. These new compounds are yellow and stable. The structure of these products were characterized by microanalysis and spectroscopic data.

EXPERIMENTAL SECTION

^{1}H-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 F254 (Merck, Darmstadt), detection with ultraviolet light (254 nm).

Preparation of S-Substituted Polyhalonitrodienes

General Procedure I

Equimolar amounts of 2-nitro-1,1,3,4,4-Pentachloro-1,3-butadiene **1** and thiols **2a** and **2b** were stirred for 36 h at room temperature 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 over $CaCl_2$ or $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel.

Preparation of S,S-Substituted Polyhalonitrodienes

General Procedure II

To a mixture of **2b** and **1** in 30 ml of ethanol 2 g of NaOH (in 10 ml water) was added at room temperature. The mixture was stirred for 1 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 over $CaCl_2$ or $MgSO_4$. The solvent was evaporated and residue was purified by column chromatography on silica gel.

*1,1,4-Tris(decylthio)-2-nitro-3,4-dichloro-1,3-butadiene (**4b**).* Compound **4b** was synthesized from **1** (2 g, 7.37 mmol) and n-decylmercaptan **2b** (2.57 g, 7.37 mmol) according to the general procedure II. Purification (CC) gave 3.8 g (75%) of **4b**. $R_f = 0.481$ (Petroleum ether). Yellow oil. —IR (film): ν = 2800, 2900 cm^{-1} (C—H), 1600 (C=C), 1290, 1540 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.7–1.0 ppm (m, 9H, 3 CH_3), 1.1–1.8 (m, 48H, 24 CH_2), 2.5–3.2 (m, 6H, 3 S—CH_2), $C_{34}H_{63}S_3NCl_2O_2$ (684.987), MS m/z 684.2.

Preparation of N,S-Substituted Polyhalonitrodienes

General Procedure III

Equimolar amounts of S-substituted polyhalonitrodienes (**3a** and **3b**) and amine derivatives were stirred in dichloromethane 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 over $CaCl_2$ or $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel.

*N-[1-(Decylthio)-2-nitro-3,4,4-trichloro-1,3-butadienyl)]-N′-[4-fluorophenyl]-piperazine (**6a**).* Synthesized from **3b** (0.2 g, 0.48 mmol) and 4-fluorophenylpiperazine **5a** (0.088 g, 0.48 mmol) according to the general procedure III. Purification (CC) gave 0.201 g (74%) of **6a**. R_f = 0.863 ($CHCl_3$). Yellow oil. —IR (film): ν = 2800, 2950, 3050 cm^{-1} (C—H), 1600 (C=C), 1280 1520 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.7–1.0 ppm (m, 3H, CH_3), 1.1–1.5 (m, 16H, $(CH_2)_8$), 1.6–1.8 (m, 2H, S—CH_2), 2.6–4.4 (m, 8H, 4 CH_2), 6.8–7.7 (m, 4H, Ar—H). $C_{24}H_{33}SN_3Cl_3FO_2$ (552.971), MS m/z 553.

*N-[1-(Decylthio)-2-nitro-3,4,4-trichloro-1,3-butadienyl)]-N′-[phenyl]-piperazine (**6b**).* Synthesized from **3b** (0.2 g, 0.48 mmol) and phenylpiperazine **5b** (0.079 g, 0.48 mmol) according to the general procedure III. Purification (CC) gave 0.175 g (67%) of **6b**. R_f = 0.617 ($CHCl_3$). Yellow oil. —IR (film): ν = 2800, 2900, 3050 cm^{-1} (C—H), 1600 (C=C), 1280, 1550 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.8–1.1 ppm (m, 3H, CH_3), 1.2–1.5 (m, 16H, $(CH_2)_8$), 1.6–1.9 (m, 2H, S—CH_2), 2.8–4.2 (m, 8H, 4 CH_2), 6.7–7.5 (m, 5H, Ar—H). $C_{24}H_{35}SN_3Cl_3O_2$ (534.981), MS m/z 535.

*N,N′-[1-(Decylthio)-2-nitro-3,4,4-trichloro-1,3-butadienyl)]-2,5-dimethylpiperazine (**8b**).* Synthesized from **3b** (0.2 g, 0.48 mmol) and 2,5-dimethylpiperazine **7** (0.056 g, 0.48 mmol) according to the General procedure III. Crystallization from methanol gave 0.19 g (45%) of **8b**. R_f = 0.652 ($CHCl_3$). —m.p. 163–164°C. —IR (KBr): ν = 2800, 2950 cm^{-1} (C—H), 1590 (C=C), 1280, 1520 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.8–1.0 ppm (m, 12H, 4 CH_3), 1.1–1.8 (m, 18H, $(CH_2)_9$), 2.8–3.4 (m, 4H, 2 CH_2), 3.8–5.0 (m, 2H, 2 CH). $C_{34}H_{54}S_2N_4Cl_6O_4$ (859.682), MS m/z 858.1.

*1-(Decylthio)-2-nitro-3,4,4-trichloro-1-(4-methylpiperidino)-1,3-butadiene (**10b**).* Synthesized from **3b** (0.2 g, 0.48 mmol) and 4-methylpiperidine **9** (0.048 g, 0.48 mmol) according to the general procedure III. Purification (CC) gave 0.17 g (74%) of **10b**. R_f = 0.8 ($CHCl_3$). Yellow oil. —IR (film): ν = 2800, 2900 cm^{-1} (C—H), 1590 (C=C), 1280, 1540 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.8–1.0 ppm (m, 6H, 2 CH_3), 1.2–1.6 (m, 16H, $(CH_2)_8$), 1.6–2.0 (m, 2H, S—CH_2), 2.8–4.1 (m, 9H, piperidine-H). $C_{20}H_{33}SN_2Cl_3O_2$ (471.971), MS m/z 472.

*1-(Decylthio)-2-nitro-3,4,4-trichloro-1-(4-fluorophenylamino)-1,3-butadiene (**12b**).* Synthesized from **3b** (0.2 g, 0.48 mmol) and 4-fluoro

aniline **11** (0.054 g, 0.48 mmol) according to the general procedure III. Purification (CC) gave 0.167 g (70%) of **12b**. R_f = 0.434 ($CHCl_3$/Petroleum ether 1:1). Yellow oil. —IR (film): ν = 2850, 2900 cm^{-1} (C—H), 1610 (C=C), 1240, 1550 (C—NO_2), 3300 (N—H). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.8–1.0 ppm (m, 3H, CH_3), 1.1–1.7 (m, 16H, $(CH_2)_8$), 2.3–2.5 (m, 2H, S—CH_2), 6.9–7.5 (m, 4H, Ar—H), 11.9 (s, 1H, NH). $C_{20}H_{26}SN_2Cl_3FO_2$ (483.864), MS m/z 484.1.

*1-(Buthylthio)-2-nitro-3,4,4-trichloro-1-(N-morpholino)-1,3-butadiene (**14a**).* Synthesized from **3a** (0.2 g, 0.61 mmol) and morpholine **13** (0.053 g, 0.61 mmol) according to the general procedure III. Crystallization from methanol gave 0.145 g (63%) of **14a**. —m.p. 92–93°C. -IR (KBr): ν = 2860, 2900, 2960 cm^{-1} (C—H), 1540, 1600 (C=C), 1290, 1325, 1450 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.8–1.2 ppm (m, 3H, CH_3), 1.3–1.9 (m, 4H, 2 CH_2), 2.8–3.2 (m, 2H, S—CH_2), 3.4–4.1 (m, 8H, $(CH_2)_2$-N-$(CH_2)_2$).

*1-(Decylthio)-2-nitro-3,4,4-trichloro-1-(N-morpholino)-1,3-butadiene (**14b**).* Synthesized from **3b** (0.2 g, 0.48 mmol) and morpholine **13** (0.0425 g, 0.48 mmol) according to the general procedure III. Crystallization from methanol gave 0.123 g (55%) of **14b**. R_f = 0.541 ($CHCl_3$). —m.p. 75–76°C. —IR (KBr): ν = 2850, 2950 cm^{-1} (C—H), 1590 (C=C), 1280, 1530 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.8–1.0 ppm (m, 3H, CH_3), 1.2–1.8 (m, 16H, $(CH_2)_8$), 2.8–3.1 (m, 2H, S—CH_2), 3.4–3.9 (m, 8H, 4 $(CH_2)_2$-N-$(CH_2)_2$). $C_{18}H_{29}SN_2Cl_3O_3$ (459.866), MS m/z 460.

*N,N′-[1-(Buthylthio)-2-nitro-3,4,4-trichloro-1,3-butadienyl)]-piperazine (**16a**).* Synthesized from **3a** (1 g, 3.07 mmol) and piperazine **15** (0.265 g, 3.07 mmol) according to the general procedure III. Crystallization from methanol gave 1.99 g (98%) of **16a**. —m.p. 186–187°C. —IR (KBr): ν = 2853, 2923, 2960 cm^{-1} (C—H), 1560, 1575 (C=C), 1270, 1280, 1510 (C—NO_2). —^{1}H-NMR ($CDCl_3$, TMS int.): 0.7–1.1 ppm (m, 3H, CH_3), 1.1–1.9 (m, 4H, 2 CH_2), 2.7–3.2 (m, 2H, CH_2), 3.2–4.2 (m, 8H, 4 CH_2).

*N,N′-[1-(Buthylthio)-2-nitro-3,4,4-trichloro-1,3-butadienyl)]-p-phenylenediamine (**18a**).* Synthesized from **3a** (0.5 g, 1.54 mmol) and p-phenylenediamine **17** (0.166 g, 1.54 mmol) according to the general procedure III. Crystallization from methanol gave 0.97 g (92%) of **18a**. —m.p. 202–203°C. —IR (KBr); ν = 2850, 2900, 2963 cm^{-1} (C—H), 1610, 1650 (C=C), 1300, 1550 (C—NO_2). —^{1}H NMR ($CDCl_3$, TMS int.): 0.7–1.1 ppm (m, 3H, CH_3), 1.1–1.8 (m, 4H, 2 CH_2), 2.2–2.7 (m, 2H, CH_2), 7.1–7.7 (m, 4H, Ar—H), 12.0 (s, 2H, 2 NH).

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