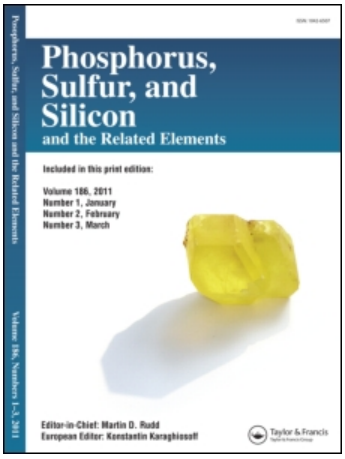

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NOVEL N,S-SUBSTITUTED DIENES BY THE REACTION OF 2-NITROTHIOSUBSTITUTED HALODIENES AND PRIMARY AMINES

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NOVEL N,S-SUBSTITUTED DIENES BY THE REACTION OF 2-NITROTHIOSUBSTITUTED HALODIENES AND PRIMARY AMINES

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*Mono(thio)substituted **1a–c** gave compounds **3a–c** and **5a** with o-toluidin (**2**) and m-toluidin (**4**) in ether. Compounds **9a–c** and **11a,b** were obtained from the reaction of compounds **1a–c** with p-fluorophenylamine (**8**) and p-fluorobenzylamine (**10**). Compounds **7a** and **15c** were obtained from the reaction of **1a** and **1c** with p-phenylendiamine (**6**) and o-phenylendiamine (**14**). Compound **13c** was synthesized from the reaction of compound **1c** with benzidine (**2**).*

Keywords: Amines; mono(thio)-substituted halodienes; N,S-thiosubstituted nitrodiene; thioether; thiol

Previously we described the synthesis of N,S-substituted diene compounds by the reaction of some monothiosubstituted dienes with amines.[1–10]

In continuation of this study, we synthesized novel N,S-substituted nitrodiene compounds and determined their structures by various techniques.

Mono(thio)substituted dienes **1a–c** gave compounds **3a–c** with o-toluidin (**2**). Compounds **5a**, **7a** and **9a–c** were obtained from the reaction of mono(thio)substituted dienes with m-toluidin (**4**), p-phenylendiamine (**6**) and p-fluoroanilin (**8**) (Scheme 1).

Reactant **1c** gave **13c** and **15c** with benzidine (**12**) and o-phenylendiamine (**14**), respectively, and compounds **1a**,**b** gave **11a**,**b** with p-fluorobenzylamine (**10**).

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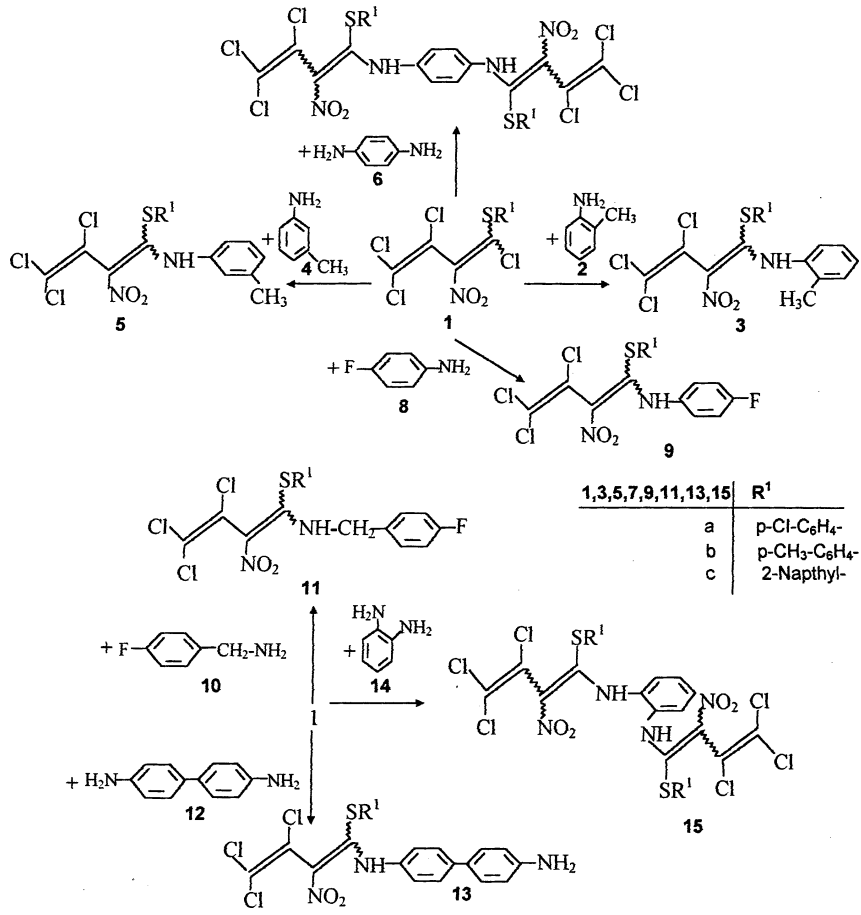

SCHEME 1

Compounds **3a–c**, **5a**, **9a–c**, **11a**,**b**, and **13c** are novel N,S-substituted 2-nitrodiene compounds. Compounds **7a** and **15c** are dibutadienyl-substituted phenylendiamine compounds with interesting structures. Also, compound **1** is a reactive 2-nitrodiene derivative. The Cl atom connected to a nitrovinyl group is exchanged simply by N- or S-nücleophiles.

Both monothiosubstituted nitrodienes and N,S-substituted dienes are formed by an addition–elimination mechanism. These compounds are novel and stable compounds. The structure of these compounds was determined by microanalysis and spectroscopic data. The ^{1}H NMR spectra of **3a–c**, **9a–c**, **5a**, **7a**, **11a**,**b**, **13c**, and **15c** showed signals at $\delta = 11.7$–12.8 ppm for the HN- groups, and the ^{1}H NMR spectra of

compound **13c** showed signals at $\delta = 1.2$–1.8 ppm characteristic for the H_2N-group.

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).
- Thin layer chromatography (TLC) plates silica 60 F_{254} (Merck, Darmstadt).

Preperation of N,S-Substituted Polyhalonitrodienes: General Procedure

Appropriate amounts 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 to the reaction mixture. 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.

3,4,4-Trichloro-1-(p-chlorophenylthio)-1-(2-methylphenylamino)-2-nitro-1,3-butadiene (3a)

Compound **3a** was synthesized from **1a** (0.1 g, 0.279 mmol) and o-toluidin (0.044 g, 0.279 mmol) according to the general procedure. The mixture was purified by crystallization in methanol. All products were synthesized the same way.

3a: yield, 0.071 g (28%), m.p. 177–178°C. $R_f = 0.6538$ (CH_2Cl_2/Hexan 1:1). IR (KBr): $\nu = 3010$, 3020 cm^{-1} (Ar—H), 1600 (C=C), 1250, 1520 (C—NO_2), 3500 (NH). ^1H NMR ($CDCl_3$, TMS int.): $\delta = 7.2$–7.4 ppm (m, 8H, Ar—H), 2.4 (s, 3H, CH_3), 12.6 (s, 1H, >NH). $C_{17}H_{12}N_2Cl_4SO_2$ (450.174) calcd.: C, 45.36; H, 2.68; N, 6.22; S, 7.12. Found: C, 45.14; H, 2.48; N, 5.98; S, 7.19.

3,4,4-Trichloro-1-(2-methylphenylamino)-1-(p-methylphenylthio)-2-nitro-1,3-butadiene (3b)

3b: yield, 0.014 g (12%), m.p. 152–153°C. $R_f = 0.6250$ (CH_2Cl_2/Hexan 1:1). IR (KBr): $\nu = 2980$, 3050 cm^{-1} (C—H), 1610 (C=C), 1290, 1530

(C—NO_2), 3480 (NH). ^{1}H NMR ($CDCl_3$, TMS int.): δ = 6.9–7.2 ppm (m, 8H, Ar—H), 1.9–2.8 (m, 6H, $2CH_3$), 12.6 (m, 1H, >NH). $C_{18}H_{15}N_2Cl_3SO_2$ (429.756) calcd.: C, 50.30; H, 3.51; N, 7.44; S, 7.46. Found: C, 49.66; H, 3.05; N, 7.42; S, 7.37.

3,4,4-Trichloro-1-(2-methylphenylamino)-1-(2-napthylthio)-2-nitro-1,3-butadiene (3c)

3c: yield, 0.014 g (8%), m.p. 133–134°C. R_f = 0.2924 (CH_2Cl_2/Hexan 1:1). IR (KBr): ν = 3100 cm^{-1} (C—H), 1620 (C=C), 1290, 1525 (C—NO_2), 3480 (NH). ^{1}H NMR ($CDCl_3$, TMS int.): δ = 7.2–7.8 ppm (m, 11H, Ar—H), 2.3 (m, 3H, CH_3), 12.8 (m, 1H, >NH). $C_{21}H_{15}N_2Cl_3SO_2$ (465.789) calcd.: C, 54.15; H, 3.24; N, 6.01; S, 6.88. Found: C, 54.35; H, 3.66; N, 6.06; S, 6.72.

3,4,4-Trichloro-1-(p-chlorophenylthio)-1-(3-methylphenylamino)-2-nitro-1,3-butadiene (5a)

5a: yield, 0.064 g (51%), m.p. 193–194°C. R_f = 0.650 (ethylacetat/petroleumether 1:2). IR (KBr): ν = 3020, 3100 cm^{-1} (C—H), 1580, 1600 (C=C), 1280, 1525 (C—NO_2). ^{1}H NMR ($CDCl_3$, TMS int.). δ = 6.9–7.2 ppm (m, 8H, Ar—H), 2.3 (s, 3H, CH_3), 12.6 (s, 1H, >NH). $C_{17}H_{12}N_2Cl_4SO_2$ (450.174) calcd.: C, 45.36; H, 2.68; N, 6.22; S, 7.12. Found: C, 45.44; H, 2.92; N, 6.18; S, 7.23.

N,N-Bis(3,4,4-trichloro-1-(p-chlorophenylthio)-2-nitro-1,3-butadienyl)-o-phenylen-diamine (7a)

7a: yield, 0.029 g (17%), m.p. 173–174°C. R_f = 0.3846 (CH_2Cl_2). IR (KBr): ν = 2980, 3010 cm^{-1} (C—H), 1590, 1600 (C=C), 1300, 1540 (C—NO_2), 3490 (NH). ^{1}H NMR ($CDCl_3$, TMS int.): δ = 6.8–7.5 ppm (m, 12H, Ar—H), 11.8 (s, 1H, >NH). $C_{26}H_{14}N_4Cl_8S_2O_4$ (794.169) calcd.: C, 39.32; H, 1.77; N, 7.05; S, 7.10. Found: C, 40.14; H, 1.89; N, 7.23; S, 7.18.

3,4,4-Trichloro-1-(p-chlorophenylthio)-1-(4-fluorophenylamino)-2-nitro-1,3-butadiene (9a)

9a: yield, 0.070 g (55%), m.p. 175–176°C. R_f = 0.560 ($CHCl_3$/petroleumether 1:1). IR (KBr): ν = 2970, 3020 cm^{-1} (C—H), 1580, 1620 (C=C), 1295, 1530 (C—NO_2), 3500 (NH). ^{1}H NMR ($CDCl_3$, TMS int.): δ = 7.2–7.4 ppm (m, 8H, Ar—H), 11.7 (s, 1H, >NH). $C_{16}H_9N_2Cl_4SFO_2$ (454.136) calcd.: C, 42.32; H, 1.99; N, 6.16; S, 7.06. Found: C, 42.43; H, 2.24; N, 6.26; S, 7.18.

3,4,4-Trichloro-1-(4-fluorophenylamino)-1-(p-methylphenylthio)-2-nitro-1,3-butadiene (9b)

9b: yield, 0.060 g (51%), m.p. 175–176°C. R_f = 0.611 ($CHCl_3$/petroleumether 1:1). IR (KBr): ν = 2970, 3010 cm^{-1} (C—H), 1590, 1610 (C=C), 1270, 1525 (C—NO_2), 3510 (NH). ^1H NMR ($CDCl_3$, TMS int.): δ = 6.8–7.4 ppm (m, 8H, Ar—H), 2.4 (m, 3H, CH_3), 11.8 (s, 1H, >NH). $C_{17}H_{12}N_2Cl_3SFO_2$ (433.719) calcd.: C, 47.07; H, 2.78; N, 6.45; S, 7.39. Found: C, 47.26; H, 3.17; N, 6.17; S, 7.88.

3,4,4-Trichloro-1-(4-fluorophenylamino)-1-(2-napthylthio)-2-nitro-1,3-butadiene (9c)

9c: yield, 0.061 g (52%), m.p. 147–148°C. R_f = 0.42 ($CHCl_3$). IR (KBr): ν = 2970, 3010 cm^{-1} (C—H), 1570, 1600 (C=C), 1290, 1520 (C—NO_2), 3500 (NH). ^1H NMR ($CDCl_3$, TMS int.): δ = 6.9–7.3 ppm (m, 10H, Ar—H), 11.8–12.4 (m, 1H, >NH). $C_{20}H_{12}N_2Cl_3SFO_2$ (469.751) calcd.: C, 51.13; H, 2.57; N, 5.96; S, 6.82. Found: C, 51.49; H, 2.79; N, 6.53; S, 6.80.

3,4,4-Trichloro-1-(p-chlorophenylthio)-1-(4-fluorobenzylamino)-2-nitro-1,3-butadiene (11a)

11a: yield, 0.10 g (81%), m.p. 177–178°C. R_f = 0.72 (ethylacetate/petroleumether 1:1). IR (KBr): ν = 2970, 3010 cm^{-1} (C—H), 1570, 1600 (C=C), 1290, 1510 (C—NO_2). ^1H NMR ($CDCl_3$, TMS int.): δ = 7.2–7.8 ppm (m, 8H, Ar—H), 4.5–4.8 (m, 2H, CH_2), 11.8 (s, 1H, >NH). $C_{17}H_{11}N_2Cl_4SFO_2$ (550.252) calcd.: C, 43.62; H, 2.36; N, 5.98; S, 6.84. Found; C, 44.15; H, 2.33, N, 5.96; S, 6.79.

3,4,4-Trichloro-1-(1-(4-fluorobenzylamino)-1-(p-methylphenylthio)-2-nitro-1,3-butadiene (11b)

11b: yield, 0.105 g (84%), m.p. 178–179°C. R_f = 0.56 ($CHCl_3$/petroleumether 1:1). IR (KBr): ν = 2980, 3000 cm^{-1} (C—H), 1560, 1600 (C=C), 1290, 1520 (C—NO_2), 3490 (NH). ^1H NMR ($CDCl_3$, TMS int.): δ = 7.2–7.4 ppm (m, 8H, Ar—H), 2.4 (s, 3H, CH_3), 4.2–4.8 (m, 2H, CH_2), 11.8 (s, 1H, >NH). $C_{18}H_{14}N_2Cl_3SFO_2$ (447.745) calcd.: C, 48.28; H, 3.15; N, 6.26; S, 7.16. Found: C, 48.73; H, 3.37; N, 6.15; S, 7.46.

N-(3,4,4-Trichloro-1-(2-napthylthio)-2-nitrobutadienyl)-1-benzidin (13c)

13c: yield, 0.062 g (42%), m.p. 234–235°C. R_f = 0.3953 (ethylacetate). IR (KBr): ν = 3000, 3010 cm^{-1} (C—H), 1600, 1610 (C=C), 1280, 1500 (C—NO_2). ^1H NMR ($CDCl_3$, TMS int.): δ = 6.8–7.8 ppm (m, 15H, Ar—H), 11.8 (s, 1H, >NH), 1.2–1.8 (m, 2H, NH_2). $C_{26}H_{18}N_3SO_2Cl_3$ (542.875) calcd.: C, 57.52; H, 3.34; N, 7.74; S, 5.90. Found: C, 57.53; H, 3.48; N, 7.63; S, 5.74.

N,N-Bis(3,4,4-trichloro-1-(2-napthylthio)-2-nitro-1,3-butadienyl)-p-phenylendiamine (15c)

15c: yield, 0.063 g (49%), m.p. 167–168°C. R_f = 0.2380 (CH_2Cl_2/petroleumether 1:1). IR (KBr): $\nu = 2980, 3015\ cm^{-1}$ (C—H), 1600 (C=C), 1290, 1540 (C—NO_2), 3490 (NH). ^1H NMR ($CDCl_3$, TMS int.): $\delta = 6.9–7.5$ ppm (m, 18H, Ar—H), 11.8 (m, 2H, >NH). $C_{34}H_{20}N_4Cl_6S_2O_4$ (824.777) calcd.: C, 50.39; H, 2.68; N, 8.12; S, 3.72. Found: C, 49.46; H, 2.43; N, 7.76; S, 3.98.

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