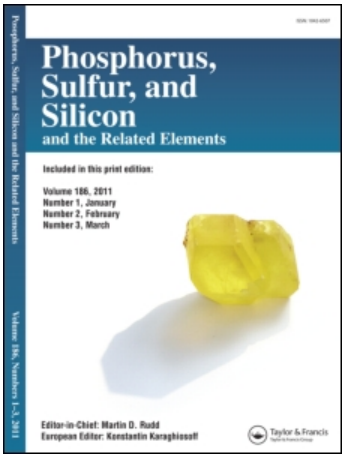

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New *N,S*-Substituted Nitrobutadienes from Mono(Arylthio)Substituted Nitrobutadienes

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To cite this Article İbiş, Cemil and Yıldırım, Hatice(2009) 'New *N,S*-Substituted Nitrobutadienes from Mono(Arylthio)Substituted Nitrobutadienes', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 2, 369 — 378
To link to this Article: DOI: 10.1080/10426500802162861
URL: http://dx.doi.org/10.1080/10426500802162861

Phosphorus, Sulfur, and Silicon, 184:369–378, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802162861

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New *N,S*-Substituted Nitrobutadienes from Mono(Arylthio)Substituted Nitrobutadienes

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*N,S-Substituted nitrobutadienes **3a–g** were synthesized from the reaction of the thiosubstituted derivatives **1a–g** with thiomorpholine **2**. The N,S-substituted nitrobutadienes **5a–g** were obtained from the reaction of the thiosubstituted butadienes **1a–g** with N-diphenylmethyl piperazine **4**. The structure of butadiene **3c** was elucidated by single crystal X-ray diffraction.*

Keywords *N*-Diphenylmethyl piperazine; mono(arylthio)substituted nitrodiene; *N,S*-substituted nitrobutadiene; thiomorpholine; X-ray diffraction

INTRODUCTION

It is known that mono-, bis-, tris-, and tetrakisheterosubstituted nitrobutadienes can be obtained from the reaction of nitrobutadienes with *N*- and *S*-nucleophilic compounds.[1,2] The synthesis of some *N,S*-substituted nitrobutadienes has been reported.[3–13] We have prepared *N,S*-substituted nitrobutadienes from the reaction of some mono(thio)substituted nitrobutadienes with piperazine and morpholine derivatives.[12–19] Substituted piperazines are important in clinical chemistry. Furthermore, some piperazine salts are used in gene transfer reactions[20–22] and show spasmolytic,[23] anthelmintic,[24] or germicidal[25] activities.

The aim of this study was the synthesis and characterization of new *N,S*-substituted-1,3-butadienes from mono(thio)substituted-1,3-butadienes.

Received 12 April 2008; accepted 26 April 2008.
We thank the Fund of Istanbul University for financial support of this work.
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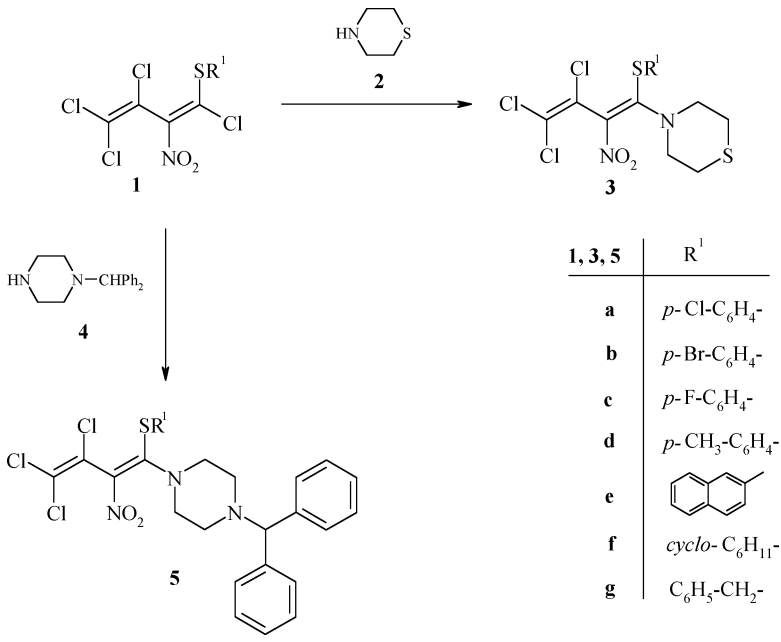

SCHEME 1

RESULTS AND DISCUSSION

The mono(thio)substituted nitrobutadienes **1a–g**[6–9] reacted with thiomorpholine **2** to form the new derivatives **3a–g**. Compounds **5a–g** were obtained from the reaction of **1a–g** with *N*-diphenylmethyl piperazine **4** (Scheme 1). The new *N*,*S*-substituted nitrobutadienes are obtained in good yields and are stable yellow solids. Composition and structure of **3a–g** and **5a–g** are shown from microanalysis and from spectroscopic data. These compounds are probably formed by an addition-elimination reaction.

The NMR signals of the thiomorpholine and piperazine ring protons of **3c** and **5c** at 30, 45 and 100°C are given in Figures 1 and 2, respectively. Broad signals are observed at $\delta = 2.36$ ppm and at $\delta = 3.69$ ppm at 30°C for the hydrogen atoms of the thiomorpholine ring in **3c**. The proton signals of thiomorpholine ring become sharper at 45°C and show a triplet at 100°C (Figure 1).

The piperazine ring protons of **5c** display in the ^{1}H NMR spectrum at 30°C broad signals at $\delta = 2.1$ ppm and at $\delta = 3.5$ ppm. For the signals of these protons, no splitting was observed at 45°C, while at 100°C a triplet at $\delta = 3.5$ ppm was detected (Figure 2).

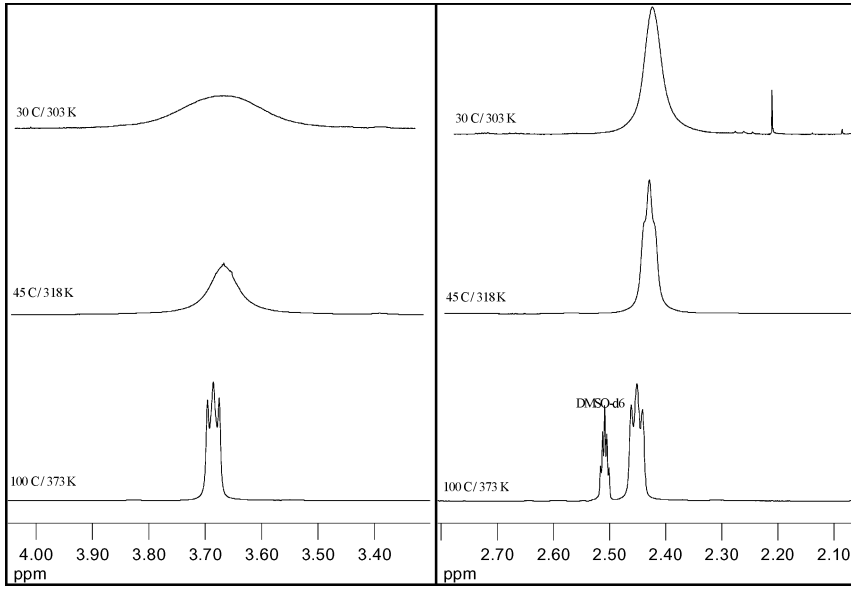

FIGURE 1 ^{1}H NMR signals of the methylene protons in **3c** at 30°C(in $CDCl_3$), at 45°C(in $CDCl_3$), and at 100°C (in DMSO-d6).

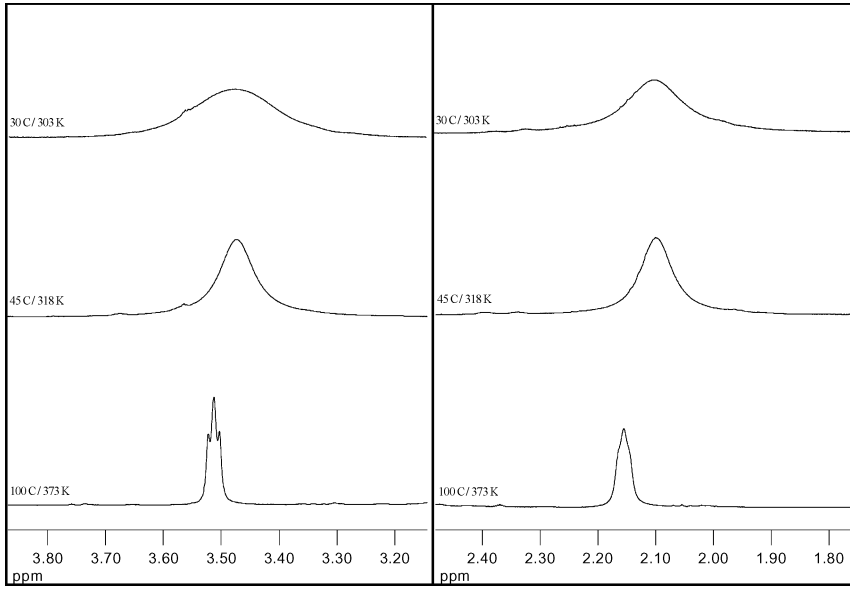

FIGURE 2 ^{1}H NMR signals of the methylene protons in **5c** at 30°C(in $CDCl_3$), at 45°C(in $CDCl_3$), and 100°C (in DMSO-d6).

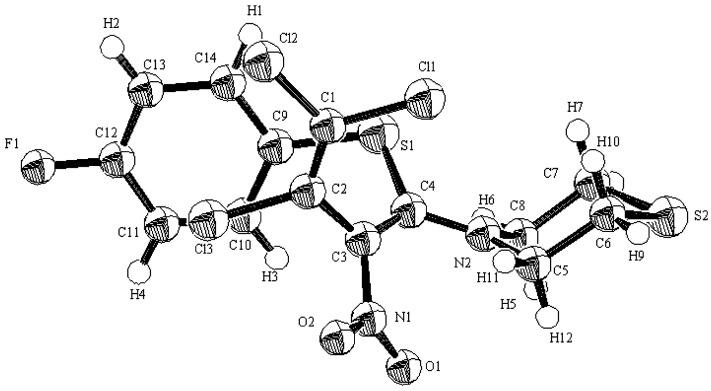

FIGURE 3 ORTEP-II view of the molecular structure of **3c** in the crystal; thermal ellipsoids are drawn at the 50% probability level.

The *Z*-isomer of **1a** has been reported before.[26] Alkylthio and piperazine substituted 2-nitrobutadienes were found to exist as the *E*-isomers.[27] For the *N*, *S*-substituted nitrobutadienes **3** and **5**, the *E*-isomers also are observed.

The thiomorpholine ring of compound **3c** adopts chair conformation (Figure 3). Bond lengths within the butadiene chain are 1.338(3), 1.453(3), and 1.400(2) Å for C2—C1, C3—C2, and C4—C3, respectively. The C1—C2—C3 bond angle is 122.3(1) degrees and the C2—C3—C4 bond angle is 123.7(1) degrees. The C4—C3—C2—C1 torsion angle is –56.4(3) degrees. The butadiene unit adopts nearly a *cis* configuration, but is not completely planar as would be expected if the two double bonds were fully conjugated. The crystallographic data and details on structure refinement for compound **3c** are summarized in Table I, selected atom distances and angles are contained in Table II.

Crystallographic data (excluding structure factors) for **3c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC—615307.[28]

EXPERIMENTAL

Melting points were measured on a Buchi B-540 capillary apparatus and are uncorrected. IR-spectra were recorded on a Shimadzu FTIR-8101 instrument. NMR spectra were obtained with a Varian Unity Inova 500 MHz instrument (499.83 MHz for ^{1}H, 125.68 MHz for ^{13}C). UV spectra were recorded with a UV-VIS spectrophotometer TU-1901;

TABLE I Crystal and Structure Refinement Data for 3c

Sum formula	$C_{14}H_{12}N_2O_2Cl_3S_2F$
M_w (g.mol^{-1})	429.74
Color	Yellow
Crystal size /mm	0.60 × 0.40 × 0.20
Crystal system	Triclinic
Space group	$P\bar{1}$
a, b, c (Å)	8.7550(4), 10.1123(6), 10.9520(5)
α, β, γ (^{0})	110.746(3), 97.178(2), 95.261(1)
Vol / Å^3	889.93(8)
Z	2
D_c / g.cm^{-3}	1.604
F(000)	436.00
μ(cm^{-1})	7.68
Reflections collected	69762
Independent reflections	5183 ($R_{int} = 0.032$)
Goodness of fit	0.913
Final R indices [I>2σ >(I)][a]	$R = 0.052$, $Rw = 0.059$
Largest diff. peak and hole (e$^-$.Å^{-3})	0.39 and –0.39

[a] $R = \sum| \mid F_o \mid - \mid F_c \mid \mid / \sum \mid F_o \mid$, $R_w = [\sum w(\mid F_o \mid - \mid F_c \mid)^2 / \sum w F_o^2]^{1/2}$

positions of the absorption maxima λ_{max} are given in nm. Microanalyses were obtained using a Carlo-Erba 1110 element analyzer. Thin-layer chromatography (TLC): silica gel 60 F_{254} foils (Merck). Column chromatography: silica gel 60 (particle size 0.063–0.20 mm, Merck).

TABLE II Selected Atom Distances (Å), Bond and Torsion Angles (Degrees) for 3c

S(2)—C(6)	1.794(2)	N(2)—C(4)	1.341(2)
N(2)—C(8)	1.475(3)	N(2)—C(5)	1.469(3)
C(2)—C(1)	1.338(3)	C(4)—C(3)	1.400(2)
C(8)—C(7)	1.509(2)	C(3)—C(2)	1.453(3)
S(2)—C(7)	1.804(3)	C(6)—C(5)	1.515(2)
C(4)—N(2)—C(8)	123.3(2)	C(4)—N(2)—C(5)	121.5(2)
C(8)—N(2)—C(5)	115.1(2)	C(3)—C(4)—S(1)	122.1(1)
C(3)—C(4)—N(2)	123.7(2)	S(1)—C(4)—N(2)	113.9(1)
C(5)—C(6)—S(2)	113.4(2)	C(2)—C(3)—C(4)	123.7(1)
C(7)—C(8)—N(2)	112.3(2)	N(2)—C(5)—C(6)	110.9(2)
C(6)—S(2)—C(7)	96.7(1)	S(2)—C(7)—C(8)	111.3(2)
C(4)—C(3)—C(2)—C(1)	−56.4(3)	C(8)—N(2)—C(4)—C(3)	150.4(2)
C(4)—N(2)—C(8)—C(7)	121.0(2)	C(8)—N(2)—C(5)—C(6)	59.9(2)
C(4)—N(2)—C(5)—C(6)	−122.9(2)	N(2)—C(4)—C(3)—C(2)	143.3(2)
F(1)—C(12)—C(13)—C(14)	178.3(2)	N(2)—C(8)—C(7)—S(2)	61.8(2)

X-Ray Structure Determination of 3c

Single crystal X-ray diffraction data for **3c** was obtained with a Rigaku R-Axis Rapid-S diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71070$ Å). The structure was solved by Direct Methods (SIR92).[29] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Crystal Structure Crystallographic Software Package.[30]

Synthesis of Nitrobutadienes 3 and 5: General Procedure

Equimolar amounts (0.3 mmol) of the mono(arylthio)substituted nitrobutadiene **1a–g** and thiomorpholine **(2)** or *N*-diphenylmethyl piperazine **(4)** were dissolved in 25 mL of CH_2Cl_2 and stirred for 6 h at room temperature. Chloroform (3×50 mL) was added to the reaction mixture. The organic layer was washed three times with 100 mL of water and dried over $CaCl_2$. The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

2-Nitro-3,4,4-trichloro-1-(4-chlorophenylthio)-1-thiomorpholinyl-1,3-butadiene (3a)

Yield: 0.114 g (96%). M.p.: 151.5–152.5°C. IR(KBr): $\upsilon = 1295$, 1530 (NO_2), 1600 (C=C), 2900 (C-H), 3100 cm^{-1} (Ar-H). ^1H NMR ($CDCl_3$): $\delta = 7.41$ (d, $J = 8.8$ Hz, 2H, Ar-H), 7.36 (d, $J = 8.8$ Hz, 2H, Ar-H), 3.69 (s, br, 4H, NCH_2), 2.39 (s, br, 4H, SCH_2). UV ($CHCl_3$): $\lambda_{max} = 390$, 248 nm. $C_{14}H_{12}Cl_4N_2O_2S_2$ (446.20): Calcd. C 37.68, H 2.71, N 6.28; Found C 38.47, H 2.70, N 6.31.

2-Nitro-3,4,4-trichloro-1-(4-bromophenylthio)-1-thiomorpholinyl-1,3-butadiene (3b)

Yield: 0.157 g (86%). M.p.: 143.4–144.7°C. IR(KBr): $\upsilon = 1295$, 1530 (NO_2), 1600 (C=C), 2900 (C-H), 3000, 3050 cm^{-1} (Ar-H). ^1H NMR ($CDCl_3$): $\delta = 7.51$ (d, $J = 8.8$ Hz, 2H, Ar-H), 7.24 (d, $J = 8.8$ Hz, 2H, Ar-H), 3.65 (s, br, 4H, NCH_2), 2.28 (s, br, 4H, SCH_2). UV ($CHCl_3$): $\lambda_{max} = 390$, 250 nm. $C_{14}H_{12}BrCl_3N_2O_2S_2$ (490.65): Calcd. C 34.27, H 2.47, N 5.71; Found C 34.47, H 2.03, N 5.48.

2-Nitro-3,4,4-trichloro-1-(4-fluorophenylthio)-1-thiomorpholinyl-1,3-butadiene (3c)

Yield: 0.117 g (99%). M.p: 116.1–117.4°C. IR(KBr): $\upsilon = 1280$, 1520 (NO_2), 1600 (C=C), 2900 (C-H), 3100 cm^{-1} (Ar-H). ^1H NMR ($CDCl_3$): $\delta = 7.43$ (ddd, $J = 8.8$, 1.9, 6.8 Hz, 2H, Ar-H), 7.14 (ddd, $J = 8.3$, 1.9, 6.4

Hz, 2H, Ar-H), 3.69 (s, br, 4H, NCH_2), 2.36 (s, br, 4H, SCH_2).^{13}C NMR (DMSO-d6): $\delta =$ 26.3, 56.6, 117.7, 118.3, 125.3, 125.9, 127.8, 136.2, 162.7, 164.7 (CF). UV ($CHCl_3$): $\lambda_{max} = 390$, 244 nm. $C_{14}H_{12}Cl_3FN_2O_2S_2$ (429.74): Calcd. C 39.13, H 2.81, N 6.52; Found C 39.63, H 2.90, N 6.37.

2-Nitro-3,4,4-trichloro-1-(4-methylphenylthio)-1-thiomorpholinyl-1,3-butadiene (3d)

Yield: 0.118 g (98%). M.p.: 141.2–142.4°C. IR(KBr): $\upsilon =$ 1290, 1520 (NO_2), 1600 (C=C), 2900, 2950 (C-H), 3050 cm^{-1} (Ar-H). ^{1}H NMR ($CDCl_3$): $\delta =$ 7.33 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.23 (d, $J = 8.3$ Hz, 2H, Ar-H), 3.64 (s, br, 4H, NCH_2), 2.38 (s, 3H, CH_3), 2.27 (s, br, 4H, SCH_2). ^{13}C NMR ($CDCl_3$): $\delta =$ 21.4, 26.5, 55.7, 120.2, 125.5, 126.7, 127.1, 131.1, 133.0, 140.5, 167.0. UV ($CHCl_3$): $\lambda_{max} = 390$, 246 nm. $C_{15}H_{15}Cl_3N_2O_2S_2$ (425.78): Calcd. C 42.31, H 3.55, N 6.58; Found C 41.71, H 3.35, N 6.57.

2-Nitro-3,4,4-trichloro-1-(2-naphthylthio)-1-thiomorpholinyl-1,3-butadiene (3e)

Yield: 0.116 g (99%). M.p.: 172.9–173.8°C. IR(KBr): $\upsilon =$ 1295, 1550 (NO_2), 1630 (C=C), 2900, 2990 (C-H), 3100 cm^{-1} (Ar-H). ^{1}H NMR ($CDCl_3$): $\delta =$ 7.97 (d, $J = 1.5$ Hz, 1H, naphthyl-H), 7.90 (d, $J = 8.3$ Hz, 1H, naphthyl-H), 7.86 (t, $J = 5.4$ Hz, 1H, naphthyl-H), 7.80 (t, $J =$ 5.4 Hz, 1H, naphthyl-H), 7.57 (m, 2H, naphthyl-H), 7.44 (dd, $J = 6.8$ Hz, 1.9 Hz, 1H, naphthyl-H), 3.72 (s, 4H, NCH_2), 2.27 (s, br, 4H, SCH_2). UV ($CHCl_3$): $\lambda_{max} = 391$, 248 nm. $C_{18}H_{15}Cl_3N_2O_2S_2$ (461.82): Calcd. C 46.81, H 3.27, N 6.07; Found C 46.08, H 3.28, N 6.25.

2-Nitro-3,4,4-trichloro-1-cyclohexylthio-1-thiomorpholinyl-1,3-butadiene (3f)

Yield: 0.128 g (80%). M.p.: 121.6–122.5°C. IR(KBr): $\upsilon =$ 1295, 1510 (NO_2), 1580 (C=C), 2850, 2900 cm^{-1} (C-H). ^{1}H NMR ($CDCl_3$): $\delta =$ 3.80 (s, br, 4H, NCH_2), 3.33 (m, 1H, S-$CH_{cyclohexyl}$), 2.71 (t, $J = 5.4$ Hz, 4H, SCH_2), 1.1–2.0 (m, 10H, cyclohexyl-H). UV ($CHCl_3$): $\lambda_{max} =$ 401, 296, 244 nm. $C_{14}H_{19}Cl_3N_2O_2S_2$ (417.80): Calcd. C 40.25, H 4.58, N 6.70; Found C 41.55, H 4.04, N 6.60.

2-Nitro-3,4,4-trichloro-1-benzylthio-1-thiomorpholinyl-1,3-butadiene (3g)

Yield: 0.125 g (84%). M.p.: 157.6–158.2°C. IR(KBr): $\upsilon =$ 1295, 1520 (NO_2), 1600 (C=C), 2800, 2900 (C-H), 3050 cm^{-1} (Ar-H). ^{1}H NMR ($CDCl_3$): $\delta =$ 7.1–7.4 (m, 5H, Ar-H), 4.05 (s, 2H, S-CH_2-Ar), 3.65 (s, br, 4H, NCH_2), 2.66 (t, $J = 5.4$ Hz, 4H, SCH_2). UV ($CHCl_3$): $\lambda_{max} = 399$,

295, 243 nm. $C_{15}H_{15}Cl_3N_2O_2S_2$ (425.78): Calcd. C 42.31, H 3.55, N 6.58; Found C 42.03, H 3.06, N 6.44.

2-Nitro-3,4,4-trichloro-1-(4-chlorophenylthio)-1-[4-(1-diphenylmethyl)-piperazine-1-yl]-1,3-butadiene (5a)

Yield: 0.095 g (60%). M.p.: 160.2–161.0°C. IR(KBr): $\upsilon = 1290$, 1520 (NO_2), 1600 (C=C), 2800, 2900 (C-H), 3050 cm^{-1} (Ar-H).^{1}H NMR ($CDCl_3$): $\delta = 7.27$ (m, 8H, Ar-H), 7.20 (d, $J = 7.8$ Hz, 4H, ArH), 7.13 (t, $J = 7.3$ Hz, 2H, ArH), 4.10 (s, 1H, CH-N), 3.50 (s, br, 4H, NCH_2), 2.10 (s, br, 4H, NCH_2). UV ($CHCl_3$): $\lambda_{max} = 387$, 246 nm. $C_{27}H_{23}Cl_4N_3O_2S$ (595.37): Calcd. C 54.47, H 3.89, N 7.06; Found C 54.91, H 3.99, N 7.56.

2-Nitro-3,4,4-trichloro-1-(4-bromophenylthio)-1-[4-(1-diphenylmethyl)-piperazine-1-yl]-1,3-butadiene (5b)

Yield: 0.100 g (66%). M.p.: 105.3–106.1°C. IR(KBr): $\upsilon = 1290$, 1540 (NO_2), 1600 (C=C), 2800, 2900 (C-H), 3020, 3050 cm^{-1} (Ar-H).^{1}H NMR ($CDCl_3$): $\delta = 7.5$ (d, $J = 8.3$ Hz, 2H, Ar-H), 7.30 (s, 2H, Ar-H), 7.22 (t, $J = 7.8$ Hz, 6H, Ar-H), 7.19 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.14 (t, $J = 7.3$ Hz, 2H, Ar-H), 4.08 (s, 1H, CH-N), 3.48 (s, 4H, CH_2-N), 2.10 (s, 4H, CH_2-N). UV ($CHCl_3$): $\lambda_{max} = 387$, 248 nm. $C_{27}H_{23}BrCl_3N_3O_2S$ (639.82): Calcd. C 50.68, H 3.62, N 6.57; Found C 50.10, H 3.53, N 6.48.

2-Nitro-3,4,4-trichloro-1-(4-fluorophenylthio)-1-[4-(1-diphenylmethyl)-piperazine-1-yl]-1,3-butadiene (5c)

Yield: 0.087 g (55%). M.p.: 189.9–191.4°C. IR(KBr): $\upsilon = 1280$, 1530 (NO_2), 1600 (C=C), 2800, 2900 (C-H), 3100 cm^{-1} (Ar-H).^{1}H NMR (DMSO-d6): $\delta = 7.53$ (ddd, $J = 8.8$, 1.9, 6.8 Hz, 2H, Ar-H), 7.34 (m, 6H, Ar-H), 7.29 (t, $J = 7.3$ Hz, 4H, Ar-H), 7.19 (t, $J = 7.3$ Hz, 2H, Ar-H), 4.25 (s, 1H, CH-N), 3.46 (s, 4H, CH_2-N), 2.10 (s, 4H, CH_2-N). ^{13}C NMR (DMSO-d6): $\delta = 50.4$, 53.8, 74.6, 118.2, 118.3, 125.0, 126.3, 127.4, 127.9, 128.3, 129.3, 136.0, 136.1, 162.7, 164.7 (CF). UV ($CHCl_3$): $\lambda_{max} = 387$, 245 nm. $C_{27}H_{23}Cl_3FN_3O_2S$ (578.91): Calcd. C 56.02, H 4.00, N 7.26; Found C 56.34, H 4.06, N 7.21.

2-Nitro-3,4,4-trichloro-1-(4-methylphenylthio)-1-[4-(1-diphenylmethyl)-piperazine-1-yl]-1,3-butadiene (5d)

Yield: 0.090 g (54%). M.p.: 95.4–97.0°C. IR(KBr): $\upsilon = 1295$, 1540 (NO_2), 1600 (C=C), 2800, 2990 (C-H), 3000, 3020 cm^{-1} (Ar-H).^{1}H NMR (DMSO-d6): $\delta = 7.36$ (t, $J = 8.1$ Hz, 6H, Ar-H), 7.29 (t, $J = 8.1$ Hz, 6H, Ar-H), 7.19 (t, $J = 6.8$ Hz, 2H, Ar-H), 4.16 (s, 1H, CH-N), 3.46 (s, 4H, NCH_2), 2.20 (s, 4H, NCH_2), 2.38 (s, 3H, CH_3).^{13}C NMR ($CDCl_3$): $\delta = 21.3$, 29.7, 50.2, 53.3, 75.5, 119.1, 125.0, 126.9, 127.4, 127.4, 128.7,

130.9, 132.9, 140.0, 141.4, 165.7. UV ($CHCl_3$): $\lambda_{max} = 388$, 243 nm. $C_{28}H_{26}Cl_3N_3O_2S$ (574.95): Calcd. C 58.49, H 4.56, N 7.31; Found C 58.16, H 4.71, N 7.07.

2-Nitro-3,4,4-trichloro-1-cyclohexylthio-1-[4-(1-diphenylmethyl)-piperazine-1-yl]-1,3-butadiene (5f)

Yield: 0.091 g (56%). M.p.: 202.2–203.3°C. IR(KBr): $\upsilon = 1280$, 1550 (NO_2), 1600 (C=C), 2800, 2950 (C-H), 3050 cm^{-1} (Ar-H).^{1}H NMR ($CDCl_3$): $\delta = 7.33$ (d, $J = 7.3$ Hz, 4H, Ar-H), 7.20 (t, $J = 7.3$ Hz, 4H, Ar-H), 7.13 (t, $J = 6.8$ Hz, 2H, Ar-H), 4.18 (s, 1H, NCH), 3.60 (s, 4H, NCH_2), 2.44 (s, 4H, NCH_2), 3.25 (m, 1H, SCH), 1.1-2.0 (m, 10H, cyclohexyl-H). UV ($CHCl_3$): $\lambda_{max} = 393$, 297, 243 nm. $C_{27}H_{30}Cl_3N_3O_2S$ (566.97): Calcd. C 57.20, H 5.33, N 7.41; Found C 57.21, H 5.07, N 7.43.

2-Nitro-3,4,4-trichloro-1-benzylthio-1-[4-(1-diphenylmethyl)-piperazine-1-yl]-1,3-butadiene (5g)

Yield: 0.190 g (74%). M.p.: 91.6–92.4°C. IR(KBr): $\upsilon = 1290$, 1520 (NO_2), 1600 (C=C), 2750, 2900 (C-H), 3000, 3020 cm^{-1} (Ar-H).^{1}H NMR ($CDCl_3$): $\delta = 7.32$ (d, $J = 7.3$ Hz, 4H, Ar-H), 7.23 (m, 7H, Ar-H), 7.13 (m, 4H, Ar-H), 4.18 (s, 1H, CH-N), 4.07 (s, 2H, S-CH_2-Ar), 3.49 (s, 4H, NCH_2), 2.44 (s, 4H, NCH_2). UV ($CHCl_3$): $\lambda_{max} = 394$, 295, 241 nm. $C_{28}H_{26}Cl_3N_3O_2S$ (574.95): Calcd. C 58.49, H 4.56, N 7.31; Found C 58.19, H 3.78, N 7.20.

REFERENCES

[1] R. V. Kaberdin, V. I. Potkin, and V. A. Zapol'skii, *Russ. Chem. Rev.*, **66,** 827 (1997).
[2] Yu. A. Ol'dekop, R. V. Kaberdin, and V. I. Potkin, *Zh. Org. Khim.,* **16,** 543 (1980).
[3] C. İbiş and Ç. Sayıl, *Phosphorus, Sulfur, and Silicon,* **92,** 39 (1994).
[4] C. İbiş, *Bull. Soc. Chim. Belg.,* **105,** 317 (1996).
[5] C. İbiş and Ç. Sayıl, *Synth. Commun.,* **24,** 2797 (1994).
[6] C. İbiş and F. S. Göksel, *Phosphorus, Sulfur, and Silicon,* **97,** 165 (1994).
[7] C. İbiş, *Phosphorus, Sulfur, and Silicon,* **118,** 49 (1996).
[8] C. İbiş, W. M. Dib Brimo, and G. Aydınlı, *Phosphorus, Sulfur, and Silicon,* **170,** 221 (2001).
[9] C. İbiş and G. Aydınlı, *Sulfur Lett.,* **23,** 67 (1999).
[10] C. İbiş and M. Onul, *Phosphorus, Sulfur, and Silicon,* **178,** 1881 (2003).
[11] C. İbiş and G. Aydınlı, *Phosphorus, Sulfur, and Silicon,* **177,** 2529 (2002).
[12] C. İbiş and Ç. Sayıl, *Rev. Roum. Chim.,* **46,** 211 (2001).
[13] C. İbiş, F. S. Göksel, and G. Aydınlı, *Phosphorus, Sulfur, and Silicon,* **178,** 777 (2003).
[14] C. İbiş and Z. Gökmen, *Phosphorus, Sulfur, and Silicon,* **143,** 67 (1998).
[15] C. İbiş, F. G. Kırbaþlar, and G. Aydınlı, *Phosphorus, Sulfur, and Silicon,* **179,** 1975 (2004).
[16] C. İbiş and M. Onul, *Phosphorus, Sulfur, and Silicon,* **180,** 2787 (2005).

[17] C. İbiş, Ç. Sayıl, and F. Özkök, *Z. Naturforsch. Teil B,* **61b,** 1174 (2006).
[18] C. İbiş, Z. Gökmen, and F. S. Göksel, *Chim. Acta Turc.,* **32,** 31 (2004).
[19] C. İbiş and G. Aydınlı, *Chim. Acta Turc.,* **33,** 23 (2005).
[20] M. Nishiyoma, T. Yamamoto, and Y. Koie, *Tetrahedron Lett.,* **39,** 617 (1998).
[21] F. Kerrigon, C. Martin; and G. H. Tomas, *Tetrahedron Lett.,* **39,** 2219 (1998).
[22] I. Solodin and T. D. Heath, *Synlett,* **7,** 619 (1996).
[23] R. Baltzly, W. S. Ide, and E. Lorz, *J. Am. Chem. Soc.,* **77,** 4809 (1955).
[24] M. Harfenist, *J. Am. Chem. Soc.,* **79,** 2211 (1957).
[25] D. R. Smith, J. W. Curry, and R. L. Eifert, *J. Am. Chem. Soc.,* **72,** 2969 (1950).
[26] C. İbiş, M. C. Sayıl, and N. G. Deniz, *Acta Cryst.,* E**62,** o800-o801 (2006).
[27] C. İbiş and N. G. Deniz, *Acta Cryst.,* E**63,** o1091-o1092 (2007).
[28] Further information may be obtained free of charge from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC-615307. E-mail: deposit@ccdc.cam.ac.uk.
[29] SIR92: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, and M. Camalli, *J. Appl. Cryst.,* **27,** 435 (1994).
[30] CrystalStructure 3.5.1: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000–2003). 9009 New Trails Dr., The Woodlands, TX 77381, USA.