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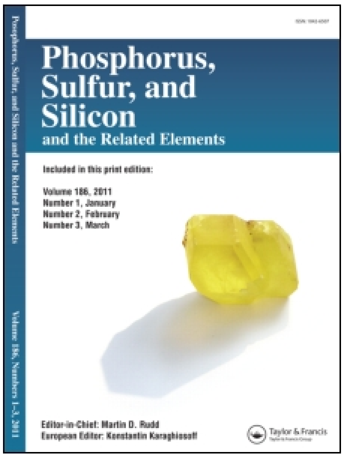

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New N,S-Substituted Dienes from Mono(thio)substituted-2-nitrohalo-1,3-diene and Some Amines

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New N,S-Substituted Dienes from Mono(thio)substituted-2-nitrohalo-1,3-diene and Some Amines

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*Mono(thio)substituted nitrodiene compound **1** reacted with **2a–f** and yielded **3a–f** in methylene chloride. Compound **1** gave **7** by the reaction with **6**. Compounds **5a–c** were obtained by the reactions of **4a–c** with **1**. **3a** also has been structurally characterized using single-crystal X-ray diffraction analyses.*

Keywords 2-Nitrohalodiene; 4-methoxythiophenol; mono(thio)substituted nitrodiene; N,S-substituted nitrodiene; piperazine; piperidine; thiosubstituted halodiene

In recent years, some mono-, di-, and tris(thio)substituted dienes were obtained from the reactions of nitrodienes with thiols and dithiols.[1–9] We have reported previously that N,S-substituted dienes were prepared from the reactions of some mono(thio)substituted dienes with some amines (primary amine, piperazine, morpholine, piperidine, etc).[10–15] The piperazine and piperidine compounds have been subject to medicinal applications and gen transfer studies due to their interesting biological activity and chemical effects.[16–21]

Our aim in this sudy was to synthesize and characterize new N,S-substituted nitrodienes. Reaction of the mono(thio)substituted diene compound "1-(4-methoxyphenylthio)-2-nitro-1,3,4,4-tetrachloro-1,3-butadiene" (**1**),[22] which is a very reactive compound with some amines, provided the corresponding N,S-substituted halodiene derivatives.

Novel N,S-substituted dienes **3a–f** were obtained via the treatment of **1** with piperazine derivatives **2a–f**. Moreover, **1** was treated with the

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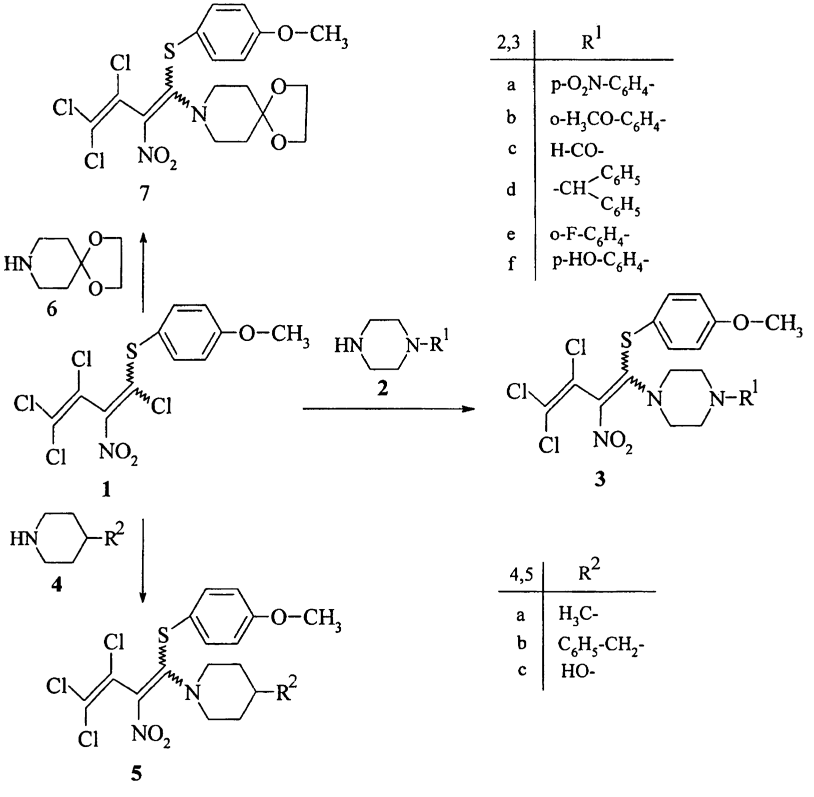
piperidine derivatives **4a–c** to give the corresponding N,S-substituted dienes **5a–c**. For the synthesis of **7**, **1** was treated with 1,4-dioxa-8-azaspiro-4,5-decane (**6**). The substitution reaction proceeds by addition-elimination reactions.[23] These novel heterocycles that are prepared are stable and they are yellow-colored compounds (Scheme 1).



2,3	R^1
a	$p\text{-}O_2N\text{-}C_6H_4\text{-}$
b	$o\text{-}H_3CO\text{-}C_6H_4\text{-}$
c	H-CO-
d	$\text{-CH}{<}^{C_6H_5}_{C_6H_5}$
e	$o\text{-}F\text{-}C_6H_4\text{-}$
f	$p\text{-}HO\text{-}C_6H_4\text{-}$

4,5	R^2
a	$H_3C\text{-}$
b	$C_6H_5\text{-}CH_2\text{-}$
c	HO-

SCHEME 1

The IR spectra of **3f** and **5c** showed a characteristic HO-band at ~3500 cm^{-1} and the IR-spectrum of **3c** showed a characteristic >C=O band at 1630 cm^{-1}.

The structures of these compounds have been established by their spectral data. The stereochemistry of **3a** was also confirmed by X-ray crystallographic analysis. The crystal of **3a** was also obtained by slow evaporation of solvent chloroform.

Experimental conditions of **3a** are summarized in Table I. An ORTEP diagram of **3a** with an atom numbering scheme is given in Figure 1,

TABLE I Crystallographic Data and Structure Refinement for Compound (3a). $\mathbf{R = \Sigma||Fo| - |Fc||/\Sigma|Fo|}$, $\mathbf{R_w = [\Sigma_w(|Fo| - |Fc|)2\,/\,\Sigma wFo2]1/2}$

Sum formula	(C21H19C13SN405)
f_w(g.mol^{-1})	545.82
Crystal dimensions (mm)	0.70 × 0.60 × 0.40
Crystal system	Triclinic
Space group	P-1
Lattice Parameters	
a (Å)	7.8400(2)
b (Å)	9.7030(3)
c (Å)	16.9628(4)
α(°)	93.898(2)
β(°)	93.879(2)
γ(°)	96.9296(13)
Vol [Å^3]	1260.67(6)
Z	2
D_{calc} (g.cm^{-3})	1.438
μ[cm^{-1}]	4.85
F(000)	560
Index ranges	$-11 <= h <= 11$ $-13 <= k <= 13$ $-23 <= l <= 23$
Reflections collected	98820
Independent reflections	7393[R(int) = 0.035]
Data/restraints/parameters	6946/0/326
Goodness-of-fit on F^2	1.081
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.063, wR = 0.099$
Largest diff. peak and hole	1.78 and −0.75 e. Å^{-3}

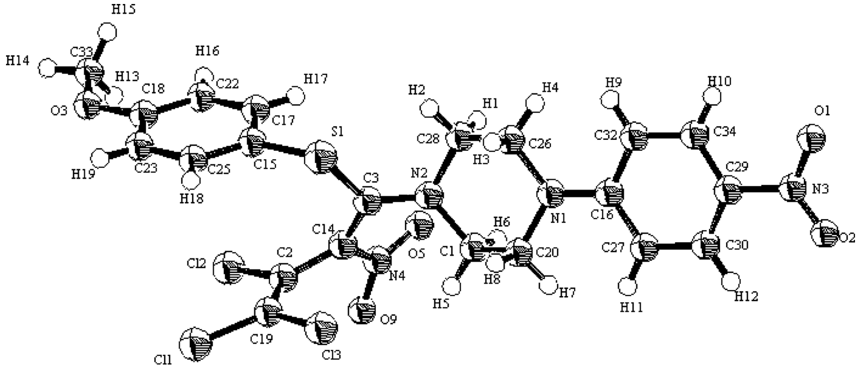


FIGURE 1 The molecular structure of compound **3a**.

TABLE II Selected Bond Lengths (Å) and Angles (°) for Compound 3a

S(1)-C(3)	1.754(2)	O(3)-C(18)	1.363(3)
S(1)-C(15)	1.774(2)	O(3)-C(33)	1.436(4)
Cl(2)-C(2)	1.737(2)	C(15)-C(17)	1.377(3)
Cl(3)-C(19)	1.714(2)	C(15)-C(25)	1.395(3)
Cl(1)-C(19)	1.714(2)	C(16)-C(27)	1.388(4)
O(5)-N(4)	1.239(2)	C(16)-C(32)	1.386(5)
N(2)-C(3)	1.338(2)	C(17)-C(22)	1.390(3)
N(2)-C(1)	1.461(3)	C(18)-C(22)	1.383(3)
N(2)-C(28)	1.457(4)	C(18)-C(23)	1.389(3)
N(4)-O(9)	1.245(3)	O(2)-N(3)	1.206(4)
N(4)-C(14)	1.413(2)	C(23)-C(25)	1.382(4)
N(1)-C(16)	1.381(3)	N(3)-C(29)	1.456(3)
N(1)-C(20)	1.460(3)	N(3)-O(l)	1.204(5)
N(1)-C(26)	1.431(5)	C(26)-C(28)	1.397(4)
C(2)-C(14)	1.452(2)	C(27)-C(30)	1.381(4)
C(2)-C(19)	1.332(3)	C(29)-C(30)	1.355(5)
C(3)-C(14)	1.402(3)	C(29)-C(34)	1.349(6)
C(1)-C(20)	1.518(3)	C(32)-C(34)	1.377(4)
C(3)-S(1)-C(15)	104.4(1)	C(27)-C(16)-N(1)	122.1(2)
C(3)-N(2)-C(1)	122.5(2)	C(32)-C(16)-N(1)	121.4(2)
C(3)-N(2)-C(28)	125.2(2)	C(22)-C(17)-C(15)	120.3(2)
C(1)-N(2)-C(28)	111.5(2)	C(22)-C(18)-C(23)	119.9(2)
O(9)-N(4)-C(14)	117.6(2)	C(22)-C(18)-O(3)	124.8(2)
O(9)-N(4)-O(5)	121.7(2)	C(23)-C(18)-O(3)	115.3(2)
C(14)-N(4)-O(5)	120.7(2)	Cl(3)-C(19)-Cl(1)	114.2(1)
C(16)-N(1)-C(20)	120.1(2)	Cl(3)-C(19)-C(2)	122.2(2)
C(16)-N(1)-C(26)	121.0(2)	Cl(1)-C(19)-C(2)	123.6(2)
C(20)-N(1)-C(26)	113.0(2)	N(1)-C(20)-C(1)	110.6(2)
C(14)-C(2)-C(19)	123.2(2)	C(17)-C(22)-C(18)	119.6(2)
C(14)-C(2)-Cl(2)	117.9(1)	C(25)-C(23)-C(18)	120.7(2)
C(19)-C(2)-Cl(2)	118.8(1)	C(29)-N(3)-O(1)	119.1(3)
C(14)-C(3)-S(1)	122.8(1)	C(29)-N(3)-O(2)	119.7(3)
C(14)-C(3)-N(2)	123.2(2)	O(1)-N(3)-O(2)	121.1(3)
S(1)-C(3)-N(2)	113.6(2)	C(15)-C(25)-C(23)	119.1(2)
C(20)-C(1)-N(2)	110.0(2)	C(28)-C(26)-N(1)	117.0(4)
C(18)-O(3)-C(33)	117.1(2)	C(30)-C(27)-C(16)	121.3(3)
N(4)-C(14)-C(2)	115.1(2)	N(2)-C(28)-C(26)	117.2(3)
N(4)-C(14)-C(3)	120.0(2)	C(30)-C(29)-C(34)	120.3(3)
C(2)-C(14)-C(3)	124.9(2)	C(30)-C(29)-N(3)	119.7(3)
C(17)-C(15)-C(25)	120.3(2)	C(34)-C(29)-N(3)	120.0(3)
C(17)-C(15)-S(1)	121.0(2)	C(27)-C(30)-C(29)	120.1(3)
C(25)-C(15)-S(1)	118.6(2)	C(34)-C(32)-C(16)	121.8(4)
C(27)-C(16)-C(32)	116.4(2)	C(29)-C(34)-C(32)	120.1(4)

and bond lengths and angles are in Table II. All physical properties and spectral data of the synthesized compounds are listed in Table III.

The C—C bond lengths of the butadiene chain are 1,332, 1.452, and 1.402 Å. respectively, for C_{19}-C_2, C_2-C_{14}, and C_{14}-C_3 for **3a**. The

TABLE III Spectral Data of the New Compounds

Product No.	M.P. (^{9}C)	Yield (%)	Mole. form. (Mol. wt.)	Analytical data cal./found C	H	N	IR (cm^{-1})	^{1}H-NMR δ (ppm)
3a	193–194	58	$C_{21}H_{19}SN_4Cl_3O_5$ (545.83)	46.21 46.08	3.50 3.34	10.26 9.87	2800, 2900, 3100 (C—H), 1600 (C═C),1290, 1520 (C—NO_2)	1.3–3.4 (m, 8H, $H_{piper.}$), 3.8–3.9 (m, 3H, $OC\mathbf{H}_3$), 6.7–8.2 (m, 8H, H_{arom})
3b	180–181	48	$C_{22}H_{22}SN_3Cl_3O_4$ (530.86)	49.77 46.27	4.17 3.77	7.91 7.28	2900, 2950, 3100 (C—H), 1590 (C═C), 1275, 1550 (C—NO_2)	1.1–2.9 (m, 9H, $H_{piper.}$), 3.7–3.9 (m, 6H, 2 $OC\mathbf{H}_3$), 6.6–7.4 (m, 8H, H_{arom})
3c	212–213	49	$C_{16}H_{16}SN_3Cl_3O_4$ (452.74)	42.44 42.07	3.56 3.34	9.28 9.18	2800, 2950, 3000 (C—H), 1590 (C═C), 1270, 1290, 1540 (C—NO_2), 1630 (C=O)	1.2–2.1 (m, 8H, $H_{piper.}$), 3.7–3.9 (m, 3H, $OC\mathbf{H}_3$, 6.7–7.4 (m, 4H, H_{arom})
3d	167–168	53	$C_{28}H_{26}SN_3Cl_3O_3$ (590.96)	56.91 56.39	4.43 4.02	7.11 6.94	2800, 2850, 3050 (C—H), 1590 (C═C), 1270, 1290, 1535 (C—NO_2)	1.8–3.6 (m, 8H, $H_{piper.}$), 3.7–3.9 (m, 3H, $OC\mathbf{H}_3$, 4.04 (S, 1H, N-CH), 6.7–7.4 (m, 14H, H_{arom})
3e	187–188	55	$C_{21}H_{19}SN_3Cl_3O_3F$ (518.83)	48.62 48.85	3.69 4.36	8.10 8.30	2800, 2900(C—H), 1590 (C═C), 1250 1540 (C—NO_2)	2.6–3.7 (m, 8H, $H_{piper.}$), 3.7–4.0 (m, 3H, $OC\mathbf{H}_3$), 6.6–7.5 (m, 8H, H_{arom})
3f	207–208	46	$C_{21}H_{20}SN_3Cl_3O_4$ (516.83)	48.80 48.25	3.90 4.58	8.13 7.91	2800, 2900, 2950 (C—H), 1590 (C═C), 1260, 1530 (C-NO_2), 3550 (C—OH)	2.6–3.7 (m, 8H, $H_{piper.}$), 3.7–3.9 (m, 3H, $OC\mathbf{H}_3$), 4.4 (s, 1H, OH) 6.6–7.5 (m-8H, H_{arom})
5a	134–135	61	$C_{17}H_{19}SN_2Cl_3O_3$ (437.77)	46.64 46.52	4.37 4.71	6.40 6.40	2800, 2950, 3000 (C—H), 1595 (C═C), 1285, 1290, 1535 (C—NO_2)	0.7–0.9 (m, 3H, $C\mathbf{H}_3$, 1.2–3.3 (m, 9H, $H_{piper.}$), 3.7–3.9 (m, 3H, $OC\mathbf{H}_3$), 6.8–7.5 (m, 4H, H_{arom})
5b	—	72	$C_{23}H_{23}SN_2Cl_3O_3$ (513.87)	53.75 53.36	4.51 4.06	5.45 5.58	2800, 2900, 3000 (C—H), 1595 (C═C), 1280, 1290, 1525 (C—NO_2)	1.1–3.2 (m, 11H, 5$C\mathbf{H}_2$ and 1 C**H**), 3.7–3.9 (m, 3H, $OC\mathbf{H}_3$, 6.8–7.4(m, 9H, H_{arom})
5c	162–163	42	$C_{16}H_{17}SN_2Cl_3O_4$ (439.74)	43.70 43.64	3.89 3.75	6.37 5.84	2800, 2950 (C—H), 1595 (C═C), 1285 1530 (C—NO_2), 3510 (C—OH)	1.4–1.7 (m, 1H, OH), 2.0–2.4 (m, 9H, H_{piper}), 3.6–3.9 (m, 3H, OCH_3), 6.8–7.5 (m, 4H, H_{arom})
7	164–165	57	$C_{18}H_{19}SN_2Cl_3O_5$ (481.78)	44.87 44.11	3.97 3.74	5.81 5.22	2850, 2950, 3000 (C—H), 1590 (C═C), 1280, 1540 (C—NO_2)	1.2–1.8 (m, 8H, H_{piper}), 3.8–3.9 (m, 3H, $OC\mathbf{H}_3$), 3.9–4.0 (m, 4H, —O—$(C\mathbf{H}_2)_2$—O—) 6.9–7.5 (m, 4H, H_{arom})

C-14, C-2, and C-19 bond angle is 123.2° and also the C-3, C-14, and C-2 bond angle is 124.9° for **3a**. As a feature of the structure of **3a**, the dihedral angle between the diene plane (S1, C3, C14, C2, C19, C12, C13, and C11 of Figure 1) and the phenyl thio plane (C18, C22, C23, C17, C15, and C25 of Figure 1) is 124.737°. The butadiene moiety is not completely planar for this compound because the two double bonds are not fully conjugated.

Crystal **3a** was mounted on an Rigaku R-Axis Rapid-S diffractometer with a graphite monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The structure was solved by SIR 92[24] and refined with CRYSTALS.[25] The positions of the H atoms bonded to C atoms were calculated (C—H distance 0.96 Å) and refined using a riding model. The H atom displacement parameters were restricted to be $1.2U_{eq}$ of the parent atom. All calculations were performed using the CrystalStructure crystallographic software package.[26] An ORTEP-II view of the molecular structure of **3a** is given in Figure 1.[27] Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-267315 for **3a**.[28]

EXPERIMENTAL SECTION

Melting points are uncorrected using a Büchi SMP 20 capillary apparatus. IR-spectra: Shimadzu FTIR-8101. ^{1}H-NMR-Spectra: Varian Inova 500 MHz. Elemental Analyzer 1110 Carlo-Erba. Thin-layer chromatography: TLC plates silica: 60 F254 (Merck, Darmstadt), detection with ultraviolet light (254 nm). Products were isolated by column chromatography on Kieselgel 60 with particle size 0.063–0.20 mm (Merck).

Preparation of N,S-Substituted Polyhalonitrodienes

Standard Work-Up Procedure

Equimolar amounts of S-substituted polyhalonitrodiene and amine derivatives were stirred in dichloromethane until the completion of the reaction. Chloroform was added to the reaction mixture. The organic layer was separated, washed with water (4 × 30 mL), and dried with $CaCl_2$ or $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography on silica gel.

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[28] Further information may be obtained from Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC-267315 for *3a.* E-mail: deposit@ccdc.cam.ac.uk