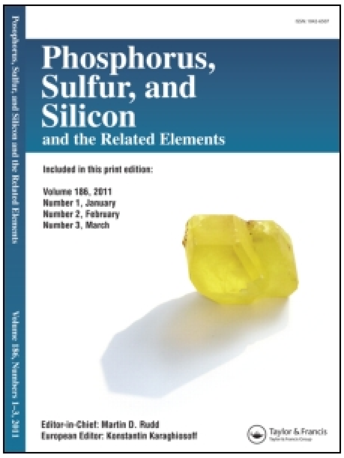


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

N,S-Substituted Nitrodienes from Naphthylthiosubstituted Nitrodienes and *S*-, *S,S*-Substituted Dienes from Hexachloro-1,3-Butadiene

Cemil İbiş[a]; Zeliha Gökmen[a]
[a] Department of Chemistry, Istanbul University, Avcilar, Istanbul, Turkey

To cite this Article İbiş, Cemil and Gökmen, Zeliha(2007) '*N,S*-Substituted Nitrodienes from Naphthylthiosubstituted Nitrodienes and *S*-, *S,S*-Substituted Dienes from Hexachloro-1,3-Butadiene', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 5, 1053 — 1059

To link to this Article: DOI: 10.1080/10426500601093838

URL: http://dx.doi.org/10.1080/10426500601093838

Phosphorus, Sulfur, and Silicon, 182:1053–1059, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601093838

N,S-Substituted Nitrodienes from Naphthylthiosubstituted Nitrodienes and *S*-, *S,S*-Substituted Dienes from Hexachloro-1,3-Butadiene

Cemil İbiş
Zeliha Gökmen
Department of Chemistry, Istanbul University, Avcilar, Istanbul, Turkey

Mono(thio)substituted dienes **1** *gave compounds* **3a–c***,* **7, 9,** *and* **11** *on reaction with pipe-razine derivatives in dry ether. N,S-substıtuted nitrodiene* **5** *was obtained from the reaction of* **1** *with 1,4-dioxospriol* **4**. *Hexachlorobutadiene* **12** *in a water-ethanol mixture in the presence of sodium hydroxide reacted with ethyleneglycol bismercaptoacetate* **13** *to give thiosubstituted thioethers* **14** *and* **15**.

Keywords Thioether; hexachloro-1,3-butadiene; *N,S*-thiosubstituted nitrodiene; piperazine

INTRODUCTION

The chemistry of nitro-compounds, especially of their halogen derivatives, has been intensively studied in recent decades. These highly reactive substances have been used to develop preparative methods for the synthesis of complex polyfunctional derivatives of different classes. We reported previously the synthesis of *N,S*-substituted dienes from the reaction of mono(thio)substituted dienes with some amines (primary amines, piperazine, morpholine, piperidine, etc.).[1–4] In recent years, some mono-, di-, and tris(thio)substituted dienes were obtained from reactions of nitrodienes with thiols and dithiols.[5–12]

Some thioethers were obtained from the reaction of hexachloro-1,3-butadiene with methanethiol in EtOH. In an US patent it was reported that these compounds exhibit biological activity (e.g., fungicidal, insecticidal, bactericidal, and herbicidal activity).[13] We described the

Received November 16, 2005; accepted October 11, 2006.
We thank the Research Fund of the University of Istanbul for financial support of this work.

Address correspondence to Cemil İbiş, Department of Chemistry, Faculty of Engineering, Istanbul University, Avcilar, Istanbul, Turkey. E-mail: ibiscml@istanbul. edu.tr

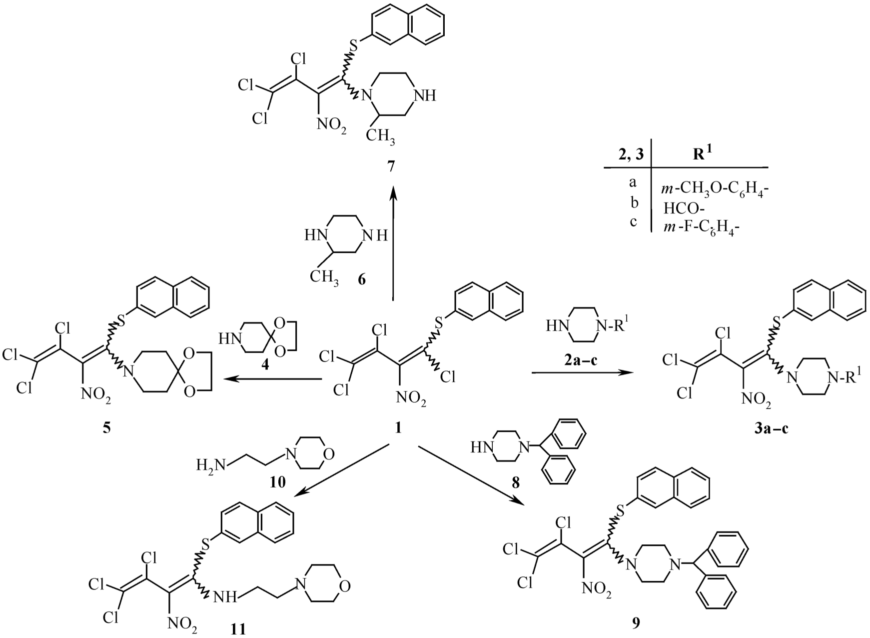
synthesis of some thioethers from the reaction of hexachlorobutadiene with some thiols.[14–18]

The aim of this work was to synthesize new *N*,*S*-, *S*-, and *S*,*S*-substituted 1,3-dienes and to determine their structures.

Piperazine compounds are important for clinical chemistry; some piperazine compounds were also used in gen-transfer reactions.[19,20] Piperidinyl derivatives show excellent biological activity.[21] Thiomorpholine compounds exhibit biological activity against respiratory tract-infection.[22–24]

RESULTS AND DISCUSSION

The tetrachloro-butadiene **1**,[25] when treated with piperazines **2**, **6**, and **8** in ether, yielded piperazinyl butadienes **3a–c**, **7**, and **9**. Compounds **5** and **11** were obtained from the reaction of **1** with 1,4-dioxa-8-azaspiro [4.5]decane **4** and 4-(2-aminoethyl)morpholine **10** in ether (Scheme 1).

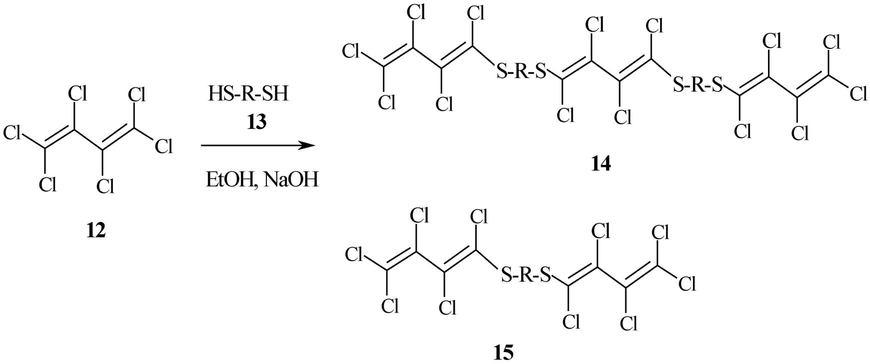


SCHEME 1

Monobutadienyl piperazine compound **7** was obtained from the reaction of **1** with 1-methylpiperazine, although we expected the formation of *N*,*S*-substituted bis(butadienyl) compound. All the reactions were made in ether at r.t. The IR spectrum of **3b** showed a band characteristic for the >C=O group, and the IR spectrum of **7** showed a band characteristic for the —NH group. The mass spectrum of compound **7** confirms its molecular mass (458.797) MS (25 eV): m/z = 458.97. NMR signals of the hydrogen atoms of the two methylene groups (—O—$(CH_2)_2$—O—) adjacent to the oxygen atoms in compound **5** are shifted to a higher field and display multiplets in the range 3.89–3.96 ppm. The new butadienes are stable compounds.

We reported previously the synthesis of mono- and bis(thio) substituted chlorobutadienes from the reaction of hexachlorobutadiene **12** with some thiols as well as the synthesis of cyclic and acyclic bis(thio)substituted chlorobutadienes from the reaction of **12** with dithiols.[26–29]

New compounds **14** and **15** were obtained from the reaction of hexachloro-1,3-butadiene **12** with ethyleneglycol bismercaptoacetate **13** in the presence of NaOH in ethanol (Scheme 2). These compounds are stable colorless oils. The IR spectra of **14** and **15** showed a band characteristic for the >C=O group. The structures of **14** and **15** result from their spectroscopic data and are supported by microanalysis (Tables I and II).



12

14

15

R= $-CH_2-CO-O-(CH_2)_2-O-CO-CH_2-$

SCHEME 2

The substitution reaction proceeds by an addition-elimination mechanism.[6] First an addition of the reagent to the C,C double bond

TABLE I Analytical and IR Spectroscopic Data of the New Chlorobutadienes

Molecular Formula (Yield %)	M.P. (°C)	Elemental Analysis Calcd. (found)				$R_{f:}$ (Solvent)	Molecular Mass MS : (m/z)	IR (cm^{-1})
		C	H	N	S			
3a $C_{25}H_{22}N_3Cl_3SO_3$	149–150	54.51	4.03	7.63	5.82	0.25 ($CHCl_3$)	—	3000, 3020 (C—H), 1280, 1500 (C—NO_2),
(45)		(54.49)	(4.20)	(7.62)	(5.96)			1540, 1600 (C=C)
3b $C_{19}H_{16}N_3Cl_3SO_3$	Oil	48.27	3.41	8.89	6.78	0.62 (EtAc.) -	—	2985 (C—H), 1550, 1590 (C=C)
(39)		(48.05)	(3.53)	(8.58)	(6.71)			1270, 1520 (C—NO_2), 1700 (C=O)
3c $C_{24}H_{19}N_3Cl_3SFO_2$	176–177	53.49	3.55	7.80	5.95	0.46 ($CHCl_3$)	539.80	2980, 3000 (C—H), 1270, 1510 (C—NO_2),
(93)		(52.85)	(3.33)	(7.73)	(6.03)			1570, 1605 (C=C)
5 $C_{21}H_{19}N_2Cl_3SO_4$	188–189	50.26	3.82	5.58	6.39	0.46 (EtAc/petrolumether)	—	3000, 3020 (C—H), 1570, 1610 (C=C)
(62)		(49.68)	(3.97)	(5.51)	(6.98)	(1:1)		1290, 1520 (C—NO_2)
7 $C_{19}H_{18}N_3Cl_3SO_2$	Oil	49.74	3.95	9.16	6.99	0.24 (EtAc)	458.97	2970, 3000 (C—H), 1595, 1620 (C=C),
(66)		(49.54)	(3.57)	(9.64)	(7.05)			1290, 1500 (C—NO_2), 3520 (NH)
9 $C_{31}H_{26}N_3Cl_3SO_2$	Oil	60.94	4.29	6.88	5.25	0.61 (EtAc/petrolumether)	—	2980, 3010 (C—H), 1570, 1600 (C=C),
(42)		(60.87)	(4.07)	(6.97)	(5.02)	(1:2)		1270, 1500 (C—NO_2)
11 $C_{20}H_{20}N_3Cl_3SO_3$	137–138	49.14	4.12	8.60	6.56	0.37 (EtAc/petrolumether)	—	3000 (C—H), 1570, 1600 (C=C),
(85)		(49.42)	(4.67)	(8.62)	(6.98)	(1:1)		1295, 1540 (C—NO_2), 3520 (NH),
14 $C_{24}H_{16}Cl_{14}S_4O_8$	Oil	27.27	1.53	—	12.13	0.45 ($CHCl_3$/petrolumether)	—	2990, 3000 (C—H), 1545, 1600 (C=C),
(25)		(27.60)	(2.00)	—	(12.99)	(2:1)	—	1720 (C=O)
15 $C_{14}H_8Cl_{10}S_2O_4$	Oil	25.52	1.22	—	9.73	0.47 ($CHCl_3$/petrolumether)	—	3010 (C—H), 1720 (C=O),
(14)		(25.64)	(1.76)	—	(9.69)	(1:1)	—	1570, 1620 (C=C)

TABLE II ^{1}H and ^{13}C NMR Data for the New Chlorobutadienes

		^{1}H/^{13}CNMR ($CDCl_3$) δ (ppm)
3a	^{1}H	6.84–8.03 (m, 11H, Ar-H), 3.81 (s, 3H, OCH_3), 2.74–3.77 (m, 8H, CH_2)
	^{13}C	49.6, 53.8, 55.7, 111.7, 120.1, 121.2, 124.1, 125.6, 127.1, 127.7, 127.9, 128.2, 129.1, 130.3, 132.8, 133.3, 134.0, 139.9, 152.5, 161.8.
3b	^{1}H	8.03 (s, 1H, CHO), 7.19–7.95 (m, 7H, Ar-H), 2.19–3.62 (m, 8H, CH_2)
3c	^{1}H	6.52–7.80 (m, 11H, Ar-H), 2.76–3.75 (m, 8H, CH_2)
	^{13}C	49.5, 53.5, 109.7, 116.5, 116.6, 123.8, 124.8, 125.8, 127.0, 127.7, 128.1, 128.2, 129.0, 130.4, 132.8, 133.3, 134.0, 138.8, 155.0, 156.9
5	^{1}H	7.24–8.00 (m, 7H, Ar-H), 3.89–3.96 (m, 4H, O-CH_2), 2.75–3.45 (m, 8H, CH_2)
	^{13}C	34.3, 34.9, 64.8, 106.4, 105.9, 126.8, 127.7, 127.9, 128.1, 128.3, 128.8, 130.3, 132.5, 133.2, 134.0, 154.5
7	^{1}H	7.33–7.95 (m, 7H, Ar-H), 2.82–3.74 (m, 6H, CH_2), 1.13 (s, 3H, CH_3), 2.24 (s, 1H, N-H)
	^{13}C	15.5, 41.8, 49.1, 51.0, 55.3, 109.8, 126.7, 126.6, 126.3, 128.2, 128.3, 129.0, 130.7, 132.6, 132.3, 134.3, 154.8
9	^{1}H	7.13–7.91 (m, 17H, Ar-H), 3.45–3.71 (m, 8H, CH_2), 4.10 (s, 1H, N-CH)
11	^{1}H	11.11 (s, 1H, NH), 7.20–7.96 (m, 7H, Ar-H), 3.27–3.71 (m, 8H, CH_2), 2.34–2.46 (m, 4H, N-CH_2)
	^{13}C	43.2, 53.0, 55.9, 66.7, 112.8, 126.3, 126.7, 127.2, 127.9, 128.0, 129.0, 130.3, 132.5, 132.8, 134.3, 158.2
14	^{1}H	3.4–3.8 (m, 4H, S-CH_2), 4.2 (s, 4H, O-CH_2)
	^{13}C	35.5, 62.4, 122.4, 125.0, 126.0, 132.6, 168.0
15	^{1}H	3.5–3.7 (m, 4H, S-CH_2-), 4.1 (s, 4H, O-CH_2)
	^{13}C	34.6, 61.9, 124.1, 126.0, 131.6, 137.7, 169.6

occurs, and in a second step the intermediate product is stabilized by elimination of hydrogen chloride.

EXPERIMENTAL

Elemental analyses were performed by a Carlo Erba 1106 elemental analyzer. Infrared spectra were recorded in KBr pellets or in Nujol mulls on a Shimadzu FTIR-8101 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian INOVA spectrometer. Mass spectra were obtained using Finnigan LCQ Avdantage Max. LC/MS. All chemicals and solvents were obtained commercially and used without purification. TLC was performed on precoated aluminum plates (Silicagel 60 F_{254}, Merck). Compound **1** was prepared according to a method reported earlier.[25]

Preparation of Trichlorobutadienes 3,5,7,9,11: General Procedure

1,3,4,4-Tetrachloro-napthyl(thio)-2-nitro-1,3-butadiene (0.1 g, 0.25 mmol) in 15 mL of dry ether and the respective amine in 15 mL of dry ether were stirred until completion of the reaction. Then chloroform (20 mL) was added to the reaction mixture. The organic layer was separated, washed with water (4 × 30 mL), and dried with $MgSO_4$. The solvent was eveporated and the residue was purified by crystallization from methanol. For analytical and spectroscopic data see Tables I and II.

Preparation of *S*- and *S*,*S*-Substituted Polyhalodienes: General Procedure

Hexachloro-1,3-butadiene **12** (2 g, 7.66 mmol) in 10 mL of ethanol and 1.610 g (7.66 mmol) of ethyleneglycol bismercaptoacetate **13** in 10 mL of ethanol were mixed, and 0.31 g NaOH in 8 mL of water was added at r.t. The mixture was stirred for 24 h. Then chloroform (20 mL) was added to the reaction mixture, and the organic layer was separated, washed with water (4 × 30 mL), and dried with $MgSO_4$. The solvent was eveporated, and compounds **14** and **15** were purified by column chromatography on silica gel with $CHCl_3$/petroleum ether (2:1) as an eluent. For analytical and spectroscopic data see Tables I and II.

REFERENCES

[1] C. İbiş, Z. Gökmen, and N. Y. Bozkurt, *Phosphorus, Sulfur, and Silicon*, **177,** 2907 (2002).
[2] C. İbiş and Z. Gökmen, *Phosphorus, Sulfur, and Silicon*, **179,** 2537 (2004).
[3] C. İbiş, F. S. Göksel, and G. Aydınlı, *Phosphorus, Sulfur, and Silicon*, **178,** 777 (2003).
[4] C. İbiş and N. Yılmaz, *Phosphorus, Sulfur, and Silicon*, **179,** 2543 (2004).
[5] Yu. A. Ol'dekop, R. V. Kaberdin, E. E. Buslouskaya, and I. A. Shingel, *Zh. Org. Khim.*, **15,** 1321 (1979).
[6] Yu. A. Ol'dekop, R. V. Kaberdin, and V. I. Potkin, *Zh. Org. Khim.*, **16,** 543 (1980).
[7] Yu. A. Ol'dekop, R. V. Kaberdin, and V. I. Potkin, *Zh. Org. Khim.*, **14,** 1594 (1978).
[8] Yu. A. Ol'dekop and R. V. Kaberdin, *Zh. Org. Khim.*, **12,** 2039 (1976).
[9] C. İbiş and Ç. Sayıl, *Phosphorus, Sulfur, and Silicon,* **86,** 55 (1994).
[10] C. İbiş, *Phosphorus, Sulfur, and Silicon,* **118,** 49 (1996).
[11] R. V. Kaberdin, V. I. Potkin, and V. P. Suboch, *Zh. Org. Khim.*, **29,** 1069 (1983).
[12] A. Roedig, C. İbiş, and G. Zaby, *Chem. Ber.*, **114,** 684 (1981).
[13] Diamond Alkali Company (Ert. H. Bluestone), U.S. Pat. No. 3021370, 1962; *Chem. Abstr.*, **57,** 3293c (1962).
[14] C. İbiş and Ç. Gürün, *Phosphorus, Sulfur, and Silicon,* **83,** 119 (1993).
[15] C. İbiş, *Liebigs Ann. Chem.*, **11**, 1873 (1984).
[16] C. İbiş, *Liebigs Ann. Chem.*, 1009 (1987).
[17] C. İbiş and Ç. Sayıl, *Phosphorus, Sulfur, and Silicon*, **92,** 39 (1994).

[18] C. İbiş, F. S. Göksel, and Ç. Sayıl, *Phosphorus, Sulfur, and Silicon*, **107,** 227 (1995).
[19] I. Soladin and T. D. Heat, *Synlett.*, **7,** 619 (1996).
[20] S. Zhao and A. K. Miller, *Tetrahedron Lett.*, **37,** 4463 (1996).
[21] V. Ceccletti and A. Fravolini, *J. Med. Chem.*, **39,** 4952 (1996).
[22] P. Besse, B. Combourie, P. Poupin, M. Sancelme, N. Truffaut, H. Veschambre, et al., *Journal Molecular Catalysis B. Enzymatic*, **5,** 403 (1998).
[23] U. Singh, B. Raju, S. Lam, J. Zhou, R. C. Gadwood, C. W. Ford, et al., *Bioorg. Med. Chem. Lett.*, **13,** 4209 (2003).
[24] J. Ong, V. Marino, D. A. S. Porker, D. I. B. Kerr, and D. J. Blythin, *Eur. J. Pharm.*, **369,** 33 (1999).
[25] C. İbiş, F. S. Göksel, and Ç. Sayıl, *Phosphorus, Sulfur, and Silicon*, **97,** 165 (1994).
[26] A. Roedig, G. Zaby, and W. Scharf., *Chem. Ber.*, **110,** 1484 (1977).
[27] C. İbiş, *Bull. Soc. Chim. Belg.,* **105,** 317 (1996).
[28] C. İbiş and Ç. Gürün, *Phosphorus, Sulfur, and Silicon,* **72,** 225 (1992).
[29] A. Roedig and G. Zaby, *Liebigs Ann. Chem.*, **10**, 1626 (1979).