Revue Roumaine de Chimie, **2007**, *52*(10), 957–960

THE REACTIONS OF NAPHTHYL AND ETHYL THIO SUBSTITUTED 2-NITRODIENE WITH AMINES

Cemil İBİŞ* and Zeliha GÖKMEN

Istanbul University, Engineering Faculty, Department of Chemistry, Avcılar-Istanbul, TURKEY

Received April 19, 2002

Thio substituted compound **1** gave **3a-d** compounds with **2a-d** compounds in CH_2Cl_2. Compounds **5a-c** were obtained from the reactions of compound **1** with piperidines **4a-c**. Compound **1** gave compound **7** with piperazine **6** and at the same time it gave compound **9** with *ortho*-phenylenediamine **8**. Compound **11, 12** and **14** were obtained from the reactions of compound **10** with piperidine, piperazine and morpholine.

INTRODUCTION

It was reported that mono-, bis- and tris butadiene compounds were synthesized from the reactions of 2-nitrodiene compounds with thiols.[1-8] It is known that the reactions of nitrodiene compound [Cl_2C=CCl-C(NO_2)=CCl_2] with some amines.[9-14] We reported the reactions of some thio substituted 2-nitrodiene compounds with some amines which we synthesized before.

In this work, we synthesized new N,S-substituted diene compounds from the reactions of naphthyl and ethyl substituted 2-nitrodiene with piperazines, piperidines, *ortho*-phenylendiamine and morpholine. The structures of these compounds result from their spectroscopic data and are supported by microanalysis.

We have obtained compound **1** from 2-nitropentachloro-1,3-butadiene [Cl_2C=CCl-C(NO_2)=CCl_2] before.[15]

It is known that several piperazine derivatives are important for clinic chemistry and gen transfer.[16,17]

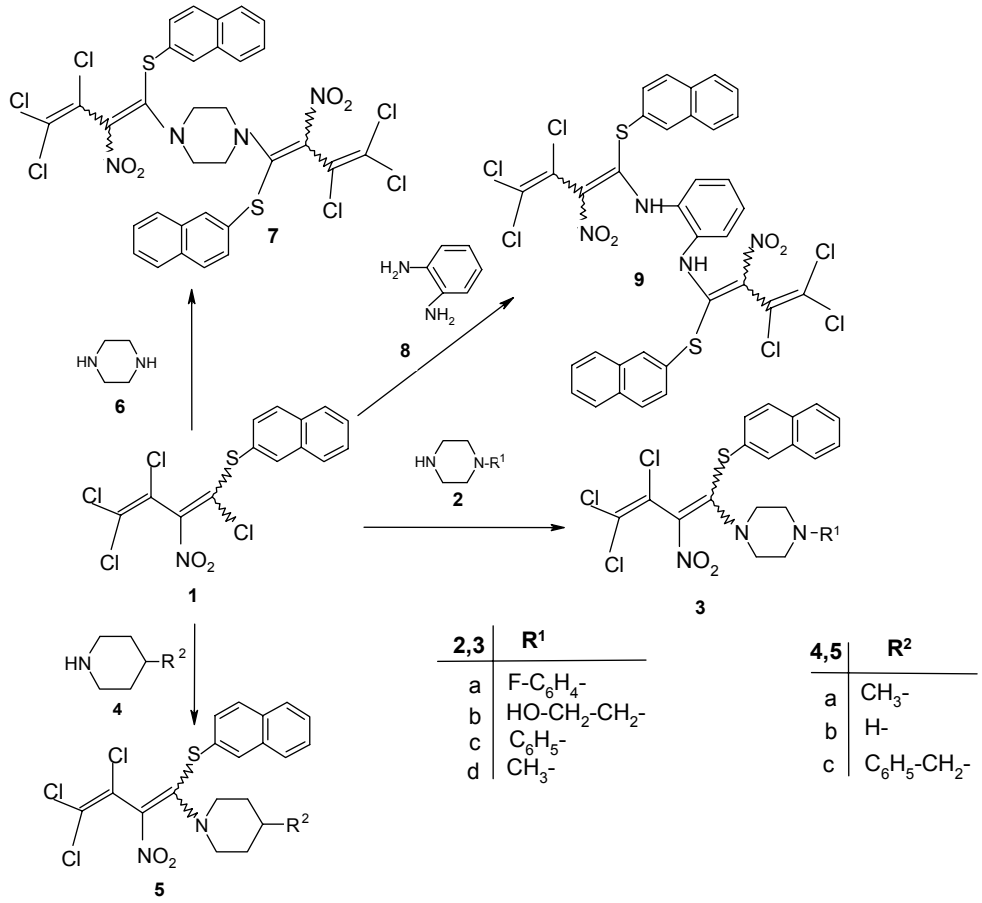
N,S-Substituted 2-nitrodiene **3a-d** compounds were obtained from the reactions of compound **1**[18] with compounds **2a-d**. The Infrared spectra of OH groups in compound **3b** shows characteristic signals for OH group at ν= 3490 cm^{-1}. Compounds **5a-c** were obtained from the reactions of compound **1** with compounds **4a-c**.

Nitrodiene compound **1** gave compound **7** with piperazine and at the same time it gave compound **9** with *ortho*phenylenediamine These compounds which are obtained from these reactions are dibutadienyl piperazine **7** and dibutadienyl amine **9** compounds. Compounds **3a-d, 5a-c, 7** and **9** were obtained from compound **1** with removing HCl. The removing HCl gives salt with amine or obtained amines. This salt gives free amine by stirring with NaOH. The ^{1}H-NMR spectra of compound **9** shown singlet signal at δ= 12.6 ppm for –NH group. (Scheme 1).

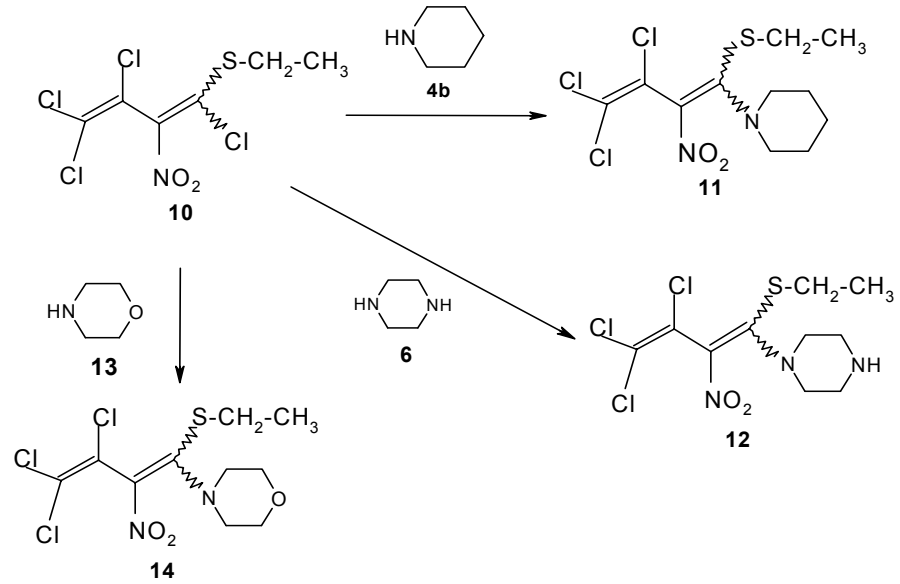
N,S-Substituted compounds **11, 14, 12** were obtained from the reactions of compound **10**[19] with piperidine, morpholine and piperazine respectively (Scheme 2).

The compounds **3a-d, 5a-c, 7, 9, 11** and **12** are yellow and stable compounds. From the spectroscopic data and related literature it can be concluded that these new compounds are formed by the substitution of chlorine atoms to the first carbon of nitrodiene with nitrogen nucleophiles. The reactions formed with addition-elimination mechanism. The structures of these compounds result from their spectroscopic data and are supported by microanalysis.

* Corresponding author: ıbıscml@istanbul.edu.tr.



Scheme 1



Scheme 2

EXPERIMENTAL

-^{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 63-200μm). –TLC plates silica 60 F_{254} (Merck, Darmstadt), detection with ultraviolet light (254nm).

Synthesis of N,S-Substituted Polyhalonitrodienes.–General Procedure*:* Appropriate amounts of 1,3,4,4-tetrachloro-1-(2-

naphthylthio)-2-nitro-1,3-butadiene **1** or 1,3,4,4-tetrachloro-1-ethylthio-2-nitro-1,3-butadiene **10** 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 separated, washed with water (4x30 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-(4-flurophenylpiperazine)-1-(2-naphthylthio)-2-nitro-1,3-butadiene **(3a)***:* Compound **3a** was synthesized from **1** (0.103 g, 0.26 mmol) and 1-(4-fluorophenyl)piperazine (**2a**) (0.047 g, 0.26 mmol) according to the General procedure. Crystallisation in methanol gave 0.096 g (69 %) of **3a.** R_f =0.6562 ($CHCl_3$/Petroleumether 2:1). -M.p. 177-178 ^oC. -IR(KBr): υ= 3000, 2970 cm^{-1} (C-H), 1550 (C=C), 1510, 1270 (C-NO_2). -^{1}H-NMR ($CDCl_3$,TMS int.) : δ= 6.6-8.1 (m, 11H, 11Ar-H), 2.6-3.9 (m, 8H, 4CH_2). $C_{24}H_{19}Cl_3FN_3O_2S$ (538.859). Calcd. C 53.49; H 3.55; N 7.79 ; found C 53.90 ; H 3.36 ; N 7.63. -MS:539.0.

3,4,4-trichloro-1-(2-hydroxy–ethylpiperazine)-1-(2-naphthylthio)-2-Nitro-1,3-butadiene **(3b):** Compound **3b** was synthesized from **1** (0.145 g, 0.37 mmol) and 1-(1-(2-hydroxyethyl)-piperazine (**2b**) (0.047 g, 0.37 mmol) according to the General procedure. Crystallisation in methanol gave 0.102 g (58 %) of **3b.** R_f =0.5 (Ethylacetate). -M.p. 188-189 ^oC. -IR(KBr): υ= 3490 cm^{-1} (OH), 3000, 2970 (C-H), 1590 (C=C), 1540, 1290 (C-NO_2). -^{1}H-NMR ($CDCl_3$,TMS int.) : δ= 7.3-8.1 ppm (m, 7H, Ar-H), 3.4-3.8 (m, 12H, 6CH_2), 1.5-2.5 (m, 1H, OH). $C_{20}H_{20}Cl_3N_3O_3S$ (488.823). calcd. C 49.14; H 4.12; N 8.59; found C 48.46 ; H 3.90 ; N 8.41.

3,4,4-trichloro-1-(2-naphthylthio)-1-(N-Phenylpiperazine)-2-Nitro-1,3-butadiene **(3c):** Compound **3c** was synthesized from **1** (0.139 g, 0.35 mmol) and N-Phenylpiperazine (**2c**) (0.057 g, 0.35 mmol) according to the General procedure. Crystallisation in methanol gave 0.115g (62 %) of **3c.** R_f=0.53 ($CHCl_3$/Petroleumether 2:1). -M.p. 195-196 ^oC. - IR(KBr,): υ= 3010, 2980 cm^{-1} (C-H), 1600, 1570 (C=C), 1500, 1290 (C-NO_2). -^{1}H-NMR ($CDCl_3$, TMS int.) : δ= 6.8-8.0 (m, 12 H, Ar-H), 2.8-4.0 (m, 8H, 4 CH_2). $C_{24}H_{20}Cl_3N_3O_2S$ (520.869). calcd. C 55.34; H 3.87; N 8.06; found C 55.44 ; H 3.78 ; N 7.99.

3,4,4-trichloro-1-(1-methylpiperazine)-1-(2-naphthylthio)--2-Nitro-1,3-butadiene **(3d):** Compound **3d** was synthesized from **1** (0.1 g, 0.25 mmol) and 1-methylpiperazine (**2d**) (0.025 g, 0.25 mmol) according to the General procedure. Crystallisation in methanol gave 0.099 g (86 %) of **3d.** R_f = 0.367 ($CHCl_3$). -M.p. 169-170 ^oC. -IR(KBr): υ= 3005, 2990 cm^{-1} (C-H), 1600 (C=C), 1525, 1280 (C-NO_2). -^{1}H-NMR ($CDCl_3$, TMS int.) : δ= 7.2-8.0 ppm (m, 7H, Ar-H), 3.2-3.8 (m, 8H, 4CH_2), 1.95-2.4 (m, 3H, CH_3). $C_{19}H_{18}Cl_3N_3O_2S$ (458.797). calcd. C 49.74; H 3.95; N 9.15; found C 49.00; H 3.70 ; N 9.10. -MS: 460.

3,4,4-trichloro-1-(4-methylpiperidino)-1-(2-naphthylthio)-2-Nitro-1,3-butadiene **(5a):** Compound **5a** was synthesized from **1 (**0.12 g, 0.30 mmol) and 4-methylpiperidine (**4a**) (0.03 g, 0.30 mmol) according to the General procedure. Crystallisation in methanol gave 0.098 g (71 %) of **5a.** R_f =0.57 ($CHCl_3$/Petroleumether 1:1). -M.p. 173-174 ^oC. - IR(KBr): υ= 3010, 2990 cm^{-1} (C-H), 1600 (C=C), 1540, 1290 (C-NO_2). -^{1}H-NMR ($CDCl_3$, TMS int.) : δ= 7.2-8.0 (m, 7H, Ar-H), 3.4-4.1 (m, 1H, CH), 3.1-3.3 (m, 4H, 2CH_2), 1.4-1.8 (m, 4H, 2CH_2), 0.5-1.0 (m, 3H, CH_3). $C_{20}H_{19}Cl_3N_2O_2S$ (457.809). calcd. C 52.47; H 4.18; N 6.11; found C 52.44 ; H 3.96 ; N 6.77. -MS: 448.0.

3,4,4-trichlro-1-(2-naphthylthio)-1-(piperidino)-2-Nitro-1,3-butadiene **(5b):** Compound **5b** was synthesized from **1 (**0.1 g, 0.25 mmol) and piperidine (**4b**) (0.022g, 0.25 mmol) according to the General procedure. Crystallisation in methanol gave 0.054 g (47 %) of **5b.** R_f =0.625 ($CHCl_3$/Petroleumether 1:1). -M.p. 165-166 ^oC. -IR(KBr): υ= 3005, 2970 cm^{-1} (C-H), 1590 (C=C), 1530, 1295 (C-NO_2). -^{1}H-NMR ($CDCl_3$, TMS int.): δ= 7.2-8.0 (m, 7H, Ar-H), 0.8-1.8, 3.2-3.8 (m, 10H, 5CH_2). $C_{19}H_{17}Cl_3N_2O_2S$ (443.782). calcd. C 51.42; H 3.86; N 6.31; found C 51.49 ; H 3.88 ; N 6.61. -MS: 444.0.

3,4,4-trichloro-1--(4-benzylpiperidino)-1-(2-naphthylthio)-2-Nitro-1,3-butadiene **(5c):** Compound **5c** was synthesized from **1 (**0.1 g, 0.25 mmol) and 4-benzylpiperidine (**4c**) (0.044g, 0.25 mmol) according to the General procedure. Crystallisation in methanol gave 0.097 g (72 %) of **5c.** R_f =0.58 ($CHCl_3$/Petrol–eumether 1:1). -M.p. 138-139 ^oC. -IR(KBr): υ= 3010, 2980 cm^{-1} (C-H), 1590 (C=C), 1510, 1280 (C-NO_2). -^{1}H-NMR ($CDCl_3$, TMS int.) : δ= 6.8-8.1 (m, 12H, Ar-H), 3.4-4.1 (m, 1H, CH), 3.0-3.3 (m, 4H, 2CH_2), 1.2-1.8 (m, 4H, 2CH_2), 2.1-2.3 (m, 2H, CH_2). $C_{26}H_{23}Cl_3N_2O_2S$ (533.908). calcd. C 58.49; H 4.34; N 5.24 ; found C 58.72; H 4.18; N 5.18.

N,N'-Bis(3,4,4-trichloro-1-(2-naphthylthio)-2-Nitro-1,3-butadienyl)-piperazine **(7):** Compound **7** was synthesized from **1 (**0.1 g, 0.025 mmol) and piperazine (**6**) (0.022g, 0.025 mmol) according to the General procedure. Crystallisation in methanol gave 0.074 g (36 %) of **7.** R_f =0.2424 (Ethylacetate). -M.p. 176-177^oC. -IR(KBr): υ= 3005, 2970 cm^{-1} (C-H), 1610, 1550 (C=C), 1500, 1290 (C-NO_2). -^{1}H-NMR ($CDCl_3$, TMS int.) : δ= 7.3-8.1 (m, 14H, Ar-H), 3.1-3.8 (m, 8H, 4 CH_2). $C_{32}H_{22}Cl_6N_4O_4S_2$ (803.403). calcd. C 47.84; H 2.76; N 6.97; S 7.08; found C 47.64; H 3.12; N 7.12 ; S 7.73 .

N,N-Bis(3,4,4-trichloro-1-(2-naphthylthio)-2-Nitro-1,3-butadienyl)-orthophenylendiamine (**9**)**:** Compound **9** was synthesized from **1** (0.1 g, 0.025 mmol) and orthophenylendiamine (**8**) (0.022g, 0.025mmol) according to the General procedure. Crystallisation in methanol gave 0.074 g (36 %) of **9.** R_f = 0.8125 (CH_2Cl_2 / Petroleumether 1:1). -M.p. 188-189 ^oC. -IR(KBr): υ= 3470, 3500 cm^{-1} (NH), 3020, 2995 (C-H), 1610, 1590 (C=C), 1520, 1290 (C-NO_2). -^{1}H-NMR ($CDCl_3$, TMS int.) : δ= 7.0-7.8 (m, 18 H, Ar-H), 12.6 (m, 2H, 2NH). $C_{34}H_{20}Cl_6N_4O_2S_2$ (825.409). calcd. C 49.47; H 2.44; N 6.78; found C 49.31; H 2.55; N 6.86.

3,4,4-trichloro-1-(2-ethylthio)-1-(4-morpholino)-2-Nitro-1,3-butadiene **(14):** Compound **14** was synthesized from **10** (0.1 g, 0.33 mmol) and morpholine (**13**) (0.029g, 0.33 mmol) according to the General procedure. Crystallisation in methanol gave 0.052 g (27 %) of **14.** R_f =0.4545 (CH_2Cl_2/Hexane 1:1). -M.p. 153-154^oC. -IR(KBr): υ= 2985, 2970 cm^{-1} (C-H), 1600 (C=C), 1530, 1285 (C-NO_2). -^{1}H-NMR ($CDCl_3$, TMS int.): δ= 3.6-4.2 ppm (m, 8H, 4CH_2), 2.9-3.1 (m, 2H, CH_2), 1.3-1.5 (m, 3H, CH_2). $C_{10}H_{13}Cl_3N_2O_3S$ (347.220). calcd. C 34.56; H 3.74; N 8.06; found C 34.36 ; H 3.74 ; N 7.93.

3,4,4-trichloro-1-(2-ethylthio)-1-(4-piperazine)-2-Nitro-1,3-butadiene **(12):** Compound **12** was synthesized from **10** (0.1 g, 0.33 mmol) and piperazine (**6**) (0.028g, 0.33 mmol) according to the General procedure. Crystallisation in methanol gave 0.047 g (42 %) of **12.** R_f =0.80 (CH_2Cl_2). -M.p. 226-227^oC. –IR (KBr): υ= 3450 cm^{-1} (N-H), 2990 (C-H), 1610, 1600 (C=C), 1520, 1300 (C-NO_2).$C_{10}H_{14}Cl_3N_3O_2S$ (345.666). calcd. C 34.64; H 4.07; N 12.12; found C 34.21 ; H 3.65 ; N 11.98.

3,4,4-trichloro-1-(2-ethylthio)-1-(4-piperidino)-2-Nitro-1,3-butadiene **(11):** Compound **11** was synthesized from **10** (0.1 g, 0.33 mmol) and piperidine (**4b**) (0.028g, 0.33 mmol) according to the General procedure. Crystallisation in methanol

gave 0.10 g (89 %) of **11.** R_f=0.481 (CH_2Cl_2/ Petroleumether 1:1). -M.p. 89-90°C. -IR(KBr): υ= 3000, 2990 cm^{-1} (C-H), 1620, 1600 (C=C), 1520, 1290 (C-NO_2). $C_{11}H_{15}Cl_3N_2O_2S$ (344.638). calcd. C 38.22; H 4.37; N 8.10; found C 38.20 ; H 4.29; N 8.0.

Acknoledgements: We thank the Research Fund of the University of Istanbul for financial support of this work.

REFERENCES

1. Yu. A. Ol'dekop, R. V. Kaberdin and V. I. Potkin, *Zh.Org. Khim.*, **1980,** *16*, 543.
2. C. İbiş, *Liebigs Ann. Chem.*, **1984,** 1873.
3. A. Roedig, G. Zaby and W. Scharf, *Chem.Ber.* **1977**, *110*, 1484.
4. C. İbiş, *Phosphorus, Sulfur and Silicon*, **1996**, *118*, 49.
5. V. I. Potkin, R. V. Kaberdin and Yu. A. Ol'dekop, *Zh.Org. Khim.*, **1986**, *22*, 1389.
6. C. İbiş and Ç. Sayıl, *Phosphorus, Sulfur and Silicon,* **1995,** *106*, 29.
7. C. İbiş, *Phosphorus, Sulfur, and Silicon*, **1997,** *130*, 79.
8. V. I. Potkin and R. V. Kaberdin, *Zh.Org. Khim.*, **1993,** *29*, 56.
9. C. İbiş and Ç. Sayıl, *Synth. Commun.*, **1994**, *29*, 2797.
10. C. İbiş and Z. Gökmen, *Phosphorus, Sulfur and Silicon*, **1998,** *143***,** 67.
11. C. İbiş and N. Yılmaz, *Phosphorus, Sulfur and Silicon*, **2000**, *159,* 87.
12. C. İbiş and G. Aydınlı, *Sulfur Letters*, **1999**, *23*, 67.
13. C. İbiş, W. M.Dıb Brımo and G. Aydınlı, *Phosphorus, Sulfur, and Silicon*, **2001,** *170*, 221.
14. V. I. Potkin and R. V. Kaberdin, *Zh.Org.Khim.*, **1994,** *30*, 1368.
15. Yu. A. Ol'dekop and R. V. Kaberdin, *Zh.Org. Khim.*, **1976,** *12*, 2039.
16. I. Soladin and T. D. Heat, *Synlett*, **1996**, *7*, 619.
17. V. Ceccletti and A. Fravolini, *J. Med. Chem.,* **1996**, *39*, 4952.
18. C. İbiş and F. S. Göksel, *Phosphorus, Sulfur and Silicon*, **1994**, *97*, 165.
19. C. İbiş and Ç. Sayıl, *Phosphorus, Sulfur and Silicon*, **1994**, *92*, 39.