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Regioselective Substitution of Vinyl Halide by *n*-Alkyl Mercaptans and Subsequent Reactions with Versatile Cyclic Secondary Amines

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Herein, we have described the preparation of several S-subtituted nitrobuta-1,3-dienes (**3a-b**) using the 4-bromo-1,1,3,4-tetrachloro-2-nitrobuta-1,3-diene (**1**) with mercaptans (**2a-b**). Afterwards, N,S-substituted nitrobuta-1,3-diene compounds (**5a**, **7b** and **9a-j**) are obtained from the interaction of versatile secondary amines with the substituted product S-substituted nitrobuta-1,3-dienes (**3a-b**) in dichloromethane. Synthesized compounds have been characterized by using IR and NMR spectroscopy methods. Structural characterization is supported by elemental analysis and by mass spectrometry with accurate mass measurement of the molecular ion.

Key Words: Nitro compounds, N,S-Substituted nitrodienes, Morpholine, Piperazine derivatives.

INTRODUCTION

The regioselective substitutions of halogen atoms of vinyl halides by -SH, -NH_2, -NHR, -OH and other nucleophilic groups is well studied reaction. Several mechanisms are known, but the most important is the S_NVinylic Mechanism, operating under mild reaction conditions and usually requiring -NO_2 (or other electron-withdrawing groups such as >C=O or -CN) activated vinyl halides[1-3]. Using appropriate reactants, the substitution of halogen atoms by nucleophilic moieties containing -SH, -NH_2, -NHR, -OH groups, *etc.*, can proceed affording different kinds of heterocyclic systems; *e.g.*, nitrogen and/or sulfur containing heterocycles prepared according to this method including imidazolidines[4], thiazolidines, dithiolanes[5], *etc*.

Aside from the viewpoint of the reactivity advantages, some subsequent reactions of the polyhalogenobuta-1,3-dienes bearing electron-withdrawing substituents such as nitro group as the exemplary starting compounds have been investigated due to finding ample use in many important fields ranging from nucleophilic substitution and ring cleavage to addition reactions[6-9]. Nitro-substituted polyhalogenobuta-1,3-diene derivatives, in particular, are being explored for their application to photosensitive materials, plant protecting agents, anti-tumour preparations[10] showing *in vitro* activity against tumours and also in controlling animal pests[11].

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Substitution reactions have been *hitherto* published dealing with the reactions of numerous nucleophilic reagents such as thiols, dithiols and amine derivatives with perhalo-2-nitrobuta-1,3-diene, perhalobuta-1,3-diene and 2*H*-perchlorobuta-1,3-diene to obtain S-, N,N-, S,S-, S,S,S-, N,N,N-, S,S,S,S-, N,S-substituted diene compounds[12-19]. The product distribution is highly sensitive to modification of the reaction conditions such as molar ratios of substrates, reagents and basicity of the reaction medium[20].

EXPERIMENTAL

Melting points were determined with a Buchi apparatus B-540 and uncorrected. All reagents and solvents were commercially available and used without further purification. TLC was carried out on Merck DC-plates (aluminum based) silica gel (60 F_{254}) for monitoring reactions. Column chromatographic separations were carried out on silica gel 60 (Merck, particle size 63-200 μm). ^{1}H NMR and ^{13}C NMR spectra were recorded with VarianUNITY INOVA spectrometers with 500 MHz frequency for ^{1}H and 125 MHz frequency for ^{13}C NMR. ^{1}H NMR spectra and ^{13}C NMR spectra in $CDCl_3$ refer to the solvent signal center at $\delta = 7.26$ and $\delta = 77.0$ ppm, respectively. IR spectra were recorded for liquids as film and for solids as (KBr) discs on a Shimadzu FTIR 8101 spectrometry. Microanalyses were carried out with a Carlo Erba Elemental Analyzer 1106. UV spectra were recorded in UV-VIS spectrophotometer TU-1901. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX MS/MS spectrometer according to either APCI or ESI techniques.

4-Bromo-1,3,4-trichloro-2-nitro-1-octylthio-buta-1,3-diene (3a): At room temperature *n*-octyl mercaptan (1.39 g, 9.5 mmol) was added to a stirred nitrodiene **1** (3 g, 9.5 mmol). After stirring for 24 h, chloroform was added to the reaction mixture. The organic layer was separated and washed with water (4 × 20 mL) and dried with $MgSO_4$. After evaporation of the solvent, the crude product was purified *via* column chromatography on silica gel as slightly yellow oil (2.17 g, 53.8 %). R_f (CCl_4) 0.57; ν_{max}/cm^{-1} 2900 (C-H_{aliph}), 1580 (C=C), 1300, 1540 (NO_2) (neat); λ_{max}/nm 350 (log ε, 4.08); ^{1}H NMR (500 MHz) δ 0.81 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.21-1.42 (m, 10H, $(CH_2)_5$), 1.68 (m, ^3J = 7.32 Hz, 2H, SCH_2CH_2), 3.07 (t, ^3J = 7.32 Hz, 2H, SCH_2; ^{13}C NMR (125 MHz) δ 14.28 (CH_3), 22.81, 28.68, 28.71, 28.95, 29.22, 31.92, 36.26 (($CH_2)_7$), 115.02 (C4), 123.36 (C3), 138.82 (C2), 157.55 (C1); Found (%): C, 33.46; H, 3.17; N, 3.30; S, 7.35. Calcd. (%) for $C_{12}H_{17}NO_2SBrCl_3$: C, 33.87; H, 4.03; N, 3.29; S, 7.53.

4-Bromo-1,3,4-trichloro-2-nitro-1-pentylthio-buta-1,3-diene (3b): *n*-Pentyl mercaptan (1.16 g, 11.08 mmol) was added dropwise to a stirred nitrodiene **1** (3.5 g, 11.08 mmol) at room temperature for 24 h within 10 min. After completion of the reaction, chloroform and water were added to the reaction mixture. Then, the aqueous phase was extracted with chloroform (3 × 20 mL). The organic layer was washed twice with H_2O and dried over anhyd. $MgSO_4$. Removal of the solvent *in vacuo* afforded a crude product that was purified *via* column chromatography on silica

gel as orange thick oil (2.64 g, 62 %). R_f (petroleum ether) 0.125; ν_{max}/cm^{-1} 2900 (C-H_{aliph}), 1590 (C=C), 1300, 1540 (NO_2) (neat); λ_{max}/nm 350 (log ε, 4.11); ^{1}H NMR (500 MHz) δ 0.86 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.27-1.41 (m, 4H, $(CH_2)_2$), 1.69 (m, ^3J 7.32 Hz, 2H, SCH_2CH_2), 3.06 (t, ^3J = 7.32 Hz, 2H, SCH_2); ^{13}C NMR (125 MHz) δ 12.79 (CH_3), 21.14, 27.15, 29.86, 34.99 ($(CH_2)_4$), 115.08 (C4), 124.05 (C3), 138.80 (C2), 156.68 (C1); m/z (ESI) 383.92 (8.1 %, M^+), 381.95 (47.84 %, M^+-H), 379.95 (100 %); Found (%): C, 28.11; H, 2.93; N, 3.94; S, 7.17. Calcd. (%) for $C_9H_{11}NO_2SBrCl_3$: C, 28.19; H, 2.89; N, 3.65; S, 8.36).

Standard work-up for the synthesis of N,S-substituted polyhalogenated nitrodienes (5a, 7b and 9a-j): A suspension of amine derivatives (**4**, **6**, **8a-e**) in 25 mL dichloromethane was added to a solution of polyhalogeno-2-nitrothiobuta-1,3-dienes (**3a-b**) in 25 mL dichloromethane at the same molar ratio. The mixture was stirred at room temperature for the required reaction time, according to TLC (typically 3-6 h). After stirring for reaction time, chloroform or dichloromethane was added to the reaction mixture. The organic layer was separated and washed with water (4 × 20 mL) and dried with $CaCl_2$ or $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel.

4-Bromo-3,4-dichloro-1-(morpholin-4-yl)-2-nitro-1-octylthio-buta-1,3-diene (5a): Synthesized according to the standard work-up as yellow crystals (181 mg, 65 %), mp 91-92 ºC. R_f ($CHCl_3$) 0.55; ν_{max}/cm^{-1} 2900 (C-H_{aliph}), 1570 (C=C), 1290, 1530 (NO_2) (KBr); λ_{max}/nm 394 (log ε, 4.06); ^{1}H NMR (500 MHz) δ 0.81 (t, ^3J = 6.83 Hz, 3H, CH_3), 1.20-1.34 (m, 10H, $(CH_2)_5$), 1.57-1.66 (m, 2H, SCH_2CH_2), 2.89 (t, ^3J = 7.32 Hz, 2H, SCH_2), 3.43-3.76 (m, 8H, CH_{2piper}); ^{13}C NMR (125 MHz) δ 13.04 (CH_3), 21.58, 27.70, 28.01, 28.75, 28.81, 30.69, 34.54 ($(CH_2)_7$), 52.62 (NCH_{2piper}), 65.41 (OCH_{2piper}), 110.53 (C4), 119.20 (C3), 129.16 (C2), 167.83 (C1); m/z (ESI) 477.48 (100 %, M^+); Found (%): C, 40.67; H, 5.76; N, 6.09; S, 6.57. Calcd. (%) for $C_{16}H_{25}N_2O_3SBrCl_2$: C, 40.35; H, 5.29; N, 5.88; S, 6.73.

4-Bromo-3,4-dichloro-2-nitro-1-(1,4-dioxa-8-azaspiro-4,5-decyl-8yl)-1-pentylthio-buta-1,3-diene (7b): Synthesized according to the standard work-up as yellow thick oil (110 mg, 79 %). R_f (CH_2Cl_2) 0.15; ν_{max}/cm^{-1} 2900 (C-H_{aliph}), 1580 (C=C), 1280, 1525 (NO_2) (neat); λ_{max}/nm 240 (log ε, 3.76); ^{1}H NMR (500 MHz) δ 0.84 (t, ^3J = 6.83 Hz, 3H, CH_3), 1.19-1.64 (m, 6H, $(CH_2)_3$), 1.78-1.81 (m, 4H, CH_{2piper}), 2.88 (t, ^3J = 7.32 Hz, 2H, SCH_2), 3.66 (br s, 4H, CH_{2piper}), 3.94 (s, 4H, O-CH_2-CH_2-O); ^{13}C NMR (125 MHz) δ 12.82 (CH_3), 21.13, 28.44, 29.84, 34.31 ($(CH_2)_4$), 50.62, 52.38 (NCH_2), 63.71 (O-CH_2-CH_2-O), 104.82 (C_{arom}), 110.92 (C4), 118.62 (C3), 129.43 (C2), 168.78 (C1); m/z (ESI) 491.37 (100 %, M^+), 489.27 (44.50 %), 409.34 (21.81 %); Found (%): C, 39.62; H, 4.84; N, 5.98; S, 6.20. Calcd. (%) for $C_{16}H_{23}N_2O_4SBrCl_2$: C, 39.20; H, 4.73; N, 5.71; S, 6.54.

4-Bromo-3,4-dichloro-2-nitro-1-[N-(1-diphenylmethyl)-piperazin-1-yl]-1-octylthio-buta-1,3-diene (9a): Synthesized according to the standard work-up as slightly orange thick oil (111 mg, 49 %). R_f ($CHCl_3$) 0.67; ν_{max}/cm^{-1} 3100 (C-H_{arom}), 2900 (C-H_{aliph}), 1590 (C=C), 1310, 1525 (NO_2) (neat); λ_{max}/nm 240 (log ε, 4.34); ^{1}H

NMR (500 MHz) δ 0.88 (t, ^3J = 6.83 Hz, 3H, CH_3), 1.26-1.36 (m, 10H, $(CH_2)_5$), 1.60-1.65 (m, 2H, SCH_2CH_2), 2.55 (br s, 4H, CH_{2piper}), 2.92 (t, ^3J = 6.83 Hz, 2H, SCH_2), 3.66 (br s, 4H, CH_{2piper}), 4.28 (s, 1H, $(C_6H_5)_2CH$), 7.19-7.42 (m, 10H, $(C_6H_5)_2$); ^{13}C NMR (125 MHz) δ 14.06 (CH_3), 22.62, 28.68, 28.70, 29.04, 29.85, 31.74, 35.49 ($(CH_2)_7$), 51.71, 53.54 (NCH_2), 75.75 ($(C_6H_5)_2CH$), 109.84 (C4), 119.89 (C3), 127.52, 127.78, 128.84 (CH_{arom}), 131.36 (C2), 141.62 (C_{arom}), 169.31 (C1); m/z (APCI) 641.79 (100 %, M^+), 537.69 (10.14 %); Found (%): C, 54.34; H, 6.54; N, 6.43; S, 4.26. Calcd. (%) for $C_{29}H_{36}N_3O_2SBrCl_2$: C, 54.30; H, 5.66; N, 6.55; S, 5.00.

4-Bromo-3,4-dichloro-2-nitro-1-[N-(4-fluorophenyl)piperazin-1-yl]-1-octylthio-buta-1,3-diene (9b): Synthesized according to the standard work-up as slightly red thick oil (242 mg, 71 %). R_f ($CHCl_3$) 0.56; ν_{max}/cm^{-1} 3020 (C-H_{arom}), 2800 (C-H_{aliph}), 1580 (C=C), 1280, 1530 (NO_2) (neat); λ_{max}/nm 242 (log ε, 4.21); ^{1}H NMR (500 MHz) δ 0.81 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.18-1.34 (m, 10H, $(CH_2)_5$), 1.58-1.64 (m, 2H, SCH_2CH_2), 2.91 (t, ^3J = 7.32 Hz, 2H, SCH_2), 3.18 (s, 4H, CH_{2piper}), 3.74 (br s, 4H, CH_{2piper}), 6.83-7.19 (m, 4H, C_6H_4); ^{13}C NMR (125 MHz) δ 14.26 (CH_3), 22.80, 28.93, 29.21, 29.97, 30.02, 31.92, 35.79 ($(CH_2)_7$), 50.73, 53.26 (NCH_2), 111.74 (C4), 116.07, 119.05 (CH_{arom}), 120.69 (C3), 130.42 (C2), 146.74 (N-C_{arom}), 157.32, 159.24 (F-C_{arom}), 169.40 (CSN); m/z (ESI) 570.47 (100 %, M^+), 522.10 (100 %, M^+-NO_2), 487.95 (38.17 %); Found (%): C, 47.35; H, 5.52; N, 7.10; S, 5.37. Calcd. (%) for $C_{22}H_{29}FN_3O_2SBrCl_2$: C, 46.41; H, 5.13; N, 7.38; S, 5.63.

4-Bromo-3,4-dichloro-2-nitro-1-[N-(2-fluorophenyl)piperazin-1-yl]-1-octylthio-buta-1,3-diene (9c): Synthesized according to the standard work-up as orange crystals, m.p. 80-81 ºC (174 mg, 52 %). R_f (CH_2Cl_2) 0.62; ν_{max}/cm^{-1} 3050 (C-H_{arom}), 2900 (C-H_{aliph}), 1580, 1565 (C=C), 1310, 1530 (NO_2) (KBr); λ_{max}/nm 243 (log ε, 4.21); ^{1}H NMR (500 MHz) δ 0.88 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.26-1.42 (m, 10H, $(CH_2)_5$), 1.66-1.72 (m, 2H, SCH_2CH_2), 2.98 (t, ^{3}J = 7.32 Hz, 2H, SCH_2), 3.24 (s, 4H, CH_{2piper}), 3.82 (br s, 4H, CH_{2piper}), 6.92-7.10 (m, 4H, C_6H_4); ^{13}C NMR (125 MHz) δ 13.04 (CH_3), 21.59, 27.70, 27.72, 28.01, 28.81, 30.70, 34.55 ($(CH_2)_7$), 49.38, 52.38 (NCH_2), 110.40 (C4), 115.39 (C3), 118.40, 122.78, 123.64, 123.67 (CH_{arom}), 127.40 (C2), 137.61 (N-C_{arom}), 153.82, 155.78 (F-C_{arom}), 169.84 (C1); m/z (ESI) 570.05 (100 %, M^+), 533.91 (10.63 %, M^+-Cl), 488.09 (21.51 %); Found (%): C, 46.85; H, 4.76; N, 7.31; S, 4.88. Calcd. (%) for $C_{22}H_{29}N_3O_2SBrCl_2F$: C, 46.41; H, 5.13; N, 7.38; S, 5.63.

4-Bromo-3,4-dichloro-2-nitro-1-(N-phenylpiperazin-1-yl)-1-octylthio-buta-1,3-diene (9d): Synthesized according to the standard work-up as slightly red thick oil (304 mg, 78 %). R_f ($CHCl_3$) 0.52; ν_{max}/cm^{-1} 3020 (C-H_{arom}), 2800 (C-H_{aliph}), 1580 (C=C), 1280, 1530 (NO_2) (neat); λ_{max}/nm 249 (log ε, 4.25); ^{1}H NMR (500 MHz) δ 0.81 (t, ^3J = 6.83 Hz, 3H, CH_3), 1.20-1.35 (m, 10H, $(CH_2)_5$), 1.58-1.65 (m, 2H, SCH_2CH_2), 2.91 (t, ^3J = 6.83 Hz, 2H, SCH_2), 3.27 (s, 4H, CH_{2piper}), 3.74 (br s, 4H, CH_{2piper}), 6.85-6.89 and 7.21-7.25 (m, 5H, CH_{arom}); ^{13}C NMR (125 MHz) δ 14.26 (CH_3), 22.81, 28.92, 28.94, 29.23, 30.04, 31.92, 35.80 ($(CH_2)_7$), 49.68, 53.26 (NCH_2), 111.68 (C4), 120.52 (C3), 116.91, 121.44, 129.64 (CH_{arom}), 130.44 (C2), 150.17

(N-C_{arom}), 168.70 (C1); m/z (ESI) 552.61 (100 %, M^+), 515.75 (10.27 %, M^+-Cl), 504.11 (38.19 %, M^+-NO_2); Found (%): C, 46.71; H, 5.12; N, 7.67; S, 5.94. Calcd. (%) for $C_{22}H_{30}N_3O_2SBrCl_2$: C, 47.21; H, 5.48; N, 7.62; S, 5.82.

4-Bromo-3,4-dichloro-2-nitro-1-[N-(4-nitrophenyl)piperazin-1-yl]-1-octylthio-buta-1,3-diene (9e): Synthesized according to the standard work-up as yellow crystal, m.p. 161-162 ºC (222 mg, 59 %). R_f ($CHCl_3$) 0.37; ν_{max}/cm^{-1} 3020 (C-H_{arom}), 2900 (C-H_{aliph}), 1610 (C=C), 1310, 1530 (NO_2) (KBr); λ_{max}/nm 383 (log ε, 4.41); ^{1}H NMR (500 MHz) δ 0.81 (t, ^3J = 6.83 Hz, 3H, CH_3), 1.20-1.65 (m, 12H, $(CH_2)_6$), 2.93 (t, ^3J = 7.32 Hz, 2H, SCH_2), 3.56-3.94 (m, 8H, CH_{2piper}), 6.74-6.77 (m, 2H, CH_{arom}), 8.07-8.09 (m, 2H, CH_{arom}); ^{13}C NMR (125 MHz) δ 14.26 (CH_3), 22.80, 28.91, 29.19, 29.22, 29.92, 31.91, 35.93 ($(CH_2)_7$, 46.85, 52.21 (NCH_2), 112.03 (C4), 120.82 (C3), 113.30, 126.19 (CH_{arom}), 130.17 (C2), 139.91 (O_2N-C_{arom}), 153.89 (N-C_{arom}), 169.44 (C1); m/z (ESI) 597.13 (100 %, M^+), 549.49 (32.13 %, M^+-NO_2), 453.55 (19.84 %); Found (%): C, 44.53; H, 5.79; N, 9.48; S, 4.97. Calcd. (%) for $C_{22}H_{29}N_4O_4SBrCl_2$: C, 44.31; H, 4.90; N, 9.39; S, 5.38.

4-Bromo-3,4-dichloro-2-nitro-1-[N-(1-diphenylmethyl)-piperazin-1-yl]-1-pentylthio-buta-1,3-diene (9f): Synthesized according to the standard work-up as slightly orange thick oil (223 mg, 57 %). R_f ($CHCl_3$) 0.57; ν_{max}/cm^{-1} 3050 (C-H_{arom}), 2850 (C-H_{aliph}), 1580 (C=C), 1320, 1530 (NO_2) (neat); λ_{max}/nm 392 (log ε, 3.99); ^{1}H NMR (500 MHz) δ 0.82 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.19-1.31 (m, 4H, $(CH_2)_2$), 1.54-1.60 (m, 2H, SCH_2CH_2), 2.48 (s, 4H, CH_{2piper}), 2.85 (t, ^3J = 6.83 Hz, 2H, SCH_2), 3.61 (br s, 4H, CH_{2piper}), 4.21 (s, 1H, $(C_6H_5)_2CH$), 7.08-7.34 (m, 10H, $(C_6H_5)_2$); ^{13}C NMR (125 MHz) δ 14.04 (CH_3), 22.34, 29.72, 31.00, 35.66 ($(CH_2)_4$), 51.84, 53.75 (NCH_2), 75.89 ($(C_6H_5)_2CH$), 108.64 (C4), 121.23 (C3), 125.52, 127.98, 129.25 (CH_{arom}), 131.52 (C2), 141.79 (C_{arom}), 168.72 (C1); m/z (ESI) 599.86 (100 %, M^+), 563.81 (12.91 %, M^+-Cl), 518.02 (11.68 %); Found (%): C, 52.19; H, 5.38; N, 6.60; S, 4.48. Calcd. (%) for $C_{26}H_{30}N_3O_2SBrCl_2$: C, 52.10; H, 5.04; N, 7.01; S, 5.35.

4-Bromo-3,4-dichloro-2-nitro-1-[N-(4-fluorophenyl)piperazin-1-yl]-1-pentylthio-buta-1,3-diene (9g): Synthesized according to the standard work-up as orange crystals, m.p. 131-132 ºC (175 mg, 62 %). R_f ($CHCl_3$) 0.45; ν_{max}/cm^{-1} 3020 (C-H_{arom}), 2900 (C-H_{aliph}), 1590 (C=C), 1280, 1530 (NO_2) (KBr); λ_{max}/nm 244 (log ε, 4.19); ^{1}H NMR (500 MHz) δ 0.84 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.23-1.35 (m, 4H, $(CH_2)_2$), 1.59-1.65 (m, 2H, SCH_2CH_2), 2.91 (t, ^3J = 7.32 Hz, 2H, SCH_2), 3.17 (s, 4H, CH_{2piper}), 3.72 (br s, 4H, CH_{2piper}), 6.81-6.94 (m, 4H, C_6H_4); ^{13}C NMR (125 MHz) δ 14.07 (CH_3), 22.36, 29.71, 31.05, 35.77 ($(CH_2)_4$), 50.62, 53.34 (NCH_2), 111.69 (C4), 118.57 (C3), 116.02, 116.20, 118.87, 118.93 (CH_{arom}), 128.53 (C2), 146.90 (N-C_{arom}), 157.19, 159.10 (F-C_{arom}), 169.44 (C1); m/z (ESI) 527.95 (100 %, M^+), 470.22 (30.53 %); Found (%): C, 43.31; H, 4.50; N, 8.13; S, 5.62. Calcd. (%) for $C_{19}H_{23}N_3O_2SBrCl_2F$: C, 43.28; H, 4.40; N, 7.97; S, 6.08.

4-Bromo-3,4-dichloro-2-nitro-1-[N-(2-fluorophenyl)piperazin-1-yl]-1-pentylthio-buta-1,3-diene (9h): Synthesized according to the standard work-up as slightly orange thick oil (168 mg, 49 %). R_f ($CHCl_3$) 0.41; ν_{max}/cm^{-1} 3050 (C-

H_{arom}), 2900 (C-H_{aliph}), 1590 (C=C), 1290, 1520 (NO_2) (neat); λ_{max}/nm 243 (log ε, 4.21); ^{1}H NMR (500 MHz) δ 0.84 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.24-1.35 (m, 4H, $(CH_2)_2$), 1.59-1.65 (m, 2H, SCH_2CH_2), 2.91 (t, ^3J = 7.32 Hz, 2H, SCH_2), 3.18 (s, 4H, CH_{2piper}), 3.75 (br s, 4H, CH_{2piper}), 6.87-7.04 (m, 4H, C_6H_4); ^{13}C NMR (125 MHz) δ 14.06 (CH_3), 22.36, 29.71, 31.06, 35.75 ($(CH_2)_4$), 50.64, 53.57 (NCH_2), 111.65 (C4), 118.51 (C3), 116.81, 119.69, 124.14, 124.92 (CH_{arom}), 128.58 (C2), 138.04 (N-C_{arom}), 155.98, 156.10 (F-C_{arom}), 169.51 (C1); m/z (ESI) 527.97 (100 %, M^+), 480.13 (100 %, M^+-NO_2), 445.88 (51.51 %); Found (%): C, 43.58; H, 4.32; N, 7.72; S, 5.75. Calcd. (%) for $C_{19}H_{23}N_3O_2SBrCl_2F$: C, 43.28; H, 4.40; N, 7.97; S, 6.08.

4-Bromo-3,4-dichloro-2-nitro-1-(N-phenylpiperazin-1-yl)-1-pentylthio-buta-1,3-diene (9i): Synthesized according to the standard work-up as slightly red crystal, m.p. 92.5-94 ºC (186 mg, 67 %). R_f ($CHCl_3$) 0.35; ν_{max}/cm^{-1} 3020 (C-H_{arom}), 2850 (C-H_{aliph}), 1600, 1590 (C=C), 1280, 1525 (NO_2) (KBr); λ_{max}/nm 247 (log ε, 4.21); ^{1}H NMR (500 MHz) δ 0.84 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.21-1.49 (m, 4H, $(CH_2)_2$), 1.59-1.65 (m, 2H, SCH_2CH_2), 2.92 (t, ^3J = 7.32 Hz, 2H, SCH_2), 3.27 (s, 4H, CH_{2piper}), 3.74 (br s, 4H, CH_{2piper}), 6.85-7.40 (m, 5H, CH_{arom}); ^{13}C NMR (125 MHz) δ 14.04 (CH_3), 22.35, 29.68, 31.06, 35.77 ($(CH_2)_4$), 49.65, 53.28 (NCH_2), 111.67 (C4), 119.18 (C3), 116.87, 129.64 (CH_{arom}), 128.52 (C2), 150.22 (N-C_{arom}), 169.48 (C1); m/z (ESI) 532.62 (100 %, M^++Na), 510.45 (6.06 %, M^+); Found (%): C, 45.13; H, 4.87; N, 8.48; S, 5.91. Calcd. (%) for $C_{19}H_{24}N_3O_2SBrCl_2$: C, 44.81; H, 4.75; N, 8.25; S, 6.29.

4-Bromo-3,4-dichloro-2-nitro-1-[N-(4-nitrophenyl)piperazin-1-yl]-1-pentylthio-buta-1,3-diene (9j): Synthesized according to the standard work-up as orange crystals, m.p. 126.5-128 ºC (227 mg, 77 %). R_f ($CHCl_3$) 0.29; ν_{max}/cm^{-1} 3050 (C-H_{arom}), 2950 (C-H_{aliph}), 1580 (C=C), 1280, 1530 (NO_2) (KBr); λ_{max}/nm 381 (log ε, 4.43); ^{1}H NMR (500 MHz) δ 0.84 (t, ^3J = 7.32 Hz, 3H, CH_3), 1.24-1.66 (m, 6H, $(CH_2)_3$), 2.93 (t, ^3J = 7.32 Hz, 2H, SCH_2), 3.43-3.93 (m, 8H, CH_{2piper}), 6.75-6.80 (m, 2H, CH_{arom}), 7.47-8.08 (m, 2H, CH_{arom}); ^{13}C NMR (125 MHz) δ 12.83 (CH_3), 21.13, 28.39, 29.83, 34.70 ($(CH_2)_4$), 45.59, 51.02 (NCH_2), 110.79 (C4), 119.46 (C3), 112.05, 124.98 (CH_{arom}), 128.98 (C2), 138.60 (O_2N-Carom), 152.67 (N-C_{arom}), 168.26 (C1); m/z (ESI) 555.28 (100 %, M^+), 502.52 (16.01 %), 508.81 (5.13 %, M^+-NO_2); Found (%): C, 41.68; H, 5.13; N, 10.21; S, 4.84. Calcd. (%) for $C_{19}H_{23}N_4O_4SBrCl_2$: C, 41.17; H, 4.18; N, 10.11; S, 5.78 %.

RESULTS AND DISCUSSION

The reaction of 4-bromo-1,1,3,4-tetrachloro-2-nitrobuta-1,3-diene (**1**) with one molar equivalent of mercaptans (**2a-b**) furnishes the substituted products alkylthio-tetrahalo-2-nitrobuta-1,3-dienes (**3a-b**) under mild conditions. Likewise, synthesized alkylthio-perhalo-2-nitrobuta-1,3-dienes' namely with **3a-b** rich substitution pattern a promising candidate for subsequent substitutions makes N,S-substituted nitrodiene compounds (**5a**, **7b** and **9a-j**). We have attempted some further reactions

of the alkylthio-perhalo-2-nitrobuta-1,3-dienes as the exemplary precursors. The subsequent vinylic substitution of the 1-alkylthio-tetrahalo-2-nitrobuta-1,3-dienes (**3a-b**) in dichloromethane by means of versatile secondary cyclic amines proceed vigorously at room temperature yielding N,S-substituted nitrodiene compounds (**5a**, **7b** and **9a-j**) (Fig. 1). In conclusion, we have synthesized novel synthesis of S-substituted nitrodiene compounds starting from the easily accessible α-nitro-β,β-dichloro vinyl moiety, unsaturated compound within **1**. It is noteworthy that spectroscopic data are in accordance with those reported before[14,21].

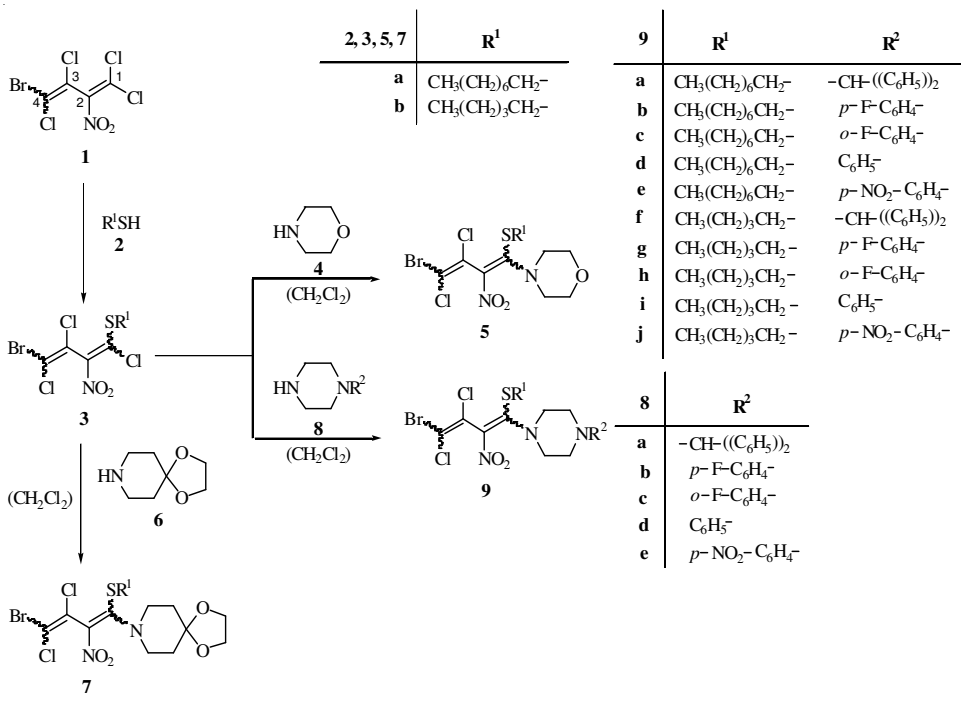

Fig. 1. Synthetic pathway of compounds **3a-b**, **5a**, **7b**, **9a-j**

Regioselective substitution is proceed these either one or two terminal halogens in the the nitrodichlorovinyl moiety of the dienes. It is known that polyhalonitrobuta-1,3-dienes are highly electrophilic compounds, capable of classical nucleophilic vinylic substitution (S_NVinylic) pathway *via* the addition-elimination route that leads to the formation of either 1-substituted-perhalonitrobuta-1,3-dienes or/and 1,1-disubstituted-perhalonitrobuta-1,3-dienes[1].

In the ^{1}H NMR spectra of compounds **9a-j**, the aromatic protons have showed typical ppm values within the range 6.81-8.09 ppm as multiplets signals from aromatic rings fall and splitting patterns (AA'BB' system).

^{13}C NMR shifts of the C-1 carbon atoms of compounds **3a** and **3b** relatively appeared in the downfield around 160 ppm, while the NO_2-bearing carbon atoms

C-2 showed their resonances at 138 ppm (the atom numbering of this compound follows the example in Fig. 1). The particular C-1 carbon atoms of the heterocyclic compounds **5a**, **7b** and **9a-j** exhibited their resonance in a range around 169 ppm, depending on the structure of the molecule, whereas the NO_2-bearing carbon atoms C-2 showed their resonances around 129 ppm. The individual C-3 and C-4 carbons each molecule of the library provides chemical shift values around 110 and 119 ppm, respectively. Additionally, employing the information from the APT ^{13}C NMR spectrum of the **9e**, we have unambiguously assigned two of four signals at 113 and 126 ppm, so it is due to -CH- of the aromatic carbon, while at 139 and 153 ppm which were assigned to quaternary carbons of the aromatic carbons.

The MS experiment for **9b** was performed in positive ion mode for ESI. The molecular ion peak [M^+] is detected at m/z 570 with strong abundance (100 %). Fragmentation of m/z 570 has yielded fragment rich product ions. The loss of a nitro group from **9b** occurs readily with 100 % at m/z 522. Notably, the other strong relative abundance of fragment ion of compound **9c** at m/z 533 appeared to be characteristic ion corresponding [M^+-Cl] being showed at m/z 570 molecular ion peak.

The UV-vis spectra of the synthesized compounds have been listed in Table-1 for each compound in $CHCl_3$ and dioxane. The spectral features for each compounds either in chloroform and dioxane observed in the UV-vis spectra showing no appreciable difference for both maximum absorption and molar absorptivity.

TABLE-1
UV-VIS DATA FOR SYNTHESIZED COMPOUNDS IN DIFFERENT SOLVENTS

Compound	Maximum absorption		Molar absorptivity	
	λ_{max}*	λ_{max}**	log ε*	log ε**
3a	350	347	4.08	4.06
3b	350	347	4.11	4.02
5a	394	386	4.06	4.01
7b	240	246	3.76	3.69
9a	240	386	4.34	3.98
9b	242	248	4.21	4.22
9c	243	247	4.21	4.23
9d	249	250	4.25	4.31
9e	383	377	4.41	4.41
9f	392	385	3.99	4.02
9g	244	246	4.19	4.24
9h	243	247	4.21	4.24
9i	247	251	4.21	4.32
9j	381	379	4.43	4.02

*$CHCl_3$; **Dioxane

Conclusion

The novel S- and N,S- substituted butadiene compounds **3a-b, 5a, 7b, 9a-j** were synthesized. Their structures were determined by micro analysis, FT-IR, ^{1}H NMR, ^{13}C NMR, MS and UV-Vis Spectroscopy. These novel compounds possess high solubility in various organic solvents such as chloroform, dichloromethane, tetrahydrofuran while insoluble in water.

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