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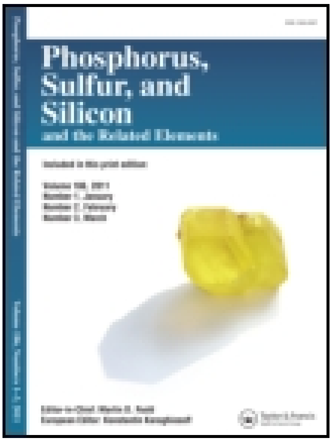

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Synthesis of Novel Thioethers and Sulfoxide Compounds

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SYNTHESIS OF NOVEL THIOETHERS AND SULFOXIDE COMPOUNDS

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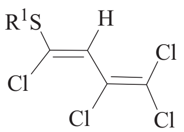
GRAPHICAL ABSTRACT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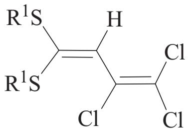
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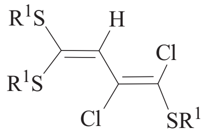
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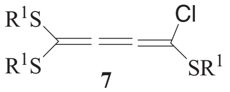
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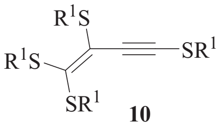
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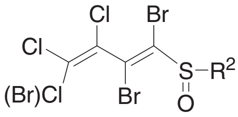
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Abstract *Thiosubstituted butadiene and butenyne compounds were synthesized from the reactions of 1,1,3,3,4,4-hexachloro-1-butene or 1,1,2,4,4-pentachlorobuta-1,3-diene with different thiols in EtOH/*H_2O *solution of NaOH. Tris(thio)substituted butadiene compound was treated with potassium tert-butoxide to obtain tris(thio)substituted butatrienyl halide compound. The novel sulfoxide compounds were synthesized from the reactions of polyhalobutadiene compounds with aliphatic thiols in* $CHCl_3$ *with m-CPBA at 0°C. The structures of the novel compounds were characterized by micro analysis, FT-IR,* ^1H*-NMR,* ^{13}C*-NMR, and MS.*

Keywords Thioethers; butatriene; sulfoxides

INTRODUCTION

Synthesis of novel butadiene and butenyne compounds containing sulfur has drawn considerable attention in organic chemistry.[1–4] One of the reasons for the synthesis of novel thioethers is an important US patent which shows the fungicidal, insecticidal, herbicidal, and nematocidal activities of a tetrakismethyl(thio)substituted butadiene compound.[5] Addition

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of sulfur to the diene structure can modify the usage of the target molecule from a sulfur-based polymer to biologically active compounds.[6,7] Thiol groups are also important in many proteins as cellular antioxidants.[8] The sulfoxides have also been paid considerable attention as synthetic intermediates to produce the biologically active compounds.[9,10]

The perhalocumulenes and sulfanyl-substituted[3]cumulenes with their unususal structures have been synthesized and reported in the literature.[11–14] The reaction of butadiene compounds with thiolates in protic or aprotic solvents leads to organyl(thio)substituted butadienes, butenynes or butatrienes.[15]

The aim of this study is the synthesis and characterization of novel thiosubstiuted butadiene, butenyne, butatriene, and sulfoxide compounds with various types of substituent.

RESULTS AND DISCUSSION

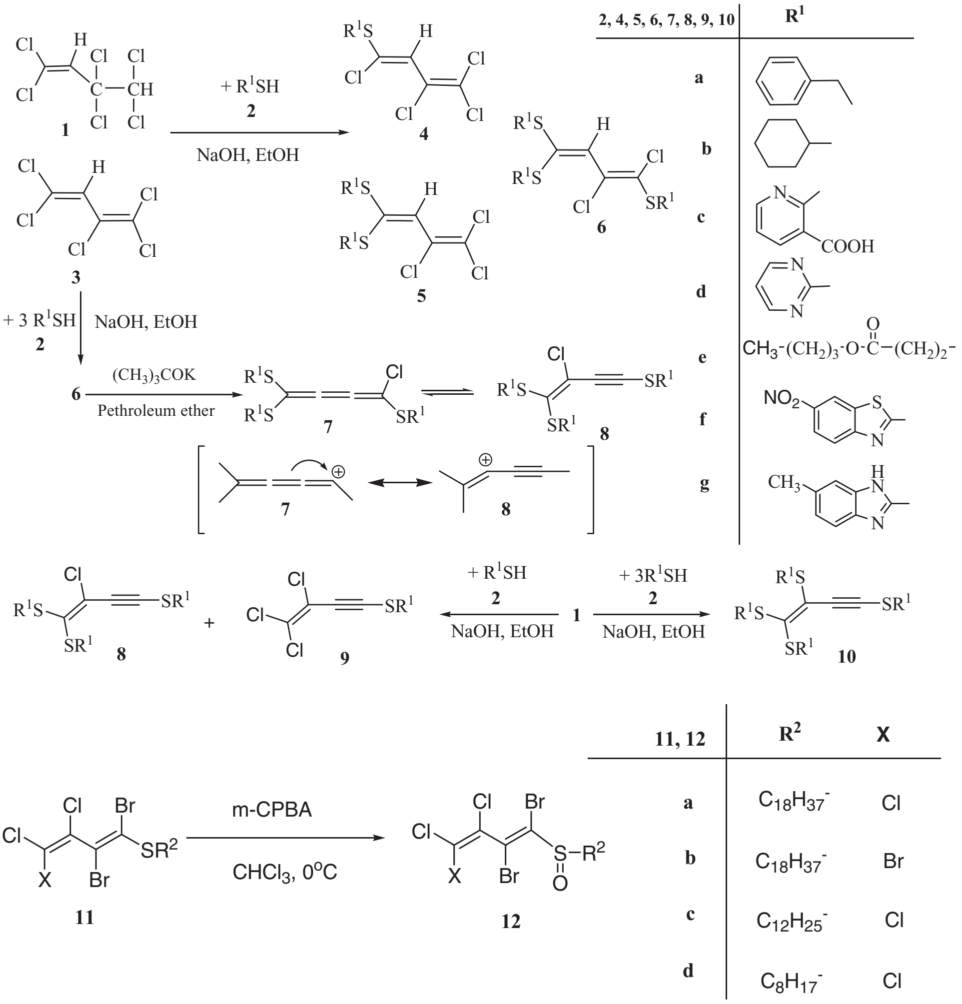
The mono(thio)substituted compound **(4c)** was synthesized from the reaction of 2H-pentachlorobutadiene **(3)** and 2-mercapto nicotinic acid **(2c)** in the presence of EtOH/H_2O solution of NaOH in good yield. (Scheme 1)

The IR spectrum of compound **(4c)** showed characteristic bands at around 2478 and 2963 cm^{-1} for the (—COOH) stretching. The reaction of 1,1,3,3,4,4-hexachloro-butene **(1)** with 2- mercaptopyrimidine **(2d)** in the presence of NaOH in ethanol at room temperature was carried out to give mono(thio)substituted compound **(4d).** The protonated molecular ion peak was observed at m/z 303 $[M+H]^+$ in the positive ion mode for ESI.

The mono(thio)substituted compound **(4f)** was synthesized from the reaction of 1,1,3,3,4,4-hexachloro-butene **(1)** and 2-mercapto-6-nitrobenzothiazole **(2f)** in the presence of EtOH/H_2O solution of NaOH. The protonated molecular ion peak of compound **(4f)** was observed at m/z 403 $[M+H]^+$ in the positive ion mode for ESI. The compound **(4g)** was synthesized from the reaction of 1,1,3,3,4,4-hexa-chloro-butene **(1)** and 2-mercapto-5-methylbenzimidazole **(2g)** in the presence of EtOH/H_2O solution of NaOH. The mass spectrum of compound **(4g)** in the negative ion mode for ESI confirms the proposed structure; the deprotonated molecular ion peak was identified at m/z 353 $[M-H]^-$. (Z)—$CCl_2 = CClCCl = CHCl$ and (E)—$CCl_2=CClCCl=CHCl$ are known from the literature.[16,17] In the ^1H NMR spectra of these compounds, the vinyl proton of *trans* isomer resonates downfield compared with the *cis* isomer. The novel mono(thio)substituted compounds **4c**, **4d**, **4f**, and **4g** gave one proton signal at around 7.00 ppm in the ^1H NMR spectra indicating (Z) isomers. The TLC experiments also gave one spot.

The bis(thio)substituted compound **(5e)** and tris(thio)substituted compound **(6e)** were synthesized from the reaction of 1,1,3,3,4,4-hexachloro-butene **(1)** and butyl-3-mercaptopropionate **(2e)** in the presence of EtOH/H_2O solution of NaOH. The ^1H NMR spectrum of compounds **(5e)** and **(6e)** exhibited the presence of vinyl protons at 5.60 and 5.61 ppm, respectively.

The reaction of 2H-pentachlorobutadiene **(3)** with three molar equivalents of benzyl mercaptan **(2a)** in the presence of NaOH in ethanol at room temperature was carried out to give tris(thio)substituted compound **(6a)**. The ^1H NMR spectrum of compound **(6a)** exhibited the presence of a vinyl proton at 6.48 ppm. Tris(thio)substituted butatriene compound **(7a)** was formed by the HCl elimination in the presence of potassium *tert*-butoxide and petroleum ether from tris(thio)substituted butadiene compound **(6a)**. The peaks at 2043 cm^{-1} in IR spectra of **(7a)** was assigned to C=C=C=C stretching vibration. The butatriene compound **(7a)** partly isomerizes to the tris(thio)butenyne compound **(8a)** at room temperature.[1]



11, 12	R^2	X
a	$C_{18}H_{37}$-	Cl
b	$C_{18}H_{37}$-	Br
c	$C_{12}H_{25}$-	Cl
d	C_8H_{17}-	Cl

Scheme 1

Tris(thio)substituted compound **(6b)** was obtained from the reaction of 2H-pentachlorobutadiene **(3)** and cyclohexanethiol **(2b)** in the presence of EtOH/H_2O solution of NaOH. The ^1H NMR spectrum of compound **(6b)** exhibited the presence of a vinyl proton at 6.88 ppm.

In our previous studies, the crystal structure of mono(thio)substituted-2-nitro-1,3-butadiene compound showed that the conjugated bond system with the EWG group, such as a nitro, has E configuration.[18] The E configuration has been also seen in the N,S-substituted-2-nitro-1,3-butadiene compounds.[19] Regarding the EWG chlorine atom, like the nitro group, it is possible to say that the compounds **6a**, **6b**, and **6e** have E configurations. The TLC experiment for compounds **6a**, **6b**, and **6e** gave one spot.

The mono-, tris- and tetrakis(thio)substituted butenyne compounds **(8e)**, **(9e)**, and **(10e)** were synthesized from the reaction of 1,1,3,3,4,4-hexa-chloro-butene **(1)** and butyl-3-mercaptopropionate **(2e)** in the presence of EtOH/H_2O solution of NaOH. The peaks at

2157, 2158, and 2157 cm^{-1} in the IR spectra of compounds **(8e)**, **(9e)**, and **(10e)** were assigned to (C≡C) stretching vibration.

The novel sulfoxide compounds **(12a–d)** were synthesized from the reactions of polyhalobutadiene compound **(11a–d)** with aliphatic thiols in $CHCl_3$ with m−CPBA at 0°C. (Scheme 1) The protonated molecular ion peak was observed at m/z (%) 617 $[M+H]^+$ at the mass spectrum of compound **(12a)** in the positive ion mode for ESI. The characteristic sulfoxide peak was observed at 1063 and 1095 cm^{-1} in the IR spectrum of compound **(12b)**. The $-CH_3$ carbon signal was seen at 14.31 ppm in the ^{13}C-NMR spectrum of compound **(12c)**. Molecular ion peak of compound **(12d)** was observed at m/z (%) 475 $[M]^+$. It is possible to say that novel compounds **12a**, **12c**, and **12d** have E-configurations because of the similar structure of compounds **6a, 6b**, and **6e**. The TLC experiments also gave one spot for these compounds.

CONCLUSION

Thiosubstituted butadiene and butenyne compounds were synthesized from the reactions of 1,1,3,3,4,4-hexachloro-1-butene or 1,1,2,4,4-pentachlorobuta-1,3-diene with different thiols in $EtOH/H_2O$ solution of with NaOH. Tris(thio)substituted butatrienyl halide compound was obtained with treating tris(thio)substituted butadiene compound with *tert*-butoxide. The novel sulfoxide compounds were synthesized from the reactions of polyhalobutadiene compounds with aliphatic thiols in $CHCl_3$ with m−CPBA at 0°C. The structures of novel thiosubstituted compounds were characterized by using spectroscopic methods.

EXPERIMENTAL

Melting points were measured using a Büchi B-540 melting point apparatus and were uncorrected. Microanalyses were performed on a Thermo Finnigan Flash EA 1112 series elemental analyzer. Infrared (IR) spectra were recorded in KBr pellets or in Nujol mulls on a Perkin Elmer Precisely Spectrum One FTIR spectrometer. The NMR spectra were recorded in $CDCl_3$ on a Varian UNITY INOVA spectrometer operating at 499.83 MHz for ^1H-NMR and 125.68 MHz ^{13}C-NMR. Chemical shifts δ are given in ppm, coupling constants in Hz. Internal standards were used: TMS for ^1H and ^{13}C resp. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS spectrometer using ion-trap mass analyzer for ESI source.

Products were isolated by column chromatography on silica gel (Fluka silica gel 60, particle size 63–200 μm). Thin-layer chromatgoraphy was performed on Merck silica gel plates ($60F_{254}$) and detection was carried out with ultraviolet light (254 nm). All reagents and solvents were of reagent-grade, obtained from commercial suppliers and used without further purification.

General Procedure 1

A mixture of 2*H*-pentachloro- 1,3-butadiene **(3)** (1.0 g, 4.4 mmol) or 1,1,3,3,4,4-hexa-chloro-butene **(1)** (1.0 g, 3.8 mmol), and thiol in ethanol (25 mL) and NaOH (1.2 g, 10 mL of water) was stirred for 24 h at room temperature. The reaction mixture was treated with water (50 mL) and extracted with CHCl3 (3 × 40 mL), and the organic layers were combined and dried (Na_2SO_4). The organic layer was evaporated and the residue was purified by column chromatography on silica gel.

General Procedure 2

An appropriate amount of tristhiosubstituted butadiene and potassium *tert*-butoxide were stirred in petroleum ether (30–50 °C) for 4 h at room temperature. Ether (3 × 40 mL) and water (50 mL) were added to the reaction mixture. The organic layer was separated and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel.

General Procedure 3

Appropriate amounts of monothiosubstituted polyhalobutadienes and 3-chlo roperbenzoic acid were mixed in chloroform (45 mL). The mixture was kept in the cold at 0°C for 24 h. After completion of the reaction, chloroform was added to the mixture and washed with 2N $NaHCO_3$ and water (4 × 30 mL). The organic layer was evaporated and the residue was purified by column chromatography on silica gel.

2-(1,1,2,4-tetrachloro-buta-1,3-dienylthio)-nicotinic acid **(4c):** Compound **(4c)** was synthesized from the reaction of 2*H*-pentachloro- 1,3-butadiene **(3)** (1.0 g, 4.4 mmol) and 2-mercaptonicotinic acid **(2c)** (0.68 g, 4.4 mmol) by the general procedure 1.

(4c): 1.72 g 57(%); m.p.: 292-294°C; R_f (Petroleum ether + Ethyl acetate 1:1): 0.47; IR (film): 3026 (=C−H_{arom}), 1567 (C=C), 2478-2963 (carboxyl –OH), 1694 (C=O); ^1H NMR ($CDCl_3$): δ 7.26 (s, 1H, H_{vinyl}), 7.48 (dd, J = 7.8 and 4.4Hz, 1H, H_{arom}), 8.36 (dd, J = 7.8 and 0.9 Hz, 1H, H_{arom}), 8.77 (dd, J = 4.4 and 0.9 Hz, 1H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 121.9, 122.3, 124.8, 125.0, 133.8, 135.7, 140.0, 153.2, 157.3 ($C_{arom,}$ $CH_{arom,}$ C_{butad}) 166.9 (C=O); $C_{10}H_5Cl_4NO_2S$ (M, 345.03). Calc: C, 34.81; H, 1.46; N, 4.06; S, 9.29. Found: C, 34.76; H, 1.73; N, 4.14 S, 9.44.

1,1,2,4-Tetrachloro-4-(pyrimidine-2-thio)-1,3-butadiene **(4d):** Compound **(4d)** was synthesized from the reaction of 1,1,3,3,4,4-hexa-chloro-butene **(1)** (1.0 g, 3.8 mmol) and 2-mercaptopyrimidine **(2d)** (0.43 g, 3.8 mmol) by the general procedure 1.

(4d): 0.20 g 17(%); Oil; R_f ($CHCl_3$): 0.53; IR (film): 3035, 2964 (=C−H_{arom}), 1552 (C=C); ^1H NMR ($CDCl_3$): δ 6.92 (s, 1H, H_{vinyl}), 7.79 (m, 3H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 117.1, 122.7, 131.6, 131.7, 131.7, 156.9, 168.6 (C_{arom}, CH_{arom}, C_{butad}); MS (ESI+): m/z 303 $[M+H]^+$; $C_8H_4Cl_4N_2S$ (M, 302.01). Calc: C, 31.82; H, 1.33; N, 9.28; S, 10.62. Found: C, 31.33; H, 1.32; N, 9.34 S, 9.72.

1,1,2,4-Tetrachloro-4-(6-nitro-benzothiazolyl-2-thio)-1,3-butadiene **(4f):** Compound **(4f)** was synthesized from the reaction of 1,1,3,3,4,4-hexa-chloro-butene **(1)** (1.0 g, 3.8 mmol) and 2-mercapto-6-nitrobenzothiazole **(2f)** (0.81 g, 3.8 mmol) by the general procedure 1.

(4f): 0.12 g 8(%); Oil; R_f ($CHCl_3$): 0.83; IR (film): 3097, 2985 (=C−H_{arom}), 1571 (C=C); ^1H NMR ($CDCl_3$): δ 7.03 (s, 1H, H_{vinyl}), 8.20 (m, 3H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 116.6, 121.9, 122.2, 124.1, 129.4, 132.9, 132.9, 135.6, 143.9, 155.7, 166.4 ($C_{arom,}$ CH_{arom}, C_{butad}); MS (ESI+): m/z 403 $[M+H]^+$; $C_{11}H_4Cl_4N_2O_2S_2$ (M, 402.10). Calc: C, 32.86; H, 1.00; N, 6.97; S, 15.95. Found: C, 32.70; H, 1.09; N, 6.34 S, 16.50.

1,1,2,4-Tetrachloro-4-(2-mercapto-5-methyl-benzimidazolyl)-1,3-butadiene **(4g):** Compound **(4g)** was synthesized from the reaction of 1,1,3,3,4,4-hexa-chloro-butene **(1)**

(1.0 g, 3.8 mmol) and 2-mercapto-5-methylbenzimidazole **(2g)** (0.43 g, 3.8 mmol) by the general procedure 1.

(4g): 0.25 g 40(%); Oil; R$_f$ (CHCl$_3$): 0.38; IR (film): 3027,2984 (=C−H$_{arom}$), 1572 (C=C), ^{1}H NMR (CDCl$_3$): δ 2.40 (s, 3H, −CH$_3$), 6.87 (s, 1H, H$_{vinyl}$), 7.45 (m, 3H, H$_{arom}$); ^{13}C NMR (CDCl$_3$): δ 20.7 (−CH$_3$), 111.9, 112.1, 122.2, 124.5, 125.6, 132.1, 132.6, 133.0, 140.4, 147.4 (C$_{arom}$, CH$_{arom}$, C$_{butad}$); MS (-ESI): *m/z* 353 [M−H]$^-$; $C_{12}H_8Cl_4N_2S$ (M, 354.08). Calc: C, 40.70; H, 2.28; N, 7.91; S, 9.06. Found: C, 40.61; H, 2.30; N, 7.44 S, 10.50.

1,1,2-Trichloro-4,4-bis(2-(butyloxycarbonyl)ethyl)thio)-1,3-butadiene **(5e):** Compound **(5e)** was synthesized from the reaction of 1,3,3,4,4-hexachloro-1-butene **(1)** (1.0 g, 3.8 mmol) and Butyl 3-mercaptopropionate **(2e)** (0.62 g, 3.8 mmol) by the general procedure 1.

(5e): 0.34 g 21(%); R$_f$ (Pethroleum ether): 0.65; IR (film): 2963, 2936 (C−H), 1744 (C=O), 1627, 1609(C=C); ^{1}H NMR (CDCl$_3$): 0.80 (m, 6H, CH$_3$), 1.58 (m, 8H, C−CH$_2$), 3.03 (m, 4H, O=C−CH), 3.60(m, 4H, S−CH$_2$), 4.05 (m, 4H, O−CH$_2$), δ 6.67 (s, 1H, H$_{vinyl}$); ^{13}C NMR (CDCl$_3$): δ 13.1 (−CH$_3$), 21.7, 28.6 (−CH$_2$), 30.9 (S−CH$_2$), 67.1 (O−CH$_2$), 113.1, 121.3, 127.6, 140.2 (C$_{butad}$), 166.8 (C=O); MS (ESI+): *m/z* 477 [M+H]$^+$; $C_{18}H_{27}Cl_3O_4S_2$ (M, 477.89). Calc: C, 45.24; H, 5.69; S, 13.42. Found: C, 44.92; H, 5.81; S, 13.74.

1,2-Dichloro-1,4,4-tris(benzylthio)-1,3-butadiene **(6a):** Compound **(6a)** was synthesized from the reaction of 2*H*-pentachloro- 1,3-butadiene **(3)** (1.0 g, 4.4 mmol) and benzylmercaptan **(2a)** (1.65 g, 13.20 mmol) by the general procedure 1.

(6a): 1.85g 63%; Oil, R$_f$ (Petroleum ether) : 0.42; IR (film): 3029, 3065 (=C−H$_{arom}$), 1574 (C=C); ^{1}H NMR (CDCl$_3$): δ 3.52 (s, 6H, CH$_2$-), 6.48 (s, 1H, H$_{vinyl}$), 7.20 (m, 15H, H$_{arom}$); ^{13}C NMR (CDCl$_3$): δ 38.5, 38.7, 43.5 (CH$_2$), 127.6, 127.8, 128.7, 128.8, 128.8, 129.2, 129.3, 129.6, 137.6 (C$_{arom,}$ CH$_{arom,}$ C$_{butad}$); MS (ESI+): *m/z* 489 [M]$^+$; $C_{25}H_{22}Cl_2S_3$ (489.54). Calc: C, 61.34; H, 4.53; S, 19.65 Found: C, 61.25; H, 4.45; S,19.32.

1,2-Dichloro-1,4,4-tris(cyclohexylthio)-1,3-butadiene **(6b):** Compound **(6b)** was synthesized from the reaction of 2*H*-pentachloro- 1,3-butadiene **(3)** (1.0 g, 4.4 mmol) and cyclohexanethiol **(2b)** (1.54 g, 13.20 mmol) by the general procedure 1.

(6b): 2.13 g 52%; Oil, R$_f$ (Petroleum ether): 0.41; IR (film): 2852-2929 (CH$_2$), 1580 (C=C); ^{1}H NMR (CDCl$_3$): 1.60 (m, 30H, −CH$_{2cyclohexyl}$), 3.05 (m, 3H, −CH$_{cyclohexyl}$), 6.88 (s, 1H, H$_{vinyl}$); ^{13}C NMR (CDCl$_3$): δ 25.7, 25.8, 25.8, 25.9, 25.9, 26.0, 26.1, 32.8, 32.9, 33.0, 33.2, 33.4, 33.5 (−CH$_{2cyclohexyl}$) 46.2, 46.3, 47.1 (−CH$_{cyclohexyl}$); 127.5, 127.6, 129.3, 140.3 (C$_{butad}$); MS (ESI+): *m/z* 465 [M]+; $C_{22}H_{34}Cl_2S_3$ (M, 465.61). Calc: C, 56.75; H, 7.36; S, 20.66. found: C, 56.50; H, 7.05; S, 19.56.

1,2-Dichloro-1,4,4-tris(2-(butyloxycarbonyl)ethyl)thio)-1,3-butadiene **(6e):** Compound **(6e)** was synthesized from the reaction of 1,3,3,4,4-hexachloro-1-butene **(1)** (1.0 g, 3.8 mmol) and Butyl 3-mercaptopropionate **(2e)** (1.85 g, 11.4 mmol) by the general procedure 1.

(6e): 0.91 g 32(%); R$_f$ (Petroleum ether): 0.60; IR (film): 2955, 2925 (C−H), 1713 (C=O), 1613, 1594(C=C); ^{1}H NMR (CDCl$_3$): δ 0.80 (m, 9H, CH$_3$), 1.20 (m, 12H, C−CH$_2$), 3.16 (m, 4H, O=C−CH), 3.61 (m, 4H, S−CH$_2$), 4.11 (m, 6H, O−CH$_2$), 6.78 (s, 1H, H$_{vinyl}$); ^{13}C NMR (CDCl$_3$): δ 13.1 (−CH$_3$), 21.7, 28.7 (−CH$_2$), 30.9 (S−CH$_2$), 65.9 (O−CH$_2$), 113.4, 123.7, 134.8, 151.9 (C$_{butad}$), 166.55 (C=O); MS (ESI+): *m/z* 605 [M+H]$^+$; $C_{25}H_{40}Cl_2O_6S_3$ (M, 603,68). Calc: C, 49.74; H, 6.68; S, 15.93. Found: C, 50.12; H, 6.56; S, 15.74.

1−Chloro-1,4,4-tris(benzylthio)-1,2,3-butatriene **(7a):** Compound **(7a)** was synthesized from the reaction of ***1***,2-Dichloro-1,4,4-tris(benzylthio)-1,3-butadiene **(6a)** (1.0 g, 2.0 mmol) and potassium *tert*-butoxide (0.45 g, 4.0 mmol) by the general procedure 2.

(7a): 1.29 69%; Oil, R_f (Petroleum ether) : 0.42; IR (film): 3028, 3064, 3084 (=C−H_{arom}), 2043 (C=C=C=C); ^{1}H NMR ($CDCl_3$): 3.91 (s, 6H,−CH_2), 7.26 (m, 15H, H_{arom}); ^{13}C NMR ($CDCl_3$): 42.5, 39.9, 39.7 (−CH_2), 127.2, 127.8, 128.8, 129.3, 129.5, 132.6, 136.7 ($C_{arom,}$ C_{butad}); MS (ESI+): *m/z* 454 $[M+H]^+$; $C_{25}H_{21}ClS_3$ (453.08) Calc: C, 66.27; H, 4.67; S, 21.23 Found: C, 66.10; H, 4.55; S, 20.19.

3-Chloro-1,4,4-(2-(butyloxycarbonyl)ethyl)thio)-1-buten-3-yne **(8e)** and ***3,4,4-trichloro-1-(2-(butyloxycarbonyl)ethyl)thio)-1-buten-3-yne*** **(9e):** Compound **(8e) and (9e)** were synthesized from the reaction of 1,3,3,4,4-hexachloro-1-butene **(1)** (1.0 g, 3.8 mmol) and butyl 3-mercaptopropionate **(2e)** (0.62 g, 3.8 mmol) by the general procedure 1.

(8e): 0.35 g 22(%); R_f (Petroleum ether + Ethyl acetate 1:1): 0.40; IR (film): 2961, 2923 (C−H), 2157 (C≡C), 1729 (C=O), 1564 (C=C); ^{1}H NMR ($CDCl_3$): 0.80 (m, 9H, CH_3), 1.28 (m, 12H, C−CH_2), 2.25 (m, 6H, CH_2−C=O), 2.98 (m, 6H, S−CH_2), 4.01 (m, 6H, O−CH_2); ^{13}C NMR ($CDCl_3$): δ 13.1, 21.7 (−CH_3, −CH_2), 28.7, 30.9 (−S−CH_2), 60.7 (−O−CH_2), 67.4, 102.5 (C≡C), 124.0, 146.8 (C=C), 166.2 (C=O); MS (ESI+): *m/z* 567 $[M]^+$; $C_{25}H_{39}ClO_6S_3$ (M, 567,22). Calc: C, 52.94; H, 6.93; S, 16.96. Found: C, 53.26; H, 6.78; S, 16.57.

(9e): 0.31 g 19(%); R_f (Petroleum ether + Ethyl acetate 1:1): 0.70; IR (film): 2957, 2923 (C−H), 2158 (C≡C), 1724 (C=O), 1546 (C=C); ^{1}H NMR ($CDCl_3$): δ 0.80 (m, 3H, −CH_3); 1.58 (m, 4H, C−CH_2), 2.63 (m, 2H, CH_2−C=O), 2.86 (m, 2H, S−CH_2), 4.11 (m, 2H, O−CH_2); ^{13}C NMR ($CDCl_3$): δ 13.1, 21.7 (−CH_3, −CH_2), 29.5 (−S−CH_2), 60.7 (O−CH2), 67.1, 91.1 (C≡C), 116.3, 129.1 (C=C), 166.2 (C=O); MS (ESI+): *m/z* 339.6 $[M+Na+H]^+$; $C_{11}H_{13}Cl_3O_2S$ (M, 315.64). Calc: C, 41.86; H, 4.15; S, 10.16. Found: C, 42.23; H, 4.33; S, 9.92.

1,3,4,4-Tetrakis(2-(butyloxycarbonyl)ethyl)thio)-1-buten-3-yne **(10e):** Compound **(10e)** was synthesized from the reaction of 1,1,3,3,4,4-hexachloro-1-butene **(1)** (1.0 g, 3.8 mmol) and Butyl 3-mercaptopropionate **(2e)** (1.85 g, 11.4 mmol) by the general procedure 1.

(10e): 1.02 g 36(%); R_f (Petroleum ether + Ethyl acetate 1:1): 0.45; IR (film): 2958, 2925 (C−H), 2157 (C≡C), 1714 (C=O), 1588, 1569 (C=C); ^{1}H NMR ($CDCl_3$): 0.81 (m, 12H,−CH_3), 1.27 (m, 16H, C−CH_2), 2.63 (m, 8H, CH_2−C=O), 3.01 (m, 8H, S−CH_2), 4.06 (m, 8H, O−CH_2);^{13}C NMR ($CDCl_3$): δ 13.9, 22.9 (CH_3, CH_2), 29.2, 29.6, 29.9 (S−CH_2), 64.4 (O−CH_2), 68.4, 91.3 (C≡C), 114.8, 129.0 (C=C), 166.4 (C=O); MS (ESI+): *m/z* 693 $[M]^+$; $C_{32}H_{52}O_8S_4$ (M, 693.01). Calc: C, 55.46; H, 7.56; N, 4.06; S, 18.51. Found: C, 55.23; H, 7.70; S, 18.04.

1,2-Dibromo-3,4,4-trichloro-1-(octadecylsulfinyl)-1,3-butadiene **(12a):** Compound **(12a)** was synthesized from the reaction of 1,2-Dibromo-3,4,4-trichloro-1-(1-octadecylthio)-1,3-butadiene **(11a)**[12] (0.7 g, 1.16 mmol) and m-Chloroperbenzoic acid (0.2 g, 1.16 mmol) at 0°C by the general procedure 3.

(12a): 0.44g (62%); m.p.:55-57°C, R_f (Pethroleum ether + $CHCl_3$ 1:2): 0.54; IR (KBr): 1560, 1610 (C=C), 2849, 2916, 2955 (C−H), 1064, 1095 (S=O). ^{1}H NMR ($CDCl_3$): δ 0.82 (t, J= 7.32Hz, 3H, CH_3), 1.46 (m, 32H, −$(CH_2)_{16}$-), 2.84 (m, J = 7.32, 2H, S−CH_2); ^{13}C NMR ($CDCl_3$): δ 14.3 (−CH_3); 22.4, 22.5, 22.9, 22.9, 28.8, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 29.8, 29.9, 29.9, 32.14 (−CH_2); 53.9 (−S−CH_2); 109.9, 115.4, 126.2, 137.9

(C_{butad}); MS (ESI+): *m/z* 617 $[M+H]^{+;}$ $C_{22}H_{37}Br_2Cl_3OS$ (M, 615.76). Calc.: C, 42.91; H, 6.06; S, 5.21. Found.: C, 43.20; H, 5.98; S, 4.98.

1,2,4-Tribromo-3,4-dichloro-1−(octadecylsulfinyl)-1,3-butadiene **(12b):** Compound **(12b)** was synthesized from the reaction of 1,2,4-Tribromo-3,4-dichloro-1-(1-octadecylthio)-1,3-butadiene **(11b)** (0.5 g, 0.77 mmol) and m-Chloroperbenzoic acid (0.13 g, 0.77 mmol) at 0°C by the general procedure 3.

(12b): 0.39g (78%); m.p.:60-62°C, R_f (Petroleum ether + $CHCl_3$ 1:2): 0.52; IR (KBr): 1558, 1609 (C=C), 2849, 2916, 2955 (C−H), 1063, 1095 (S=O). ^1H NMR ($CDCl_3$): δ 0.81 (t, $J = 7.32$Hz, 3H, CH_3), 1.48 (m, 32H, $-(CH_2)_{16}$-), 2.83 (m, $J = 7.32$, 2H, S−CH_2); ^{13}C NMR ($CDCl_3$): δ 14.3 (CH_3); 22.4, 22.5, 22.9, 22.9, 23.6, 28.8, 28.8, 29.3, 29.5, 29.7, 29.7, 29.8, 29.8, 29.8, 29.8, 29.9, 32.1 (−CH_2); 56.5 (−S−CH_2); 111.5, 116.6, 127.4, 137.7 (C_{butad}); MS (ESI+): *m/z* 661 $[M+H]^+$; $C_{22}H_{37}Br_3Cl_2OS$ (M, 660.21). Calc: C, 40.02; H, 5.65; S, 4.86. Found: C, 39.77; H, 5.02; S, 4.21.

1,2-Dibromo-3,4,4-trichloro-1−(dodecylsulfinyl)-1,3-butadiene **(12c):** Compound **(12c)** was synthesized from the reaction of 1,2-Dibromo-3,4,4-trichloro-1-(1-dodecylthio)-1,3-butadiene **(11c)**[12] (0.5 g, 0.77 mmol) and m-Chloroperbenzoic acid (0.13 g, 0.77 mmol) at 0°C by the general procedure 3.

(12c): 0.35 g (55%); Oil, R_f (Petroleum ether + $CHCl_3$ 1:2): 0.59; IR (KBr): 1560, 1610 (C=C), 2849, 2916, 2955 (C−H), 1064, 1095 (S = O). ^1H NMR ($CDCl_3$): δ 0.82 (t, $J = 7.32$Hz, 3H, CH_3), 1.46 (m, 32H, $-(CH_2)_{16}$-), 2.84 (m, $J = 7.32$, 2H, S−CH_2); ^{13}C NMR ($CDCl_3$): δ 14.3 (−CH_3); 22.4, 22.5, 22.9, 23.0, 29.3, 29.5, 29.7, 29.8, 29.8, 32.1 (CH_2); 53.9 (S−CH_2); 109.9, 115.4, 126.2, 137.9 (C_{butad}); MS (ESI+): *m/z* 533 $[M+H]^+$; $C_{16}H_{25}Br_2Cl_3OS$ (M, 531.60). Calc.: C, 36.15; H, 4.74; S, 6.03. Found.: C, 35.76; H, 4.22; S, 6.91.

1,2-Dibromo-3,4,4-trichloro-1-(octylsulfinyl)-1,3-butadiene **(12d):** Compound **(12d)** was synthesized from the reaction of 1,2-Dibromo-3,4,4-trichloro-1-(1-octyllthio)-1,3-butadiene **(11d)**[12] (0.5 g, 0.77 mmol) and m-Chloroperbenzoic acid (0.13 g, 0.77 mmol) at 0°C by the general procedure 3.

(12d): 0.59 g (67%); Oil, R_f (Petroleum ether + $CHCl_3$ 1:2): 0.63; IR (KBr): 1561, 1609 (C=C),2845, 2913, 2953 (C−H), 1063, 1095 (S=O). ^1H NMR ($CDCl_3$): δ 0.81 (t,J = 7.32Hz, 3H, CH_3), 1.46 (m, 32H, $-(CH_2)_{16}$-), 2.83 (m, $J = 7.32$, 2H, S−CH_2); ^{13}C NMR ($CDCl_3$): δ 14.3 (−CH_3); 22.4, 22.5, 29.3, 29.8, 29.9, 32.2 (CH_2); 53.3 (S−CH_2); 111.8, 116.4, 127.2, 137.8 (C_{butad}); MS (ESI+): *m/z* 475 $[M]^+$; $C_{12}H_{17}Br_2Cl_3OS$ (M, 475.49). Calc.: C, 30.31; H, 3.60; S, 6.74. Found.: C, 30.65; H, 3.81; S, 7.14.

REFERENCES

1. Ibis, C. *Liebigs Ann. Chem.* **1984,** 11, 1873-1877.
2. Roedig, A.; Zaby, G. and Scharf, W. *Chem. Ber.* **1977,** 110, 1484-1491.
3. Roedig, A.; Zaby, G. *Chem. Ber.* **1979,** 10, 1614-1625.
4. Roedig, A.; Ibis, C. and Zaby, G. *Chem. Ber.* **1981,** 114(2), 684-698.
5. *Diamond Alkali Company* (Ert. H. Bluestone), U.S. Patent 3 021 270 13 Feb. **1962**.
6. Goyot, Q.; Gingra, M. *Tetrahedron Lett.* **2009,** 50, 1977-1981.
7. Tank, R.; Pathak, U.; Singh, A.; Gupta, A.; Gupta, D. C. *React. Funct. Polym.* **2009,** 69, 224-228.
8. Tong, G. C.; Cornwell, W. K.; Means, G. E. *Toxicol. Lett.* **2004,** 147, 127-131.
9. Padmanabhan, S.; Lavin, R. C.; Durant, G. J. *Tetrahedron Asymmetr.* **2000,** 11, 3455-3645.
10. Kaczorowska, K.; Kolarska, Z.; Mitka, K.; Kowalski, P. *Tetrahedron.* **2005,** 61, 8315-8327.
11. Martin, E. L; Sharkey, W. H. *J. Am. Chem. Soc.* **1959,** 81, 5256-5258.

12. Ibis, C.; Sahin, A. *Bull. Korean Chem. Soc.* **2010,** 31(8), 2255-2260.
13. Ibis, C.; Beyazit, N. *Arkıvoc.* **2010,** 9, 244-256.
14. Schmidt, A.; Rahimi, A.; Gjikaj, M. *Synthesis.* **2009,** 14, 2371-2378.
15. Roedig, A.; Zaby, G. *Liebigs Ann. Chem.* **1979,** 10, 1606-1613.
16. Botta, D.; Mantica, E.; Castellani, L.; Dotelli, G.; Zetta, L. *Magn. Reson. Chem.* **1998,** 36, 885-891.
17. Roedig, A.; Kloss, R. *Liebigs Ann. Chem.* **1958,** 612, 1-10.
18. Ibis, C.; Ozkok, F. *Acta Chim. Slov.* **2012,** 59, 294-301.
19. Ibis, C.; Sayil, C.; Ozkok, F. *Z. Naturforsch.* **2006,** 61b, 1174-1179.