The synthesis of new thiosubstituted butadienes, butenynes and butatrienes

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Abstract
By treatment of the pentachlorobutadiene 1 and of the tetrachlorobromobutadiene 9 with thiolates in ethanol, a very fast and extensive replacement of chlorine was observed even at room temperature. The reaction of 1 with three molar equivalents of thiolates lead to butadienes with two, three, four and five organylthio groups. Tris(thio)-substituted butadienes 3a-c tetrakis(thio)-substituted butadiene 4a were treated with potassium tert-butoxide to form tris(thio)-substituted butatrienyl halide compounds 12a-c and tetrakis(thio)-substituted butatriene 14a, respectively. The butatrienyl halides 12a-c obtained partly isomerizes to give butenynes 13a-c at room temperature and without catalyst.

Keywords: Thiosubstituted butadienes, butenynes, butatrienes, thiol, HCl elimination

Introduction
Polyhalogenobutadienes have been used as model substrates for studying of the process of vinylic substitution (S_NVin). There are various possibilities of the use of these compounds for the synthesis of numerous polyfunctional products. The reactions of 2H- and 1H-pentachlorobutadienes, 1,3-di-H- and 2,3-di-H-hexachlorobutenes with some thiols are well documented and mono- and polythiosubstituted compounds, mostly butadiene derivatives, have been obtained by this way.1-7

It is known that some thiosubstituted butadienes exhibit high biological activity. Industrial research has long focused on biological applications of thiosubstituted compounds as insecticides, herbicides, fungicides, and bactericides.8 5-lipoxygenase inhibition effect of 1-thiosubstituted butadienes also reported.9 Butenynes and butatrienes are very valuable compounds for their use in polymer chemistry. Unlike alkanes and most alkenes, cumulenes tends to be rigid, which makes them appealing for molecular nanotechnology.10-12 Thiosubstituted compounds are used as
electronic conductors, ferromagnets, electron-accepting supramolecules, optical materials in material chemistry and as stabilizers in polymer chemistry.  

Schmidt et al. have synthesised thiosubstituted butatrienes and 1,3-butadienes from the reaction of a tetrakis(pyridinium)-substituted butadiene with some thiolates. In an earlier study, Block et al. have used perhalogenohydrocarbons as starting material to obtain perthio-1,3-butadienes, -1-buten-3-ynes and -1,2,3-butatrienes. In this work, we report another efficient method for the synthesis of novel thiosubstituted butadiene, butenyne and butatriene compounds.

**Results and Discussion**

The reactions of 2H-pentachlorobutadiene with three molar equivalents of thiols in the presence of NaOH in ethanol at room temperature were carried out to give bis-, tris-, tetrakis- and pentakis(thio)-substituted butadienes, 2d, 3a-c, 4a, 5a and tetrakis(thio)-substituted butenyne 6d. New mono(thio)-substituted butenyne compounds 7a, 7c, 7e-i were obtained from the reactions of 2H-pentachlorobutadiene and 10e-i, from the reactions of 2H-1,1,3,4-tetrachloro-4-bromobutadiene with one molar equivalent of thiols at the same reaction conditions. Monothiosubstituted polyhalogenobutadienes 8a, 8c, 8e-i and 11h were synthesized from the bromination of mono(thio)-substituted butenyne compounds in an apolar solvent (Scheme 1).

Compounds 3a, 4a and 5a were obtained from the reaction of 2H-pentachlorobutadiene with three molar equivalents of thiol a. In the possible reaction mechanism of 5a, it is thought that perchlorobutenyne formed by HCl elimination from 2H-pentachlorobutadiene firstly and then tetrakis(thio)-substituted butenyne and tetrakis(thio)-substituted butatriene intermediates were occurred via addition of four molar of thiol a to perchlorobutenyne. These intermediates both were stabilized by mesomery. In the last step of the mechanism, 5a was obtained by addition of one molar of thiol a to tetrakis(thio)-substituted butenyne or tetrakis(thio)-substituted butatriene. 1H-NMR spectra of 2d, 3a-c, 4a and 5a exhibited the presence of vinyl proton as a singlet at approximately 6.50 ppm. The mass spectrum of 3a confirmed the estimated structure; two main peaks were observed at m/z 683.62 and 648.77 corresponding to [M]+ and [M-Cl]+, respectively. The IR spectra of butenyne derivatives 6d, 7a, 7c, 7e-i and 10e-i showed the characteristic strong band at 2147 and 2152 cm⁻¹ for C≡C group. In the 13C-NMR spectra of these compounds, two alkyne carbons provide chemical shift values around 85.11 and 92.07 ppm. In the ESI-MS spectrum of 10h showed a molecular ion peak at m/z 455.93 and the fragmentation of molecular ion peak at m/z 375 corresponding to the loss of a bromine atom. New thiosubstituted polyhalobutadiene compounds 8a, 8c, 8e-i and 11e-i were formed by the electrophilic addition of Br₂ to butenynes. It is evidence for successful bromination reaction that the IR spectra of these compounds showed no absorption band around 2147 or 2152 cm⁻¹.
Scheme 1. General synthesis methods of butadienes and butenynes.

Tris(thio)-substituted butatriene compounds 12a-c were formed by HCl elimination in the presence of potassium tert-butoxide from tris(thio)-substituted butadienes 3a-c. These butatriene compounds 12a-c partly isomerize to the tris(thio)-substituted butenynes 13a-c even at room temperature, in a solvent medium. Tetrakis(thio)-substituted butatriene 14a, obtained from 4a by HCl elimination, is more stable than 12a-c. This stability was proved by IR spectrum of 14a that there was no typical absorption band at 2142-2157 cm⁻¹ region corresponding to C≡C group. Addition of I₂ to butatriene compounds 12a and 14a were performed in apolar solvent at room temperature to give 15a and 16a. Electrophilic addition reaction mechanism proceeds via an iodonium cation (Scheme 2).
Scheme 2. The synthesis and iodination of butatriene compounds.

The solvolysis of butatrienyl halides gives the ambident vinyl cation which has positive charge on a disubstituted carbon in both mesomorphic structures (x and y). The possible isomerization mechanism of 1-chloro-1,4,4-tris(4-methylphenylthio)butatriene have been explained in the previous study by our group (Scheme 3).  

Scheme 3. The possible isomerization mechanism of butatrienyl halides to butenynes.

12a and 12c obtained under the action of potassium tert-butoxide, are stable solid compounds. The peaks at 2037 and 2043 cm⁻¹ in the IR spectra of 12a and 12c was assigned to C=C=C=C stretching vibration, respectively. 12b, yellow oily compound, easily isomerizes to 1-buten-3-yne 13b at room temperature without catalyst. IR spectrum of 12b showed C≡C stretching band at 2143 cm⁻¹ next to butatriene band at 2043 cm⁻¹. However, in the solvent medium, stable butatrienyl halides 12a and 12c are solvolyzed to give the ambident allenyl cation which isomerizes to butyne compounds 13a and 13c. 12a-c cannot be isolated from the isomeric mixture by the chromatographic techniques. IR, Mass spectra and elemental analyses results confirmed that these compounds are the isomeric mixture...
of tris(thio)-substituted butatriene and tris(thio)-substituted butenylene. IR spectrum of the isomeric mixture of 12a and 13a showed characteristic absorption bands at 2037 and 2142 cm\(^{-1}\) due to C=C=C=C and C≡C groups, respectively. The ESI-MS in the positive ion mode of the mixture of compounds 12a and 13a, displays an ion of \(m/z\) 648.84 assigned to the protonated molecular ion peak \([M+H]^+\). The major ion of \(m/z\) 459.90 in the ESI-MS/MS of 12a and 13a indicates the loss of \(–SC_6H_4Br\) group. The presence of isomer mixture was also confirmed by the \(^{13}\)C-NMR spectrum, in which more signals than expected chemical shifts were observed and two internal alkynes appeared at 86.24 and 93.19 ppm.

Thiosubstituted butadiene and butenylene compounds showed maximum absorption of the range 244-266 nm in CHCl\(_3\), the maximum absorption wavelengths of butatriene compounds were observed between 367-392 nm.

**Experimental Section**

**General.** Melting points were measured on Buchi B-540 capillary apparatus and are uncorrected. IR-spectra were recorded on Shimadzu FTIR-8101. NMR spectra were recorded on Varian Unity Inova 500 MHz. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS Spectrometer using ion-trap mass analyzer for both APCI or ESI source. UV spectra were recorded on UV-VIS Spectrophotometer TU-1901. Microanalyses were obtained by using a Carlo-Erba 1110 element analyser. Thin-layer chromatography (TLC) : E. Merck silica gel 60 F\(_{254}\) foils. Column chromatography: Silica gel 60 ( particle size 0.063-0.20 mm, E. Merck ).

**General procedure 1**

2H-pentachlorobutadiene 1 (1 g, 4.4 mmol) and thiols (13.2 mmol) were stirred in a mixture of EtOH (30 mL) and aqueous solution of NaOH (1.2 g and 8 ml water) for 30 min. at room temperature. Ether was added to the reaction mixture and the organic layer was separated, washed with water (4x30 mL), and dried with MgSO\(_4\). The solvent was evaporated and the residue was purified by column chromatography over silica gel (petroleum ether/chloroform or petroleum ether).

**1,2-Dichloro-1,4,4-tris(4-bromophenylthio)-1,3-butadiene (3a).** Yield 40%; White solid, mp: 80-82\(^{\circ}\)C. R\(_f\) (Petroleum ether): 0.35; IR (KBr, cm\(^{-1}\)): 1580 (C=C), 3100 (=C–H; arom); UV-vis(CHCl\(_3\)): \(\lambda_{max}(log\epsilon) = 244\) nm (5.1), 266 (5.0), 330 (4.8); \(^1\)H NMR (499.83 MHz, CDCl\(_3\)): \(\delta\) 6.49 (s, 1H, vinyl-H), 7.02-7.42 (m, 12H, H\(_{arom}\)); \(^{13}\)C NMR (125.68 MHz, CDCl\(_3\)): \(\delta\) 130.91, 131.01, 131.38, 131.45, 132.81, 133.05, 133.34, 133.40 (CH\(_{arom}\)), 121.48, 122.12, 122.26, 126.32, 126.69, 130.32, 130.52, 130.91, 139.69 (C\(_{arom}\) and C\(_{butad}\)); MS (+ESI): \(m/z\) 683.62 [M]\(^+\), 648.77 [M-Cl]\(^+\); C\(_{22}\)H\(_{13}\)S\(_3\)Cl\(_2\)Br\(_3\) (M, 684.15). Calcd. C, 38.62; H, 1.91; S, 14.06. Found C, 38.61; H, 1.85; S, 14.66.
2-Chloro-1,1,4,4-tetakis(4-bromophenylthio)-1,3-butadiene (4a). Yield 12%; Yellow solid, mp: 135-137°C. Rf [Petroleum ether/CCI₄ (1:1)]: 0.42; IR (KBr, cm⁻¹): 1502, 1563 (C=C), 3079 (=C-H_arom); ¹H NMR (499.83 MHz, CDCl₃): δ 6.76 (s, 1H, vinyl-H), 6.78-7.34 (m, 16H, H_arom); ¹³C NMR (125.68 MHz, CDCl₃): δ 121.59, 122.61, 123.16, 123.20, 129.85, 130.98, 131.13, 131.79, 131.82, 132.03, 132.16, 132.21, 132.25, 132.52, 133.04, 133.96, 134.49, 135.41 ve 139.61 (CH_arom, C_arom and C_butadi) ; C₂₈H₁₇S₄ClBr₄ (M, 836.76). Calcd. C, 40.19; H, 2.05; S, 15.33. Found C, 40.87; H, 1.95; S, 15.59.

1,1,2,4,4-Pentakis(4-bromophenylthio)-1,3-butadiene (5a). Yield 6%; Yellow solid, mp:157-159°C. Rf [Petroleum ether/CHCl₃ (1:1)]: 0.13, IR (KBr, cm⁻¹): 1561 (C=C), 3074 (=C-H_arom); ¹H NMR (499.83MHz, CDCl₃): δ 6.34 (s, 1H, vinyl-H), 6.81-7.44 (m, 20H, H_arom); ¹³C NMR (125.68 MHz, CDCl₃): δ 121.92, 122.06, 122.64, 122.77, 123.07, 130.15, 131.28, 131.50, 131.90, 132.10, 132.27, 132.38, 132.51, 132.67, 133.20, 133.29, 134.06, 134.38, 135.17, 137.83, 141.31 (CH_arom, C_arom, C_butadi); C₃₃H₂₁S₄Br₅ (M, 989.39). Calcd. C, 41.28; H, 2.14; S, 16.20. Found C, 40.93; H, 2.05; S, 16.82.

1,2-Dichloro-1,4,4-tris(4-fluorophenylthio)-1,3-butadiene (3b). Yield 42%; Oil, Rf [Petroleum ether/CHCl₃ (1:1)]: 0.40; IR (film, cm⁻¹): 1589 (C=C), 3068 (=C-H_arom); UV-vis(CHCl₃): λ_max (log ε) = 257 nm (4.6), 326 (4.5); ¹H NMR (499.83 MHz, CDCl₃): δ 6.48 (s, 1H, vinyl-H), 7.02-7.48 (m, 12H, H_arom); ¹³C NMR (125.68 MHz, CDCl₃): δ 116.15, 116.32, 116.58, 116.65, 116.76, 116.83, 125.69, 127.03, 127.64, 128.36, 133.94, 135.19, 135.25, 135.71, 135.77, 135.98, 136.05, 142.56, 162.37, 164.13, 164.37 (CH_arom, C_arom and C_butadi); MS (+ESI): m/z 500.97 [M⁺], 464.96 [M-Cl]+, 373.93 [M-SC₆H₄F]+; C₂₂H₁₃Cl₂S₃F₃ (M, 500.7). Calcd. C, 52.69; H, 2.61; S, 19.18. Found C, 53.19; H, 2.99; S, 18.14.

1,2-Dichloro-1,4,4-tris(2-naphthylthio)-1,3-butadiene (3c). Yield 34%; White solid, mp: 143-145°C. Rf [Petroleum ether/CHCl₃ (1:1)]: 0.30; IR (KBr, cm⁻¹): 1580 (C=C), 3050 (=C-H_arom); UV-vis(CHCl₃): λ_max (log ε) = 259 nm (4.9); ¹H NMR (499.83 MHz, CDCl₃): δ 6.55 (s, 1H, vinyl-H), 7.25-7.84 (m, 21H, H_arom); ¹³C NMR (125.68 MHz, CDCl₃): δ 126.71, 126.79, 126.86, 126.96, 127.09, 127.17, 127.80, 127.95, 127.99, 128.36, 128.61, 129.02, 129.11, 129.23, 129.66, 129.75, 129.88, 129.93, 130.11, 130.12, 132.29, 132.48, 132.99, 133.13, 133.19, 133.63, 133.74, 133.77, 142.11 (CH_arom, C_arom and C_butadi); MS (+ESI): m/z 597.80 [M⁺], 560.97 [M-Cl]+; C₃₄H₂₂Cl₂S₃ (M, 597.64). Calcd. C, 68.33; H, 3.71; S, 16.10. Found C, 68.24; H, 3.82; S, 16.07.

1,1,2-Trichloro-4,4-bis(n-ethylthio)-1,3-butadiene (2d). Yield 41%; Oil, Rf (Hexane): 0.70; IR (film, cm⁻¹): 1546 (C=C), 2870, 2927, 2971 (C-H). ¹H NMR (499.83 MHz, CDCl₃): δ 6.18 (s, 1H, vinyl-H), 2.74-2.82 (m, J = 7.32 Hz, 4H, S-CH₂), 1.19-1.25 (m, J = 7.32 Hz, 6H, CH₃); ¹³C NMR (125.68 MHz, CDCl₃): δ 119.28, 121.53, 124.98, 142.34 (C_butadi), 128.6, 13.98 (CH₃), 26.93, 27.03 (CH₂); MS (+ESI): m/z 279.41 [M+H]+; C₃₄H₁₁Cl₂S₂ (M, 277.66). Calcd. C, 34.61; H, 3.99; S, 23.10. Found C, 34.92; H, 4.02; S, 23.65.

1,1,2,4-Tetrakis(n-ethylthio)-1-butene-3-ylene (6d). Yield 27%; Oil, Rf (Hexane): 0.35; IR (film, cm⁻¹): 1531 (C=C), 2144 (C=C), 2872, 2930, 2958 (C-H). ¹H NMR (499.83 MHz, CDCl₃): δ 2.62-2.90 (m, J = 7.32 Hz, 8H, S-CH₂), 1.18-1.47 (m, J = 7.32 Hz, 12H, CH₃); ¹³C NMR (125.68 MHz, CDCl₃): δ 87.59, 89.40, 124.60, 139.82 (C_butene); 27.59, 27.18, 27.03, 26.92 (CH₂); 13.95,
General procedure 2

2H-pentachlorobutadiene 1 (1 g, 4.4 mmol) or 2H-1,1,3,4-tetrachloro-4-bromobutadiene 9 (1 g, 3.7 mmol) and thiols (4.4 mmol for the reaction with 1, 3.7 mmol for the reaction with 9) were stirred in a mixture of EtOH (30 mL) and aqueous solution of NaOH (1.2 g and 8 mL water) for 30 min. at room temperature. Ether was added to the reaction mixture. The organic layer was separated and washed with water (4x30 mL), and dried with MgSO4. The solvent was evaporated and the products were purified by column chromatography over silica gel (petroleum ether).

1,1,2-Trichloro-4-(4-bromophenylthio)-1-buten-3-yn (7a). Yield 65%; White solid, mp: 68-69 °C. Rf (Petroleum ether): 0.67; IR (KBr, cm⁻¹): 2157 (C=C), 3025 (=C-Harom); UV-vis(CHCl₃): λmax (logs) = 266 nm (4.0); ¹H NMR (499.83 MHz, CDCl₃): δ 7.20-7.45 (m, 4H, Harom); ¹³C NMR (125.68 MHz, CDCl₃): δ 128.50, 128.66, 132.67, 132.87 (Carom ), 87.78, 91.03, 112.85, 121.66, 130.39, 134.58 (Carom and C butenyl); EIMS: m/z 341.9 [M⁺]; C₁₀H₈Cl₂SBr (M, 342.50). Calcd. C, 50.70; H, 1.17; S, 9.36. Found C, 50.67; H, 1.12; S, 9.25.

1,1,2-Trichloro-4-(2-naphthylthio)-1-buten-3-yn (6e). Yield 43%; White solid, mp: 71-73 °C. Rf (Petroleum ether): 0.71; IR (KBr, cm⁻¹): 2149 (C=C), 3032 (=C-Harom); UV-vis(CHCl₃): λmax (logs) = 259 nm (5.2); ¹H NMR (499.83 MHz, CDCl₃): δ 7.39-7.85 (m, 7H, Harom); ¹³C NMR (125.68 MHz, CDCl₃): δ 88.88, 90.67, 113.04, 124.64, 125.94, 126.74, 127.36, 127.52, 128.00, 128.13, 128.26, 129.63, 132.62, 133.97 (Carom, CHarom, Cbutenyl); C₁₄H₁₁Cl₂S (M, 313,5). Calcd. C, 53.20; H, 2.85; S, 10.40. Found C, 53.68; H, 2.38; S, 9.63.

1,1,2-Trichloro-4-(1-octythio)-1-buten-3-yn (7e). Yield 52%; Oil, Rf (Petroleum ether): 0.87; IR (film, cm⁻¹): 2152 (C≡C), 2855, 2925 (C-H). UV-vis(CHCl₃): λmax (logs) = 244 nm (4.6); ¹H NMR (499.83 MHz, CDCl₃): δ 0.8 (t, J = 7.32 Hz, 3H, CH₃), 1.2-1.4 (m, 10H, -(CH₂)₅- ), 1.70 (m, 2H, S-CH₂-CH₂), 2.75 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.04 (CH₃); 21.62, 27.14, 27.99, 28.08, 28.33, 30.75, 35.09 (CH₂); 85.08, 92.04, 112.01, 123.88 (Cbutenyl); EIMS: m/z 300.1 [M⁺]; C₁₂H₁₇Cl₂S (M, 299.69). Calcd. C, 48.09; H, 5.72; S, 10.69. Found C, 48.31; H, 5.82; S 10.44.

1,1,2-Trichloro-4-(1-decylthio)-1-buten-3-yn (7f). Yield 41%; Oil, Rf (Petroleum ether): 0.75; IR (film, cm⁻¹): 2147 (C≡C), 2855, 2925 (C-H). UV-vis(CHCl₃): λmax (logs) = 244 nm (4.1); ¹H NMR (499.83 MHz, CDCl₃): δ 0.81 (t, J = 7.32Hz, 3H, CH₃), 1.2-1.4 (m, 14H, -(CH₂)₅- ), 1.69 (m, 2H, S-CH₂-CH₂), 2.73 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.09 (CH₃); 21.67, 27.15, 28.05, 28.09, 28.29, 28.44, 28.52, 30.89, 35.09 (CH₂); 85.10, 92.07, 112.03, 123.84 (Cbutenyl); EIMS: m/z 326.1 [M⁺]; C₁₄H₂₁Cl₂S (M, 327, 743). Calcd. C, 51.30; H, 6.46; S, 9.78. Found C, 51.37; H, 6.81; S, 9.93.

1,1,2-Trichloro-4-(1-dodecylthio)-1-buten-3-yn (7g). Yield 48%; Oil, Rf (Petroleum ether): 0.85; IR (film, cm⁻¹): 2152 (C≡C), 2854, 2925 (C-H). UV-vis(CHCl₃): λmax (logs) = 244 nm (5.1); ¹H NMR (499.83 MHz, CDCl₃): δ 0.79 (t, J=7.32Hz, 3H, CH₃), 1.2-1.4 (m, 18H, -(CH₂)₉- ), 1.69 (m, 2H, S-CH₂-CH₂), 2.75 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.07

13.93, 13.62, 13.13 (CH₃); MS (+ESI): m/z 292.94 [M⁺]; C₁₂H₂₀S₄ (M, 292.55); Calcd. C, 49.27; H, 6.89; S, 43.84. Found 49.85; H, 6.02; S, 44.05.
(CH₃); 21.67, 27.14, 28.03, 28.32, 28.34, 28.42, 28.54, 28.60, 28.62, 30.90, 35.10 (CH₂); 85.10, 92.06, 112.02, 123.87 (C_{butenylene}); EIMS: m/z 354.2 [M]+; C₁₆H₂₅Cl₃S (M, 355.80); Calcd. C, 54.01; H, 7.08; S, 9.01. Found C, 54.14; H, 7.22; S, 9.49.

### 1,1,2-Trichloro-4-(1-hexadecylthio)-1-butene-3-yne (7h).

Yield 32%; Oil, R_f (Petroleum ether); 0.86; IR (film, cm⁻¹): 2152 (C=C), 2855, 2925 (C-H). UV-vis(CHCl₃): λ_{max} (logε) = 243 nm (4.1);

1H NMR (499.83 MHz, CDCl₃): δ 0.88 (t, J = 7.32 Hz, 3H, CH₃), 1.2-1.4 (m, 26H, -(CH₂)₁₁₋₁₃), 1.76 (m, 2H, S-CH₂-CH₂), 2.80 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.09 (CH₃); 21.69, 27.15, 28.05, 28.08, 28.35, 28.36, 28.44, 28.47, 28.56, 28.64, 28.67, 28.69, 28.71, 30.93, 35.10 (CH₂); 85.11, 92.07, 112.04, 123.86 (C_{butenylene}); C₂₀H₃₅Cl₃S (M, 411.50) Calcd. C, 58.30; H, 8.02; S, 7.77. Found C, 58.25; H, 8.75; S, 7.55.

### 1,1,2-Trichloro-4-(1-octadecylthio)-1-butene-3-yne (7i).

Yield 23%; Oil, R_f (Petroleum ether); 0.82; IR (film, cm⁻¹): 2157 (C=C), 2855, 2925 (C-H). UV-vis(CHCl₃): λ_{max} (logε) = 243 nm (4.5);

1H NMR (499.83 MHz, CDCl₃): δ 0.86 (t, J = 7.32 Hz, 3H, CH₃), 1.2-1.4 (m, 30H, -(CH₂)₁₅₋₁₃), 1.76 (m, 2H, S-CH₂-CH₂), 2.80 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.09 (CH₃); 21.69, 27.15, 27.54, 28.05, 28.09, 28.35, 28.37, 28.44, 28.47, 28.56, 28.59, 28.60, 28.64, 28.67, 28.71, 30.94, 35.10 (CH₂); 85.11, 92.06, 112.03, 123.85 (C_{butenylene}); C₂₂H₃₇Cl₃S (M, 439.96) Calcd. C, 60.06; H, 8.47; S, 7.28. Found C, 60.61; H, 8.49; S, 7.29.

### 1-Bromo-1,2-dichloro-4-(1-octylthio)-1-butene-3-yne (10e).

Yield 67%; Oil, R_f (Petroleum ether); 0.85; IR(film, cm⁻¹): 2146 (C=C), 2855, 2956 (C-H). UV-vis(CHCl₃): λ_{max} (logε) = 242 nm (4.5);

1H NMR (499.83 MHz, CDCl₃): δ 0.82 (t, J = 7.32 Hz, 3H, CH₃), 1.22-1.47 (m, 10H, -(CH₂)₅₋₇), 1.70 (m, 2H, S-CH₂-CH₂), 2.74 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.04 (CH₃); 21.62, 27.14, 28.00, 28.08, 28.09, 30.75, 35.22 (CH₂); 86.70, 91.37, 112.55, 123.27 (C_{butenylene}); C₁₂H₁₁SCl₂Br (M, 344.14) Calcd. C, 41.88; H, 4.98; S, 9.32. Found C, 41.31; H, 5.02; S, 9.63.

### 1-Bromo-1,2-dichloro-4-(1-decylthio)-1-butene-3-yne (10f).

Yield 60%; Oil, R_f (Petroleum ether); 0.77; IR(film, cm⁻¹): 2146 (C=C), 2855, 2925 (C-H). UV-vis(CHCl₃): λ_{max} (logε) = 242 nm (4.0);

1H NMR (499.83MHz, CDCl₃): δ 0.81 (t, J=7.32Hz, 3H, CH₃), 1.2-1.4 (m, 14H, -(CH₂)₇₋₁₃), 1.70 (m, 2H, S-CH₂-CH₂), 2.74 (t, J=7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.07 (CH₃); 21.65, 27.13, 28.04, 28.27, 28.42, 28.43, 28.49, 30.87, 35.21 (CH₂); 86.69, 92.23, 113.84, 123.27 (C_{butenylene}); C₁₄H₂₁Cl₂BrS (M, 372.19) Calcd. C, 45.18; H, 5.68; S, 8.61. Found C, 45.22; H, 5.42; S, 8.42.

### 1-Bromo-1,2-dichloro-4-(1-dodecylthio)-1-butene-3-yne (10g).

Yield 63%; Oil, R_f (Petroleum ether); 0.82; IR (film, cm⁻¹): 2147 (C=C), 2853, 2924 (C-H). UV-vis(CHCl₃): λ_{max} (logε) = 243 nm (5.1);

1H NMR (499.83 MHz, CDCl₃): δ 0.81 (t, J = 7.32Hz, 3H, CH₃), 1.19-1.35 (m, 18H, -(CH₂)₀₋₉), 1.71 (m, 2H, S-CH₂-CH₂), 2.74 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.08 (CH₃); 21.67, 27.14, 28.05, 28.33, 28.40, 28.43, 28.55, 28.61, 28.62, 30.91, 35.04 (CH₂); 86.70, 91.38, 112.54, 122.68 (C_{butenylene}); C₁₆H₂₅Cl₂BrS (M, 400.25) Calcd. C, 48.01; H, 6.29; S, 8.01. Found C, 47.96; H, 6.18; S, 8.27.

### 1-Bromo-1,2-dichloro-4-(1-hexadecylthio)-1-butene-3-yne (10h).

Yield 50%; Oil, R_f (Petroleum ether); 0.83; IR (film, cm⁻¹): 2146 (C=C), 2851, 2921 (C-H). UV-vis(CHCl₃): λ_{max}}
1-Bromo-1,2-dichloro-4-(1-octadecylthio)-1-buten-3-yne (10i). Yield 44%; Oil, Rf (Petroleum ether): 0.79; IR (film, cm⁻¹): 2148 (C=C), 2853, 2923 (C-H). UV-vis(CHCl₃): λ_max (logε) = 244 nm (3.9); ¹H NMR (499.83 MHz, CDCl₃): δ 0.81 (t, J = 7.32 Hz, 3H, CH₃), 1.2-1.4 (m, 26H, -(CH₂)₁₅-), 1.71 (m, 2H, S-CH₂-CH₂), 2.73 (t, J=7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.09 (CH₃); 21.68, 27.13, 27.15, 28.04, 28.33, 28.35, 28.39, 28.42, 28.44, 28.55, 28.63, 28.65, 28.67, 28.69, 30.92, 35.07 (NH₂), 86.69, 91.36, 110.60, 125.47 (C-butynyl); C₂₂H₃₃Cl₂BrS (M, 484.41); Calcd. C, 54.78; H, 7.67; S, 6.04.

General procedure 3
Tris- or tetrakis-thiosubstituted butadiene compound (0.9 mmol) in 50 mL Petroleum ether (30-50 °C) was mixed with potassium tert-butoxide (0.2 g, 1.8 mmol) for 4h at room temperature. For 12c, Tetrahydoruran was used as solvent instead of Petroleum ether. Ether and water added to the reaction mixture and then organic layer was separated, dried with anhydrous MgSO₄. The solvent was evaporated and the residue was purified by column chromatography over silica gel (petroleum ether/chloroform).

1-Chloro-1,4,4-tris(4-bromophenylthio)-1,2,3-butatriene (12a) and 2-Chloro-1,1,4-tris(4-bromophenylthio)-1-buten-3-yne (13a). Yield 82%; Bright yellow crystalline solid, mp: 119-121°C. Rf (Petroleum ether): 0.35; IR (KBr, cm⁻¹): 2037, 859 (C=C=C=C), 2142 (C≡C), 1576 (C=C), 3073 (═C-H). UV-vis(CHCl₃): λ_max (logε) = 384 nm (4.9); ¹H NMR (499.83 MHz, CDCl₃): δ 7.12-7.44 (m, 12H, H_arom). UV-vis(CHCl₃): λ_max (logε) = 384 nm (4.9); ¹H NMR (499.83 MHz, CDCl₃): δ 7.12-7.44 (m, 12H, H_arom) ¹³C NMR (125.68 MHz, CDCl₃): δ 86.24, 93.19, 101.80, 115.53, 120.08, 120.76, 122.19, 122.49, 123.25, 127.17, 128.47, 128.97, 129.15, 129.81, 130.07, 130.22, 130.57, 130.83, 130.97, 131.23, 131.31, 131.45, 131.46, 131.47, 131.60, 132.19, 133.00, 134.23, 134.52, 137.53, 145.88, 153.13 (C_arom, CH_arom, C_butatriene, C_butenyl); MS (+ESI): m/² 648.84 [M+H]⁺; C₂₂H₁₂ClBr₃S₃ (M, 647.50); Calcd. C, 40.80; H, 1.85; S, 14.83. Found C, 40.67; H, 1.23; S, 15.63.

1-Chloro-1,4,4-tris(4-fluorophenylthio)-1,2,3-butatriene (12b) and 2-Chloro-1,1,4-tris(4-fluorophenylthio)-1-buten-3-yne (13b). Yield 76%; Oil, Rf [Petroleum ether/CHCl₃ (1:1): 0.40; IR (film, cm⁻¹): 2043, 870 (C=C=C=C), 2143 (C≡C), 1589 (C=C), 3068 (═C-H_arom). UV-vis(CHCl₃): λ_max (logε) = 316 nm (5.0); ¹H NMR (499.83 MHz, CDCl₃): δ 7.12-7.51 (m, 12H, H_arom) ¹³C NMR (125.68 MHz, CDCl₃): δ 86.07, 93.75, 110.00, 114.69, 115.93, 116.11, 116.29, 116.57, 116.75, 116.82, 126.95, 127.49, 128.53, 129.10, 129.16, 130.94, 132.51, 132.57, 133.90, 133.97, 135.12, 135.92, 135.99, 136.58, 140.26, 143.03, 161.64, 162.35, 163.37, 163.62, 164.33, 164.43 (C_arom, CH_arom, C_butatriene, C_butenyl); MS (+ESI): m/² 465.13 [M]⁺; C₂₂H₁₂ClF₃S₃ (M, 464.97); Calcd. C, 56.83; H, 2.60; S, 20.69. Found C, 57.0; H, 2.93; S, 21.07.
1-Chloro-1,4,4-tris(2-naphtylthio)-1,2,3-butatriene (12c) and 2-Chloro-1,1,4-tris(2-naphtylthio)-1-buten-3-ynne (13c). Yield 67%; Yellow crystalline solid, mp: 185-187 °C. Rf [Petroleum ether/CHCl₃ (1:1)]: 0.30; IR (KBr, cm⁻¹): 2043, 856 (C=C=C=C), 2141 (C=C), 1588 (C=C), 3055 (=C-H_arom). UV-vis(CHCl₃): λ_max (logε) = 392 nm (4.2); ¹H NMR (499.83 MHz, CDCl₃): δ 7.29–7.85 (m, 21H, H_arom). ¹³C NMR (125.68 MHz, CDCl₃): δ 109.76, 118.94, 122.85, 125.97, 126.28, 126.44, 126.55, 126.60, 126.69, 126.72, 126.76, 126.78, 126.83, 126.86, 126.91, 126.93, 127.04, 127.06, 127.14, 127.42, 127.63, 127.78, 127.80, 127.87, 127.89, 127.90, 127.92, 127.97, 128.03, 128.32, 128.57, 128.62, 128.99, 129.01, 129.08, 129.20, 129.28, 129.64, 129.72, 129.86, 129.90, 129.91, 130.06, 131.14, 132.06, 132.26, 132.46, 133.16, 134.30 (C_arom, C_H_arom, C_butatriene, C_butenyne); MS (+APCI): m/z 561.31 [M]+; C₄₈H₂₁Cl₃S₃ (M, 561.18). Calcd. C, 40.80; H, 1.85; S, 14.83. Found C, 40.67; H, 1.23; S, 15.03.

General procedure 4

Monothiosubstituted butenylene compound (1.5 mmol) and bromine (0.25 g, 1.5 mmol) were stirred in CCl₄ (30mL) for 3h at room temperature. Ether was added to the reaction mixture and extracted with 100 ml of 3% aqueous solution of Na₂S₂O₃ twice. The organic layer was separated, washed with water (4x30 mL), dried with anhydrous MgSO₄. The solvent was evaporated and the residue was purified by column chromatography over silica gel (petroleum ether).

1,2-Dibromo-3,4,4-trichloro-1(4-bromophenylthio)-1,3-butenadiene (8a). Yield 82%; White solid, mp: 60-62 °C. Rf (Petroleum ether): 0.67; IR (film, cm⁻¹): 1599, 1564 (C=C), 3080 (C-H_arom); UV-vis(CHCl₃): λ_max (logε) = 243 (4.02); ¹H NMR (499.83MHz, CDCl₃): δ 7.18-7.48 (m, 4H, H_arom); ¹³C NMR (125.68 MHz, CDCl₃): δ 118.97, 121.83, 123.36, 129.67, 131.57, 131.78, 132.88, 134.79; C₁₀H₄Br₂Cl₃S (M, 502, 27) Calcd. C, 37.91; H, 1.03; S, 7.32. Found C, 37.90; H, 1.03; S, 7.32.

1,2-Dibromo-3,4,4-trichloro-1-(2-naphtylthio)-1,3-butenadiene (8c). Yield 63%; White solid, mp: 65-67 C. Rf (Petroleum ether): 0.71; IR (KBr, cm⁻¹): 1585, 1538 (C=C), 3054 (C-H_arom); UV-vis(CHCl₃): λ_max (logε) = 241 (4.05); ¹H NMR (499.83MHz, CDCl₃): δ 7.16-7.92 (m, 7H, H_arom); ¹³C NMR (125.68 MHz, CDCl₃): δ 110.75, 118.94, 122.85, 125.97, 126.28, 126.44, 126.84, 126.97, 127.80, 128.03, 129.43, 131.15, 132.94; C₁₄H₇Br₂Cl₃S (M, 473.44) Calcd. C, 35.52; H, 1.49; S, 6.77. Found C, 34.92; H, 1.03; S, 7.22.

1,2-Dibromo-3,4,4-trichloro-1-(1-octyldithio)-1,3-butenadiene (8e). Yield 65%; Oil, Rf (Petroleum ether): 0.85; IR (film, cm⁻¹): 2855, 2927 (C-H), 1538, 1599 (C=C), UV-vis(CHCl₃): λ_max (logε) = 246 nm (5.3); ¹H NMR (499.83 MHz, CDCl₃): δ 0.8 (t, J = 7.32Hz, 3H, CH₃); 1.20-1.35 (m, 10H, -CH₂-); 1.58 (m, 2H, S-CH₂-CH₂), 2.89 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz,
CDCl₃; δ 13.05 (CH₃); 21.61, 27.46, 28.00, 28.04, 28.08, 30.74, 35.76 (CH₂); 109.84, 116.85, 123.69, 128.43 (C₈butadiene); C₁₂H₁₇Cl₃Br₂S (M, 459.50) Calcd. C, 31.37; H, 3.73; S, 6.98. Found C, 31.61; H, 3.49; S, 7.09.

1,2-Dibromo-3,4,4-trichloro-1-(1-decythio)-1,3-butadiene (8f). Yield 78%; Oil, Rₜ(Petroleum ether): 0.75; IR (film, cm⁻¹): 2854, 2924 (C-H), 1538, 1599 (C=C), UV-vis(CHCl₃): λₑ,max (log e) = 244 nm (5.1); ¹H NMR (499.83 MHz, CDCl₃): δ 0.81 (t, J = 7.32 Hz, 3H, CH₃), 1.19-1.34 (m, 10H, -(CH₂)₅- ), 1.58 (m, 2H, S-CH₂-CH₂), 2.89 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.09 (CH₃); 21.65, 28.05, 28.08, 28.27, 28.42, 28.49, 28.62, 30.87, 35.75 (CH₂); 109.82, 116.85, 123.69, 128.48 (C₈butadiene); C₁₄H₂₁Cl₃Br₂S (M, 487.50) Calcd. C, 34.46; H, 4.30; S, 6.56. Found C, 34.09; H, 4.97; S, 7.08.

1,2-Dibromo-3,4,4-trichloro-1-(1-dodecythio)-1,3-butadiene (8g). Yield 92%; Oil, Rₜ(Petroleum ether): 0.90; IR (film, cm⁻¹): 1598, 1539 (C=C), 2854, 2954 (C-H). UV-vis(CHCl₃): λₑ,max (log e) = 243 nm (5.0); ¹H NMR (499.83 MHz, CDCl₃): δ 0.82 (t, J = 7.32 Hz, 3H, CH₃), 1.19-1.34 (m, 26H, -(CH₂)₁₃- ), 1.58 (m, 2H, S-CH₂-CH₂), 2.92 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.09 (CH₃); 21.67, 27.45, 28.04, 28.07, 28.32, 28.41, 28.45, 28.53, 28.61, 30.90, 35.75 (CH₂); 109.81, 116.85, 123.69, 128.48 (C₈butadiene); C₁₆H₂₅Cl₃Br₂S (M, 515.50) Calcd. C, 37.24; H, 4.84; S, 6.20. Found C, 38.01; H, 4.85; S, 6.55.

1,2-Dibromo-3,4,4-trichloro-1-(1-hexadecylthio)-1,3-butadiene (8h). Yield 86%; Oil, Rₜ(Petroleum ether): 0.86; IR (film, cm⁻¹): 1598 (C=C), 2853, 2923 (C-H). UV-vis(CHCl₃): λₑ,max (log e) = 245 nm (4.8); ¹H NMR (499.83 MHz, CDCl₃): δ 0.81 (t, J = 7.32 Hz, 3H, CH₃), 1.18-1.35 (m, 26H, -(CH₂)₁₃- ), 1.56 (m, 2H, S-CH₂-CH₂), 2.89 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.09 (CH₃); 21.68, 27.45, 28.04, 28.07, 28.35, 28.41, 28.46, 28.53, 28.62, 28.65, 28.68, 28.69, 30.92, 35.75 (CH₂); 109.82, 116.85, 123.68, 128.47 (C₈butadiene); C₂₀H₃₃Cl₃Br₂S (M, 571.50) Calcd. C, 42.03; H, 5.78; S, 5.60. Found C, 41.95; H, 5.85; S, 5.55.

1,2-Dibromo-3,4,4-trichloro-1-(1-octadeylthio)-1,3-butadiene (8i). Yield 76%; Oil, Rₜ(Petroleum ether): 0.80; IR (film, cm⁻¹): 2855, 2925 (C-H), 1550 (C=C). UV-vis(CHCl₃): λₑ,max (log e) = 244 nm (4.4); ¹H NMR (499.83 MHz, CDCl₃): δ 0.81 (t, J = 7.32 Hz, 3H, CH₃), 1.18-1.38 (m, 30H, -(CH₂)₁₅-), 1.58 (m, 2H, S-CH₂-CH₂), 2.92 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.09 (CH₃); 21.68, 27.46, 27.53, 28.04, 28.08, 28.35, 28.42, 28.46, 28.53, 28.62, 28.63, 28.65, 28.67, 28.69, 28.76, 30.92, 35.76 (CH₂); 109.84, 116.85, 123.69, 128.48 (C₈butadiene); C₂₂H₃₇Cl₃Br₂S (M, 599.77) Calcd. C, 44.05; H, 6.22; S, 5.34. Found C, 44.52; H, 6.35; S, 5.12.

1,2-Dibromo-3,4,4-trichloro-1-(1-hexadecylthio)-1,3-butadiene (11h). Yield 88%; Oil, Rₜ(Petroleum ether): 0.83; IR (film, cm⁻¹): 1594 (C=C), 2853, 2923 (C-H). UV-vis(CHCl₃): λₑ,max (log e) = 244 nm (5.3); ¹H NMR (499.83 MHz, CDCl₃): δ 0.81 (t, J = 7.32 Hz, 3H, CH₃), 1.19-1.35 (m, 26H, -(CH₂)₁₃- ), 1.58 (m, 2H, S-CH₂-CH₂), 2.89 (t, J = 7.32, 2H, S-CH₂) ¹³C NMR (125.68 MHz, CDCl₃): δ 13.11 (CH₃); 21.69, 27.46, 28.06, 28.10, 28.36, 28.43, 28.44, 28.47, 28.55, 28.63, 28.66, 28.68, 28.70, 30.93, 35.75 (CH₂); 109.58, 118.25, 123.64, 128.41 (C₈butadiene); C₂₀H₃₃Cl₂Br₂S (M, 616.36) Calcd. C, 38.93; H, 5.35; S, 5.19. Found C, 38.25; H, 5.69; S, 4.97.
**General procedure 5**

Arylthiosubstituted butatriene compound (1.5 mmol) and iodine (0.38 g, 1.5 mmol) were stirred in CCl₄ (30 mL) for 3 h at room temperature. Ether was added to the reaction mixture and extracted with 100 ml of 3% aqueous solution of Na₂S₂O₅ twice. The organic layer was separated, washed with water (4x30 mL), dried with anhydrous MgSO₄. The solvent was evaporated and the residue was purified by column chromatography over silica gel (petroleum ether/chloroform).

1-Chloro-2,3-diiodo-1,4,4-tris(4-bromophenylthio)-1,3-butadiene (15a). Yield 87%; Oil, Rₐ (Petroleum ether): 0.35; IR (film, cm⁻¹): 1563 (C=C), 3077 (=C-Harom). ¹H NMR (499.83 MHz, CDCl₃): δ 6.84-7.46 (m, 12H, Harom); ¹³C NMR (125.68 MHz, CDCl₃): δ 61.92, 67.46, 99.76, 102.30, 102.54, 102.79, 121.41, 121.65, 121.70, 122.58, 129.37, 129.86, 130.19, 130.47, 130.49, 130.55, 130.60, 130.69, 130.73, 130.76, 130.80, 131.50, 131.54, 131.61, 132.20, 132.30, 133.07, 133.13, 133.18, 133.39, 133.84, 133.92, 134.18, 138.46, 139.45; (CHarom, Carom, Cbutadien) MS (+ESI): m/z 775.32 [M-I]⁺; C₂₂H₁₂Br₃ClI₂S₃ (M, 901.50). Calcd. C, 29.31; H, 1.34; S, 10.67. Found C, 29.88; H, 1.93; S, 11.09.

2,3-Diiodo-1,1,1,4-tetrakis(4-bromophenylthio)-1,3-butadiene (16a). Yield 76%; Light yellow crystalline solid, mp: 135-137 °C; Rₐ [Petroleum ether/CCl₄ (1:1)]: 0.42; IR (KBr, cm⁻¹): 1564 (C=C), 3076 (=C-Harom). ¹H NMR (499.83 MHz, CDCl₃): δ 6.88-7.25 (m, 16H, Harom); ¹³C NMR (125.68 MHz, CDCl₃): δ 131.98, 132.02, 133.58, 134.16 (CHarom), 68.40, 106.04, 122.67, 122.74, 131.81, 139.28 (Carom and Cbutadiene); MS (+ESI): m/z 1052 [M⁺]; C₂₈H₁₂Br₄I₂S₄ (M, 1054.11). Calcd. C, 31.90; H, 1.53; S, 12.17. Found C, 32.23; H, 1.75; S, 12.88.

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