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Synthesis of New Sulfanyl-, Sulfinyl-, and Sulfonyl-Substituted Polychlorobuta-1,3-dienes[1]

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Abstract—New R-sulfanyl-substituted polychlorobuta-1,3-dienes were synthesized by reactions of hexachloro-1,3-butadiene or 1,1,2,4,4-pentachlorobuta-1,3-diene with dimethylbenzenethiols, heptane-1-thiol, and 4-methyl-7-sulfanyl-2*H*-chromen-2-one. Some sulfides were oxidized to the corresponding sulfoxides and sulfones or brominated with bromine. Among the synthesized compounds, the coumarin derivative, 4-methyl-7-(1,2,3,4,4-pentachlorobuta-1,3-dien-1-ylsulfanyl)-2*H*-chromen-2-one showed fluorescence properties. 1,1′,1″-[3,4-Dichlorobuta-1,3-diene-1,1,4-triyltris(sulfanediyl)]tris(2,4-dimethylbenzene) reacted with potassium *tert*-butoxide in petroleum ether to afford a mixture of isomeric 1,1′,1″-[4-chlorobuta-1,2,3-triene-1,1.4-triyltris(sulfanediyl)]tris(2,4-dimethylbenzene) and 1,1′,1″-[2-chlorobut-1-en-3-yne-1,1,4-triyltris(sulfanediyl)]-tris(2,4-dimethylbenzene). The GC/MS method was found to be useful for the separation of some sulfanyl-substituted butadiene isomer mixtures. The synthesized compounds were characterized by elemental analyses, mass spectrometry, UV-Vis, IR, and NMR (^{1}H, ^{13}C) or fluorescence spectroscopy.

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Thioethers have found widespread use in the synthesis of biologically active compounds and various drugs [1–3]. For instance, aryl sulfides have received considerable attention because of their applications in some drugs commonly used for the treatment of diabetes and Alzheimer's and Parkinson's diseases [1]. Also, sulfoxides are useful intermediates in the synthesis of drugs and natural products [4]. Haloalkyl sulfones possess biological properties such as herbicidal, bactericidal, antifungal, and insecticidal activity [5]. Furthermore, [3]cumulenes are generally unstable compounds which have received attention in chemistry [6].

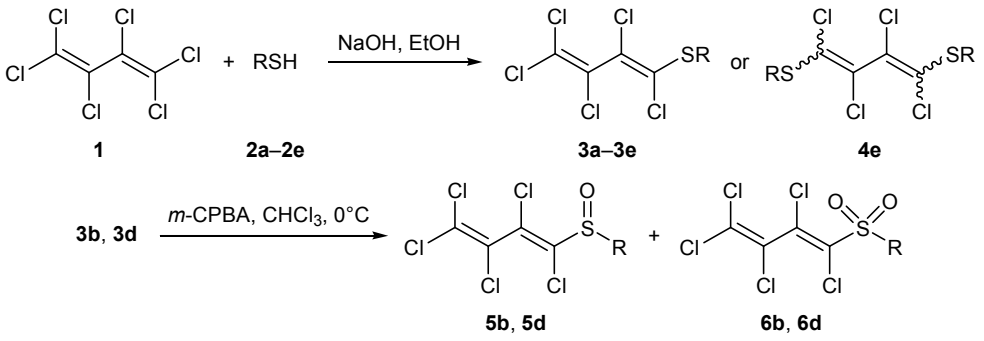
Sulfanyl-, sulfinyl-, and sulfonyl-substituted butadienes or butenynes were synthesized previously from polyhalodienes [7–16]. In particular, we described [7] the synthesis of a new series of sulfanyl-substituted butadienes, butenynes, and [3]cumulenes starting from 1,1,2,4,4-pentachlorobuta-1,3-diene and their bromination, iodination, or oxidation. In the present work we report the synthesis of mono-, bis-, and tris-sulfanyl-substituted butadienes, butenynes and their bromination and oxidation to sulfoxides/sulfones, as well as the synthesis of tris(sulfanyl)[3]cumulene starting from 1,1,2,4,4-pentachlorobuta-1,3-diene.

The reaction of hexachlorobuta-1,3-diene (**1**) with thiols **2a**–**2d** in ethanol in the presence of NaOH gave monosulfanyl derivatives **3a**–**3d**, whereas coumarin derivative **2e** reacted with **1** to produce mono- or bis-sulfanyl-substituted compound **3e** or **4e**, depending on the reactant ratio (Scheme 1). Sulfides **3b** and **3d** were oxidized with *m*-chloroperoxybenzoic acid in chloroform at 0°C; as a result, mixtures of the corresponding sulfoxides **5b**, **5d** (major product, 60–65%) and sulfones **6b**, **6d** (minor product, 10%) were obtained. The products were isolated by silica gel column chromatography. Compounds **5b** and **5d** exhibited characteristic S=O stretching bands at 1088 and 1077 cm^{-1}, respectively, in the IR spectra. Sulfones **6b** and **6d** showed peaks at 1338, 1156 cm^{-1} and 1341, 1143 cm^{-1} (νSO_2), respectively. In the ^{1}H NMR spectra of **5b**, **5d**, **6b**, and **6d**, protons of the methyl groups and aromatic rings gave signals in a lower field than in the spectra of initial sulfides **3b** and **3d**, which clearly indicated oxidation of the sulfur atom to sulfoxide or sulfonyl group. The mass spectra of these compound were also consistent with the proposed structures.

The ^{13}C NMR spectrum of coumarin derivative **3e** contained a signal at δ_C 160.07 ppm due to the carbonyl carbon atom, and a carbonyl stretching band at 1752 cm^{-1} was observed in the IR spectrum of **3e**. The aromatic protons in the coumarin fragment resonated

[1] The text was submitted by the authors in English.

Scheme 1.



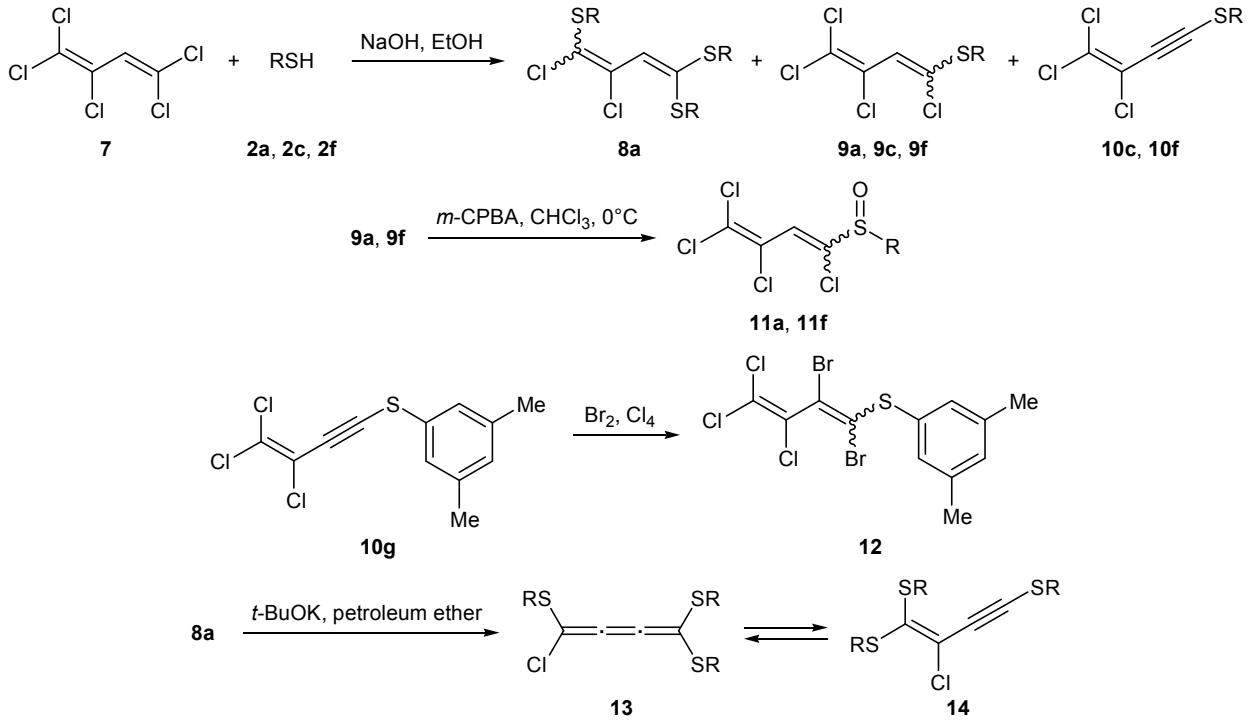
2–**6**, R = 2,4-$Me_2C_6H_3$ (**a**), 2,5-$Me_2C_6H_3$ (**b**), 3,4-$Me_2C_6H_3$ (**c**), C_7H_{15} (**d**), 4-methyl-2-oxo-2*H*-chromen-7-yl (**e**).

in the ^{1}H NMR spectrum of **3e** at δ 6.25 (s), 7.26 (d.d), 7.31 (s), and 7.54 ppm (d). The ESI mass spectrum of **3e** showed the protonated molecular ion peak with *m*/*z* 417.0 $[M + H]^+$ (calculated for $C_{14}H_7Cl_5O_2S$ 416.54). Taking into account that thiol **2e** exhibits fluorescence, we expected that compound **3e** fluoresces as well. In fact, compound **3e** in chloroform ($c = 10^{-4}$ M) showed an emission maximum at λ 395.1 nm in the fluorescence spectrum, which corresponded to the maximum at λ 359.1 nm in the fluorescence excitation spectrum (see figure).

The reactions of 1,1,2,4,4-pentachlorobuta-1,3-diene (**7**) with thiols **2a**, **2c**, and **2f** under analogous conditions (NaOH, EtOH) afforded compound **8a**, **9a**, **9c**, **9f**, **10c**, and **10f**. Sulfides **9a** and **9f** were oxidized to sulfoxides **11a** and **11f** with *m*-CPBA in $CHCl_3$ at 0°C (Scheme 2).

Compounds **9** were formed as mixtures of *E* and *Z* isomers. The isomers of **9c** were separated by GC/MS (different retention times of two isomers). The mass spectra of both isomers showed the same molecular ion peak (EI) with *m*/*z* 328.0 ($C_{12}H_{10}Cl_4S$, calcd. 328.09) and close similarity of the fragmentation patterns. In the ^{1}H NMR spectrum of **9c** we observed two vinyl proton signals at δ 6.11 and 6.44 ppm. Likewise, compound **9f** was a mixture of two isomers (GC/MS).

Scheme 2.



2, **8**–**11**, R = 2,4-$Me_2C_6H_3$ (**a**), 3,4-$Me_2C_6H_3$ (**c**), 2,6-$Me_2C_6H_3$ (**f**); **13**, **14**, R = 2,4-$Me_2C_6H_3$.

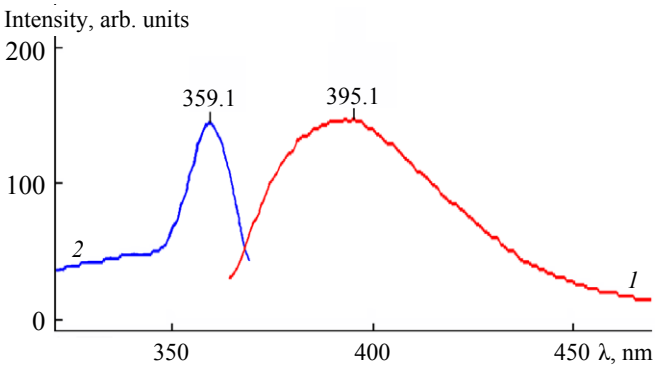
Treatment of **10g** [7] with bromine resulted in the formation of 1,2-dibromo-3,4,4-trichloro-1-(2,4-dimethylphenylsulfanyl)buta-1,3-diene (**12**) as a mixture of two isomers (GC/MS). The IR spectrum of **12** lacked C≡C stretching band typical of initial butenyne **10g** (2155 cm^{-1}), and no signals at δ_C 88.18 and 89.14 ppm [7] were observed in its ^{13}C NMR (APT) spectrum, indicating bromine addition to the triple bond.

Tris-sulfanyl [3]cumulene **13** was synthesized by elimination of HCl from **8a** by the action of potassium *tert*-butoxide in petroleum ether. The IR spectrum of **13** contained an absorption band at 2040 cm^{-1} characteristic of the C=C=C=C cumulene system. Presumably, [3]cumulene **13** exists in equilibrium with butenyne isomer **14**, as follows from the presence of a band at 2137 cm^{-1} (νC≡C) in the IR spectrum. The mass spectrum of **13**/**14** showed the protonated molecular ion peak with *m*/*z* 495.0 $[M + H]^+$.

EXPERIMENTAL

The melting points were obtained on a Buchi B-540 apparatus. The IR spectra were measured in KBr using a Perkin Elmer Spectrum One FTIR instrument. The mass spectra were recorded on a Thermo Finnigan LCQ Advantage MAX system using ion-trap mass analyzer for ESI or APCI source. The GC/MS data were obtained on a Thermo Finnigan Trace DSQ system equipped with an EI source. The ^1H and ^{13}C (APT) NMR spectra were recorded on a Varian Unity Inova spectrometer (500 and 125 MHz, respectively) using $CDCl_3$ as solvent and TMS an internal standard. The elemental analyses (C, H, S) were obtained on a Thermo Finnigan Flash EA 1112 Series elemental analyzer. The UV-Vis spectra were measured on a Perkin Elmer Lambda 35 UV/Vis spectrophotometer from solutions in chloroform. The fluorescence and fluorescence excitation spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Column chromatography was carried out using silica gel (Kieselgel 60, 70–230 mesh, Merck). Kieselgel 60 F-254 plates (Merck) were used for thin-layer chromatography.

1,1,2,3,4-Pentachloro-4-(R-sulfanyl)buta-1,3-dienes 3a–3d (*general procedure*). A solution of 1.2 g of sodium hydroxide in 10 mL of water was added to an equimolar mixture of hexachlorobuta-1,3-diene (**1**) and thiol **2a**–**2d** in 25 ml of ethanol, and the mixture was stirred for 24 h at room temperature. The mixture was then diluted with ~50 mL of water and extracted with chloroform (3×40 mL), the combined extracts were dried over sodium sulfate and evaporated, and the residue was purified by silica gel column chromatography with petroleum ether as eluent.



(*1*) Fluorescence and (*2*) fluorescence excitation spectra of compound **3e** in chloroform.

2,4-Dimethyl-1-(1,2,3,4,4-pentachlorobuta-1,3-dien-1-ylsulfanyl)benzene (3a) was synthesized from 2 g (7.7 mmol) of hexachlorobuta-1,3-diene (**1**) and 1.06 g (7.7 mmol) of **2a**. Yield 0.56 g (20%), transparent oil, R_f 0.7 (petroleum ether). IR spectrum, ν, cm^{-1}: 1545, 1602 (C=C), 3011 (C–H_{arom}). UV spectrum, λ_{max}, nm (logε): 239 (4.16), 259 (4.13). ^1H NMR spectrum, δ, ppm: 2.27 s (3H, CH_3), 2.31 s (3H, CH_3), 6.95 d.d (1H, H_{arom}, ^3J = 7.6, ^4J = 1.2 Hz), 7.04 s (1H, H_{arom}), 7.31 d (^1H, H_{arom}, J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.73 (CH_3), 20.23 (CH_3), 118.93, 124.19, 124.22, 124.45, 126.57 (CH), 130.71 (CH), 133.34, 135.44 (CH), 139.96, 141.68. Mass spectrum (+APCI): *m*/*z* 361.8 $[M]^+$. Found, %: C 39.75; H 2.51; S 8.82. $C_{12}H_9Cl_5S$. Calculated, %: C 39.76; H 2.50; S 8.84. *M* 362.54.

1,4-Dimethyl-2-(1,2,3,4,4-pentachlorobuta-1,3-dien-1-ylsulfanyl)benzene (3b) was synthesized from 1.31 g (5.0 mmol) of **1** and 0.69 g (5.0 mmol) of **2b**. Yield 0.36 g (20%), transparent oil, R_f 0.7 (petroleum ether). IR spectrum, ν, cm^{-1}: 1547, 1603 (C=C), 3019 (C–H_{arom}). UV spectrum: λ_{max} 260 nm (logε 4.09). ^1H NMR spectrum, δ, ppm: 2.25 s (3H, CH_3), 2.30 s (3H, CH_3), 7.10 d (1H, H_{arom}, J = 7.8 Hz), 7.08 d.d (1H, H_{arom}, ^3J = 7.8, ^4J = 1.0 Hz), 7.25 s (1H, H_{arom}). ^{13}C NMR spectrum (APT), δ_C, ppm: 19.25 (CH_3), 19.68 (CH_3), 119.46, 124.15, 124.46, 127.36, 129.62 (CH), 130.25 (CH), 133.03, 135.47, 135.57 (CH), 138.47. Mass spectrum (+ESI): *m*/*z* 362.0 $[M]^+$. Found, %: C 39.75; H 2.50; S 8.83. $C_{12}H_9Cl_5S$. Calculated, %: C 39.76; H 2.50; S 8.84. *M* 362.54.

1,2-Dimethyl-4-(1,2,3,4,4-pentachlorobuta-1,3-dien-1-ylsulfanyl)benzene (3c) was synthesized from

0.61 g (2.4 mmol) of **1** and 0.32 g (2.4 mmol) of **2c**. Yield 0.17 g (20%), colorless viscous oil, R_f 0.6 (*n*-hexane). ^{13}C NMR spectrum, δ_C, ppm: 18.62 (CH_3), 18.69 (CH_3), 119.44, 124.16, 124.44, 124.97, 129.56, 131.27, 133.27, 134.68, 136.90, 137.87. Mass spectrum (+ESI): *m*/*z* 363.3 $[M + H]^+$. Found, %: C 39.75; H 2.50; S 8.82. $C_{12}H_9Cl_5S$. Calculated, %: C 39.76; H 2.50; S 8.84. *M* 362.54.

1,1,2,3,4-Pentachloro-4-(heptylsulfanyl)buta-1,3-diene (3d) was synthesized from 2 g (7.7 mmol) of **1** and 1 g (7.7 mmol) of **2d**. Yield 0.82 g (30%), transparent oil, R_f 0.8 (*n*-hexane). IR spectrum, ν, cm^{-1}: 1378, 1465, 2856, 2928, 2957 (C–H), 1545, 1601 (C=C). UV spectrum: λ_{max} 285 nm (log ε 3.93). ^{1}H NMR spectrum, δ, ppm: 0.82 t (3H, CH_3, *J* = 7.1 Hz), 1.16–1.30 m (6H, CH_2), 1.35 quint, 2H, CH_2, *J* = 7.2 Hz), 1.58 quint (2H, CH_2, *J* = 7.4 Hz), 2.91 m (2H, CH_2S). ^{13}C NMR spectrum (APT), δ_C, ppm: 14.24 (CH_3); 22.58, 28.63, 28.94, 30.00, 31.38, 34.20 (CH_2); 121.16, 125.55, 125.59, 134.50 (C=C). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 355.8 (8), 221.8 (36), 56.8 (100), 42.9 (46), 256.7 (9), 320.9 (5). Found, %: C 37.03; H 4.23; S 9.00. $C_{11}H_{15}Cl_5S$. Calculate, %: C 37.05; H 4.24; S 8.99. *M* 356.57.

4-Methyl-7-(1,2,3,4,4-pentachlorobuta-1,3-dien-1-ylsulfanyl)-2*H*-chromen-2-one (3e). A solution of 1.2 g of sodium hydroxide in 10 mL of water was added to a mixture of 2.0 g (7.7 mmol) of hexachlorobuta-1,3-diene (**1**) and 1.5 g (7.7 mmol) of coumarin **2e** in 25 mL of ethanol, and the mixture was stirred for 24 h at room temperature. The mixture was then adjusted to pH 2 with aqueous HCl and extracted with chloroform (3×40 mL), the extracts were combined, dried over Na_2SO_4, and evaporated, and the residue was purified by silica gel column chromatography with methylene chloride as eluent. Yield 0.64 g (20%), white solid, mp 141°C, R_f 0.8 (CH_2Cl_2). IR spectrum, ν, cm^{-1}: 1754 (C=O), 1598, 1620 (C=C). UV spectrum, λ_{max}, nm (log ε): 328 (4.38), 240 (4.37), 284 (4.27). Fluorescence spectrum ($CHCl_3$, $c = 10^{-4}$ M): λ_{max}(excit.) 359.07 nm, λ_{max}(fl.) 395.07 nm. ^{1}H NMR spectrum, δ, ppm: 2.38 s (3H, CH_3), 6.25 s (1H, H_{arom}), 7.26 d.d (1H, H_{arom}, ^3J 8.30, ^4J 1.96 Hz), 7.31 s (1H, H_{arom}), 7.54 d (1H, H_{arom}, *J* = 8.30 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.82 (CH_3), 116.18, 120.56, 120.67, 124.67, 125.51, 126.10, 126.52, 127.98, 131.45, 134.94, 151.77, 153.76; 160.07 (C=O). Mass spectrum (+ESI): *m*/*z* 417.0 $[M + H]^+$. Found, %: C 40.35; H 1.67; S 7.71. $C_{14}H_7Cl_5O_2S$. Calculated, %: C 40.37; H 1.69; S 7.70. *M* 416.54.

7,7′-[1,2,3,4-Tetrachlorobuta-1,3-dien-1,4-diylbis(sulfanediyl)]bis(4-methyl-2*H*-chromen-2-one) (4e). A solution of 1.4 g of sodium hydroxide in 15 mL of water was added to a mixture of 1.0 g (3.85 mmol) of hexachlorobutadiene **1** and 1.5 g (7.7 mmol) of 4-methyl-7-sulfanyl-2*H*-chromen-2-one (**2e**) in 25 mL of ethanol, and the mixture was stirred for 24 h at room temperature. The mixture was adjusted to pH 2 with aqueous HCl and extracted with chloroform (3× 40 mL), the extracts were combined, dried over Na_2SO_4, and evaporated, and the residue was purified by silica gel column chromatography using methylene chloride as eluent. Yield 0.66 g (30%), yellow solid, mp 236-241°C (decomp.). R_f 0.7 (EtOAc). IR spectrum, ν, cm^{-1}: 1734 (C=O), 1597, 1622 (C=C). UV spectrum, λ_{max}, nm (log ε): 330 (4.74), 239 (4.55), 291 (4.54). ^{13}C NMR spectrum, δ_C, ppm: 17.60 (CH_3), 113.40, 113.93, 113.94, 118.07, 121.11, 122.47, 123.53, 124.27, 130.07, 139.84, 150.80, 152.98; 159.11 (C=O). Mass spectrum (+ESI): *m*/*z* 573.1 $[M + H]^+$. Found, %: C 50.35; H 2.45; S 11.20. $C_{24}H_{14}Cl_4O_4S_2$. Calculated, %: C 50.37; H 2.47; S 11.21. *M* 572.32.

1,4-Dimethyl-2-(1,2,3,4,4-pentachlorobuta-1,3-diene-1-sulfinyl)benzene (5b) and 1,4-dimethyl-2-(1,2,3,4,4-pentachlorobuta-1,3-diene-1-sulfonyl)-benzene (6b). A solution of 109 mg (0.3 mmol) of sulfide **3b** in 10 mL of chloroform was added at 0°C to a solution of 52 mg (0.3 mmol) of *m*-chloroperoxybenzoic acid in 10 mL chloroform, and the mixture was stirred for 96 h at 0°C. The mixture was then treated with 2N NaOH and washed with water, and the organic layer was separated and dried over Na_2SO_4. The solvent was evaporated, and the residue was subjected to silica gel column chromatography ($CHCl_3$) to isolate **5b** and **6b**.

Compound **5b**. Yield 68 mg (60%), light yellow oil, R_f 0.7 (CH_2Cl_2). IR spectrum, ν, cm^{-1}: 1088 (S=O), 1607, 1555 (C=C). UV spectrum: λ_{max} 246 nm (log ε 4.22). ^{1}H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3), 2.36 s (3H, CH_3), 7.06 d (1H, H_{arom}, *J* = 7.81 Hz), 7.19 d (1H, H_{arom}, *J* = 7.32 Hz), 7.71 s (1H, H_{arom}). ^{13}C NMR spectrum (APT), δ_C, ppm: 18.48 (CH_3), 21.33 (CH_3), 110.00, 126.48, 129.02, 130.97, 131.07, 131.10, 132.64, 133.03, 137.44, 138.04. Mass spectrum (+ESI): *m*/*z* 378.8 $[M + H]^+$. Found, %: C 38.06; H 2.41; S 8.46. $C_{12}H_9Cl_5OS$. Calculated, %: C 38.08; H 2.40; S 8.47. *M* 378.53.

Compound **6b**. Yield 12 mg (10%), light yellow oil, R_f 0.8 ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1338, 1156

(SO_2), 1605, 1557 (C=C). UV spectrum ($CHCl_3$): λ_{max} 251 nm (log ε 4.24). ^{1}H NMR spectrum, δ, ppm: 2.39 s (3H, CH_3), 2.49 s (3H, CH_3), 7.17 d (1H, H_{arom}, J = 7.81 Hz), 7.31 d (1H, H_{arom}, J = 7.81 Hz), 7.87 s (1H, H_{arom}). ^{13}C NMR spectrum (APT), δ_C, ppm: 19.77 (CH_3), 21.07 (CH_3), 119.11, 124.19, 126.25, 131.09, 131.42, 132.87, 135.73, 135.91, 136.07, 136.79. Mass spectrum (EI): m/z 393.8. Found, %: C 36.51; H 2.30; S 8.11. $C_{12}H_9Cl_5O_2S$. Calculated, %: C 36.53; H 2.30; S 8.13. M 394.53.

1,1,2,3,4-Pentachloro-4-(heptane-1-sulfinyl)-buta-1,3-diene (5d) and 1,1,2,3,4-pentachloro-4-(heptane-1-sulfonyl)buta-1,3-diene (6d). A solution of 0.2 g (0.56 mmol) of sulfide **3d** in 10 mL of chloroform was added at 0°C to a solution of 0.19 g (1.12 mmol) of *m*-chloroperoxybenzoic acid in 10 mL of chloroform, and the mixture was stirred for 96 h at 0°C. The mixture was then treated as described above for **5b** and **6b** to isolate sulfoxide **5d** and sulfone **6d**.

Compound **5d**. Yield 136 mg (65%), light yellow oil, R_f 0.5 ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1077 (S=O), 1611, 1559 (C=C), 2856, 2926 (C–H). UV spectrum: λ_{max} 242 nm (log ε 3.89). ^{1}H NMR spectrum, δ, ppm: 0.82 t (3H, CH_3), 1.16–1.32 m (6H, CH_2), 1.33–1.48 m (2H, CH_2), 1.68 quint (2H, CH_2), 2.76–3.00 m (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 14.20 (CH_3); 22.44, 22.70, 28.86, 28.98, 31.65, 52.99 (CH_2); 123.21, 126.86, 131.06, 142.55 (C=C). Mass spectrum (+ESI): m/z 372.8 $[M + H]^+$. Found, %: C 35.44; H 4.06; S 8.60. $C_{11}H_{15}Cl_5OS$. Calculated, %: C 35.46; H 4.06; S 8.61. M 372.57.

Compound **6d**. Yield 20 mg (10%), light yellow oil, R_f 0.8 ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1341, 1143 (SO_2), 1603 (C=C), 2857, 2926 (C–H). UV spectrum: λ_{max} 250 nm (log ε 4.05). ^{1}H NMR spectrum, δ, ppm: 3.28 t (2H, CH_2S, J = 7.81 Hz), 1.78 quint (2H, CH_2, J = 7.81 Hz), 1.39 quint (2H, CH_2, J = 7.32 Hz), 1.23 m (6H, CH_2), 0.82 t (3H, CH_3, J = 6.83 Hz). ^{13}C NMR spectrum (APT), δ_C 14.19 (CH_3), 22.31, 22.68, 28.38, 28.83, 31.55, 54.29 (CH_2); 124.00, 126.33, 132.69, 134.78 (C=C). Mass spectrum (EI): m/z 388.0 $[M]^+$. Found, %: C 34.01; H 3.87; S 8.23. $C_{11}H_{15}Cl_5O_2S$. Calculated, %: C 34.00; H 3.89; S 8.25. M 388.57.

1,1′,1″-[3,4-Dichlorobuta-1,3-diene-1,1,4-triyl-tris(sulfanediyl)]tris(2,4-dimethylbenzene) (8a) and 2,4-dimethyl-1-(1,3,4,4-tetrachlorobuta-1,3-dien-1-ylsulfanyl)benzene (9a). A solution of 1.4 g of sodium hydroxide in 10 mL of water was added to a mixture of 2.0 g (8.8 mmol) of pentachlorobutadiene **7** and 3.65 g (26.4 mmol) of 2,4-dimethylbenzenethiol in 30 mL of ethanol, and the mixture was stirred for 24 h at room temperature. The mixture was treated with ~50 mL of water and extracted with chloroform (3× 40 mL), the combined extracts were dried over Na_2SO_4 and evaporated, and the residue was subjected to silica gel column chromatography with *n*-hexane as eluent to isolate compounds **8a** and **9a**.

Compound **8a**. Yield 1.87 g (40%), yellow oil, R_f 0.8 ($CHCl_3$–*n*-hexane, 1:2). IR spectrum, ν, cm^{-1}: 1601, 1543 (C=C). UV spectrum, λ_{max}, nm (log ε): 244 (4.39), 321 (4.29). ^{13}C NMR spectrum, δ_C, ppm: 19.12, 19.35, 19.66, 20.15 (CH_3); 108.76, 119.48, 119.81, 126.00, 126.29, 126.39, 126.58, 130.15, 130.42, 130.52, 132.13, 133.86, 133.94, 134.08, 134.69, 134.88, 138.09, 138.83, 138.90, 140.51, 141.16. Mass spectrum (+ESI): m/z 531.0 $[M + H]^+$. Found, %: C 63.24; H 5.30; S 18.08. $C_{28}H_{28}Cl_2S_3$. Calculated, %: C 63.26; H 5.31; S 18.09. M + H 531.63.

Compound **9a**. Yield 0.23 g (8%), light yellow oil, R_f 0.6 (*n*-hexane). IR spectrum, ν, cm^{-1}: 1566, 1602 (C=C). UV spectrum, λ_{max}, nm (log ε): 268 (4.06), 239 (4.01). ^{1}H NMR spectrum, δ, ppm: 2.24 s (3H, CH_3), 2.31 s (3H, CH_3), 6.42 s (1H, 2′-H), 6.92 d.d (1H, H_{arom}, ^3J = 7.80, ^4J = 1.46 Hz), 6.99 s (1H, H_{arom}), 7.27 d (1H, H_{arom}, J = 7.81 Hz). ^{13}C NMR spectrum (APT), δ_C, ppm: 20.96, 21.45 (CH_3); 123.88 ($C^{2'}$); 127.72, 131.84, 135.52 (CH_{arom}); 122.24, 124.79, 126.52, 138.57, 140.39, 142.04. Mass spectrum (EI), m/z (I_{rel}, %): 328.0 (50), 293.1 (38), 256.1 (100), 220.1 (30), 148.1 (40), 105.1 (55), 77.0 (69). Found, %: C 43.92; H 3.06; S 9.75. $C_{12}H_{10}Cl_4S$. Calculated, %: C 43.93; H 3.07; S 9.77. M 328.09.

2,4-Dimethyl-1-(1,3,4,4-tetrachlorobuta-1,3-diene-1-sulfinyl)benzene (11a). A solution of 70 mg (0.21 mmol) of compound **9a** in 10 mL of chloroform was added at 0°C to a solution of 36 mg (0.21 mmol) of *m*-chloroperoxybenzoic acid in 10 mL of chloroform, and the mixture was stirred for 48 h at 0°C. The mixture was then treated with 2 N NaOH and washed with water, the organic layer was separated, dried over Na_2SO_4, and evaporated, and the residue was purified by silica gel column chromatography with *n*-hexane as eluent. Yield 60 mg (81%), yellow oil, R_f 0.6 ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1074 (S=O), 1603 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.30 s (3H, CH_3), 2.48 s (3H, CH_3), 7.0 s (1H, 2′-H), 7.12 d (1H, H_{arom}), 7.45 s (1H, H_{arom}), 7.53 d (1H, H_{arom}). Mass spectrum (+ESI): m/z 344.9 $[M + H]^+$; calculated for $C_{12}H_{10}Cl_4OS$: M 344.1.

Dimethyl(1,3,4,4-tetrachlorobuta-1,3-dien-1-ylsulfanyl)benzenes 9c, 9f and dimethyl(3,4,4-trichlorobut-3-en-1-yn-1-ylsulfanyl)benzenes 10c, 10f (*general procedure***).** A solution of 1.2 g of sodium hydroxide in 10 mL of water was added to a mixture of equimolar amounts of pentachlorobutadiene **7** and dimethylbenzenethiol **2c** or **2f** in 25 mL of ethanol [1 g (4.4 mmol) of **7** and 608 mg (4.4 mmol) of **2c** in the synthesis of **9c** and **10c**; 0.8 g (3.5 mmol) of **7** and 480 mg (3.5 mmol) of **2f** in the synthesis of **9f** and **10f**], and the mixture was stirred for 24 h at room temperature. The mixture was then diluted with ~50 mL of water and extracted with chloroform (3×40 mL), the combined extracts were dried over Na_2SO_4 and evaporated, and the residue was subjected to silica gel column chromatography with petroleum ether as eluent to isolate compounds **9c** and **10c** or **9f** and **10f.**

1,2-Dimethyl-4-(1,3,4,4-tetrachlorobuta-1,3-dien-1-ylsulfanyl)benzene (9c, isomer mixture, 37:63**).** Yield 116 mg (8%), light yellow oil, R_f 0.7 (*n*-hexane). IR spectrum, ν, cm^{-1}: 1595, 1567 (C=C), 1383, 2970, 2861 (CH_3), 3018 (C–H_{arom}). UV spectrum: λ_{max} 265 nm (logε 4.18). ^1H NMR spectrum, δ, ppm: 2.18 s (6H, CH_3), 2.19 s (3H, CH_3), 2.20 s (3H, CH_3), 7.04 d (1H, H_{arom}, ^3J = 7.81 Hz), 7.09 d (1H, H_{arom}, ^3J = 7.81 Hz), 7.12 d.d (1H, H_{arom}, ^3J = 7.81, ^4J = 1.96 Hz), 7.14–7.19 m (2H, H_{arom}), 7.21 s (1H, H_{arom}), 6.11 s and 6.44 s (1H each, 2′-H). ^{13}C NMR spectrum (APT), δ_C, ppm: 19.79, 19.85, 19.90, 19.91 (CH_3); 130.71, 131.16, 131.18, 131.75, 134.65, 135.22 (CH_{arom}); 120.31, 125.30 ($C^{2'}$); 122.00, 122.35, 124.70, 124.81, 127.21, 127.47, 137.99, 138.33, 138.51, 138.54, 139.05, 139.15. Mass spectrum (EI): *m*/*z* 328.0 $[M]^+$. Found, %: C 43.92; H 3.05; S 9.77. $C_{12}H_{10}Cl_4S$. Calculated, %: C 43.93; H 3.07; S 9.77. *M* 328.09.

1,2-Dimethyl-4-(3,4,4-trichlorobut-3-en-1-yn-1-ylsulfanyl)benzene (10c). Yield 206 mg (16%), light yellow solid, mp 39°C, R_f 0.6 (petroleum ether). IR spectrum, ν, cm^{-1}: 2154 (C≡C), 1383, 2861, 2969 (CH_3), 1596 (C=C), 3015 (C–H_{arom}). UV spectrum: λ_{max} 255 nm (logε 4.74). ^1H NMR spectrum, δ, ppm: 2.18 s (3H, CH_3), 2.19 s (3H, CH_3), 7.06 d (1H, H_{arom}, *J* = 7.8 Hz), 7.11 d.d (1H, H_{arom}, ^3J = 7.8, ^4J = 1.9 Hz), 7.15 s (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 18.33, 18.75 (CH_3); 88.59, 88.62 (C≡C); 111.84, 123.89, 126.14, 126.22, 127.42, 129.77, 135.39, 137.23. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 292.0 (46), 220.1 (100), 185.1 (19), 135.1 (2), 77.0 (27). Found, %: C 49.41; H 3.12; S 11.02. $C_{12}H_9Cl_3S$. Calculated, %: C 49.42; H 3.11; S 11.00. *M* 291.63.

1,3-Dimethyl-2-(1,3,4,4-tetrachlorobuta-1,3-dien-1-ylsulfanyl)benzene (9f, isomer mixture**).** Yield 80 mg (7%), light yellow oil, R_f 0.7 (*n*-hexane). Mass spectrum (EI): *m*/*z* 327.8. Found, %: C 43.92; H 3.06; S 9.75. $C_{12}H_{10}Cl_4S$. Calculated, %: C 43.93; H 3.07; S 9.77. *M* 328.09.

1,3-Dimethyl-2-(3,4,4-trichlorobut-3-en-1-yn-1-ylsulfanyl)benzene (10f) [7]**.** Yield: 307 mg (30%), light yellow oil, R_f 0.8 (petroleum ether). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 291.8 (41), 219.9 (71), 184.9 (75), 134.9 (66). Found, %: C 49.41; H 3.12; S 11.02. $C_{12}H_9Cl_3S$. Calculated, %: C 49.42; H 3.11; S 11.00. *M* 291.63.

1,3-Dimethyl-2-(1,3,4,4-tetrachlorobuta-1,3-diene-1-sulfinyl)benzene (11f) was synthesized as described above for **11a** from 80 mg (0.24 mmol) of **9f**. Yield 40 mg (54%), R_f 0.5 ($CHCl_3$). IR spectrum: ν 1069 cm^{-1} (S=O). Mass spectrum (+ESI): *m*/*z* 345.1 $[M + H]^+$. Found, %: C 41.90; H 2.92; S 9.31. $C_{12}H_{10}Cl_4OS$. Calculated, %: C 41.89; H 2.93; S 9.32. *M* 344.1.

1-(1,2-Dibromo-3,4,4-trichlorobuta-1,3-dien-1-ylsulfanyl)-3,5-dimethylbenzene (12, isomer mixture, 40:60**).** A solution of 15.4 μL (0.3 mmol) of bromine in 50 mL of carbon tetrachloride was added to 88 mg (0.3 mmol) of **10g** [7]. The mixture was stirred for 5 h, washed with a solution of 3 g of $Na_2S_2O_6$ in 100 mL of water, and the organic layer was separated, washed with water, and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by silica gel column chromatography using *n*-hexane as eluent. Yield 37 mg (27%), light yellow oil, R_f 0.7 (*n*-hexane). IR spectrum, ν, cm^{-1}: 1579, 1601 (C=C), 3034 (C–H_{arom}). ^1H NMR spectrum, δ, ppm: 2.25 s (6H, CH_3), 2.26 s (6H, CH_3), 6.93 s (1H, H_{arom}), 6.97 s (3H, H_{arom}), 7.00 s (2H, H_{arom}). ^{13}C NMR spectrum (APT), δ_C, ppm: 20.17, 20.20 (CH_3); 129.15, 129.96, 130.36, 130.70 (CH_{arom}); 110.18, 118.28, 123.29, 123.38, 123.66, 125.88, 127.19, 127.22, 129.97, 130.36, 138.03, 138.08. Mass spectrum (EI): *m*/*z* 452.0 $[M]^+$. Found, %: C 31.91; H 2.00; S 7.12. $C_{12}H_9Cl_3Br_2S$. Calculated, %: C 31.93; H 2.01; S 7.10. *M* 451.44.

1,1′,1″-[4-Chlorobuta-1,2,3-triene-1,1.4-triyltris(sulfanediyl)]tris(2,4-dimethylbenzene) (13) and 1,1′,1″-[2-chlorobut-1-en-3-yne-1,1,4-triyltris(sulfanediyl)]tris(2,4-dimethylbenzene) (14) (isomer mixture**).** A solution of 96 mg (0.18 mmol) of **8a** in 40 mL of petroleum ether was added to 20 mg (0.18 mmol) of potassium *tert*-butoxide. The mixture was stirred for 4 h, washed with water, and extracted

with diethyl ether (3×60 mL). The combined extracts were dried over Na_2SO_4 and evaporated to give a mixture of isomers **13** and **14**. Yield 80 mg (90%), yellow oil, R_f 0.8 (*n*-hexane–$CHCl_3$, 1:1). IR spectrum, ν, cm^{-1}: 2040 (C=C=C=C), 2137 (C≡C), 1601, 1574 (C=C). ^1H NMR spectrum, δ, ppm: 2.1–2.3 m (36H, CH_3), 7.0–7.2 m (18H, H_{arom}). Mass spectrum (+ESI), *m*/z: 495.0 $[M + H]^+$, 358.0 $[M + H – SR]^+$. Calculated for $C_{28}H_{27}ClS_3$: *M* 495.2.

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