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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gpss20

Synthesis of Novel Thioethers from Polyhalobutadienes and Thiols

Nihal Onul^a, Wafaa M. Dib Brimo^a & Cemil Ibis^a

^a Division of Organic Chemistry, Department of Chemistry, Faculty of Engineering , Istanbul University , 34320, Avcilar, Istanbul, Turkey Published online: 31 Oct 2011.

To cite this article: Nihal Onul , Wafaa M. Dib Brimo & Cemil Ibis (2011) Synthesis of Novel Thioethers from Polyhalobutadienes and Thiols, Phosphorus, Sulfur, and Silicon and the Related Elements, 186:11, 2180-2188, DOI: <u>10.1080/10426507.2011.583615</u>

To link to this article: <u>http://dx.doi.org/10.1080/10426507.2011.583615</u>

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Phosphorus, Sulfur, and Silicon, 186:2180–2188, 2011 Copyright © Taylor & Francis Group, LLC ISSN: 1042-6507 print / 1563-5325 online DOI: 10.1080/10426507.2011.583615

SYNTHESIS OF NOVEL THIOETHERS FROM POLYHALOBUTADIENES AND THIOLS

Nihal Onul, Wafaa M. Dib Brimo, and Cemil Ibis

Division of Organic Chemistry, Department of Chemistry, Faculty of Engineering, Istanbul University, 34320 Avcilar, Istanbul, Turkey

GRAPHICAL ABSTRACT



Abstract Substituted perchlorobutadienes were synthesized from the reactions of hexachloro-1,3-butadiene with some thiols in ethanol in the presence of sodium hydroxide. The oxidation products were obtained from the reactions of thioethers with m-chloroperbenzoic acid. The structures of the new compounds were characterized by microanalysis and spectroscopic data.

Keywords Hexachloro-1,3-butadiene; thiols; thioethers; sulphones; sulphoxides

INTRODUCTION

In our previous studies, we have carried out the reaction of hexachlorobutadiene with thiols and dithiols in various solvents such as DMSO, DMF, and EtOH.^{1–11} The treatment of hexachlorobutadiene with thiols and dithiols yielded mono(thio) substituted, bis(thio) substituted halogenobutadiene compounds, and cyclic or acylic thioethers.^{12–14}

Recently, significant attention was paid to compounds with high sulfur content such as thioethers, as they play some key roles in biochemistry, nanochemistry, polymer chemistry, supramolecular chemistry, and material chemistry.^{15–18} Additionally, it was reported in

Received 8 February 2011; accepted 19 April 2011.

Address correspondence to Cemil Ibis, Department of Chemistry, Faculty of Engineering, Istanbul University, 34320 Avcilar, Istanbul, Turkey. E-mail: ibiscml@istanbul.edu.tr

some patents issued in the United States that thio-substituted butadiene compounds exhibit biological activities as interesting molecules in the field of pharmacology.¹⁹

As for halogenobutadienes, they are suitable for dielectrics, refrigerants, and heat transfer agents, and they can be used as aerosols, lubricants, and floatation agents. Many halogenobutadienes exhibit high antitumor activities.^{20–22}

The aim of this work was to synthesize novel *S*- and *S*,*S*- substituted halogenobutadiene compounds by carrying out reactions of hexachlorobutadiene with some thiols, and to characterize the structure of these novel compounds.

RESULTS AND DISCUSSION

As shown in Scheme 1, novel compounds were obtained by reactions of hexachloro-1,3-butadiene (1) with acyclic, cyclic, and aromatic thiols 2a-1 in ethanol in the presence of sodium hydroxide.



Scheme 1

Oxidation of sulfide compounds 3a, 3d, 3f, and 7^8 was carried out using one equivalent of metachloroperbenzoic acid (m-CPBA) at 0 °C to yield the sulfoxides 5a, 5d, 5f, 8, and the sulfones 6f and 9.

The ¹H NMR spectra of **3a–c** and **4a–c** exhibit signals at about δ 2.5–2.9 ppm due to the SCH₂ protons. Studies on bis-thiosubstituted butadienes have shown that substitution occurs at positions 1 and 4.^{1,6,13} The ¹³C NMR spectra of **3a–h** show four signals due to the butadiene skeleton. As expected, two signals for the symmetric carbons of butadiene were observed in the ¹³C NMR spectra of **4a–h**. The ¹³C NMR shifts of the C-4 carbon atoms of butadiene in compounds **3a–h** appeared around 125 ppm. On the other hand, C-4 and C-1 carbon atoms of butadiene in compounds **4a–h** appeared around 131 ppm in the ¹³C NMR spectra. The quaternary carbons of **3e** and **4e** appeared at δ 52 and 49 ppm in the ¹³C NMR spectra. The ¹H NMR spectra of **3g** and **4g** showed triplet signals corresponding to S–CH₂ proton at about δ 2.9 ppm and a multiplet for aromatic protons at about δ 7.1–7.4 ppm.

In multiple reaction monitoring (MRM), a precursor mass ion is selected for each compound in the first quadrupole (Q1) and then fragmented in the collision cell (Q2) to yield a diagnostic product ion monitored by the third quadrupole (Q3). A signal is detected only if the selected precursor ion from Q1 yields a selected product ion in Q3, so in the MRM mode each ionized compound gives distinct precursor-to-product ion transitions that are diagnostic for the presence of that particular compound.

Two MRM transitions were monitored for each compound. Q3 detects a selected mass of product ions generated by collision-induced dissociation of the precursor ions selected in Q1. The precursor ion (Q1) mass spectrum of 4f is given in Figure 1 and the product ion mass spectrum is given in Figure 2.

The precursor ion peak $[M+H]^+$ was detected at m/z 549.2 with strong abundance. Fragmentation of m/z 549.2 is shown in Figure 2. The peak of compound **4f** was caused by successive losses of chloro substituents. The transitions of the precursor ions to the productions m/z 549.2 \rightarrow 514.2, m/z 549.2 \rightarrow 478.1 and m/z 549.2 \rightarrow 443.2 were monitored for **4f**.



Figure 1 The precursor ion mass spectrum of 4f.



Figure 2 The product ion mass spectrum of 4f.

Aromatic protons of **3i**, **3j**, **3k**, **and 4j** appeared at about δ 6.5–7.5 in the ¹H NMR spectrum. Also, these compounds showed characteristic absorptions of aromatic C–H at around 3000 cm⁻¹ in the IR spectrum.

The IR spectrum of compounds **31** and **41** showed characteristic C–O–C absorption at around $1080-1160 \text{ cm}^{-1}$.

The bands at 1070, 1035, and 1060 cm⁻¹ in the IR spectrum of **5a**, **5d**, **5f**, and **8** were assigned to S=O stretching vibration, respectively. SO₂ group of **5f** and **9** were observed in the spectrum at 1150, 1300, and 1350 cm⁻¹. Those oxidation products were also characterized by mass spectrometry.

All of the compounds provided data conclusive to the proposed chemical structures.

EXPERIMENTAL

Melting points were measured on Büchi B-540 capillary apparatus and were uncorrected. IR spectra (cm⁻¹) were recorded on an FTIR spectrometer Shimadzu IR Prestige 21 model Diamond, ATR method. ¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova spectrometer at 499.83 MHz for ¹H and 125.48 MHz for ¹³C by using CDCl₃ as solvent and TMS as internal standard. Mass spectra were obtained on a hybrid triple quadrupole linear ion trap mass spectrometer (4000 QTRAP, ABSciex). The 4000 QTRAP was operated in the triple quadruple mass spectrometer mode using an electrospray ionization (ESI) source in the experiments presented here. Elemental analyses (C, H, S) were conducted using the Thermo Finnigan Flash EA 1112 elemental analyzer; their results were found to be in good agreement ($\pm 0.2\%$) with the calculated values. Products were isolated by column chromatography on silica gel (Fluka Silica gel 60, particle size 63–200 μ m). Kieselgel 60 F-254 plates (Merck) were used for thin layer chromatography (TLC). All chemicals were reagent grade and were used without further purification. Moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes.

Preparation of S-Substituted Polyhalobutadienes

General Procedure I. Equimolar amounts of 1,1,2,3,4,4-hexachloro-1,3-butadiene 1 in 10 mL of ethanol and thiols in 10 mL EtOH were mixed and NaOH (1.2 g in 8 mL of water) was added at room temperature. The mixture was stirred for 24 h until completion of the reaction (TLC). CHCl₃ (30 mL) was added to the reaction mixture and the organic layer was separated, washed with water (4 $\hat{1}$ 30 mL), and dried over anhydrous sodium sulfate. The residue was subjected to a separation by column chromatography using hexane as eluent. This afforded pure samples after evaporation of the solvents.

General Procedure II. Compounds **3a**, **3d**, **3f**, and **7** (1 mol) in 30 mL of CHCl₃ were mixed with m-cpba moles) in 30 mL of CHCl₃ at 0 °C for 24 h; 2N NaOH (30 mL) was added, and then CHCl₃ (30 mL) was added to the reaction mixture. The organic layer was separated and washed with water (4 Î 30 mL) and dried over anhydrous sodium sulfate. The residue was subjected to a separation by column chromatography using chloroform as eluent to afford pure samples after evaporation of the solvents.

1,1,2,3,4-Pentachloro-4-(pentylthio)-1,3-butadiene (3a) and 1,2,3,4-tetrachloro-1,4-bis(pentylthio)-1,3-butadiene (4a): Compounds 3a and 4a were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (2.0 g, 7.66 mmol) and 1-pentanethiol (2a) (0.79 g, 7.66 mmol) according to General Procedure I.

3a: Oil, yield 1.6 g (64%). R_f : 0.91 (hexane). IR (film) $\nu = 2900, 2950$ (CH), 1610 (C=C). ¹H NMR: $\delta = 0.83$ (t, J = 6.83 Hz, 3H, CH₃), 1.23–1.36 (m, 4H, CH₂), 1.56–1.61 (m, 2H, CH₂), 2.95 (t, J = 7.32 Hz, 2H, SCH₂). ¹³C NMR: $\delta = 12.86$ (CH₃), 21.14, 28.46, 29.60, 32.93 (CH₂), 119.89, 124.3, 125, 133.25 (C_{butadiene}). MS (+ESI): m/z: 329 [M+H]⁺, 293 [M+H–Cl]⁺, 257 [M+H–2Cl]⁺; C₉H₁₁Cl₅S (328.51). Calcd.%: C, 32.9; H, 3.38; S, 9.76. Found%: C, 32.55; H, 3.24; S, 9.77.

4a: Oil, yield 1.0 g (33%). R_f : 0.73 (hexane). IR (film) $\nu = 2930, 2970$ (CH), 1600 (C=C). ¹H NMR: $\delta = 0.8$ –0.9 (m, 6H, 2 CH₃), 1.23–1.36 (m, 8H, 4 CH₂), 1.54–1.64 (m, J = 7.32 Hz, 4H, 2 CH₂), 2.6–2.9 (m, 4H, 2 SCH₂). ¹³C NMR: $\delta = 12.93$ (CH₃), 21.29, 29.95, 31.77, 38.23 (CH₂), 123.95, 131.88 (C_{butadiene}). MS (+ESI): m/z: 397 [M+H]⁺, 362 [M+H–Cl]⁺, 327 [M+H–2Cl]⁺; C₁₄H₂₂Cl₄S₂ (396.27). Calcd.%: C, 42.43; H, 5.60; S, 16.18. Found%: C, 42.52; H, 5.80; S, 16.25.

1,1,2,3,4-Pentachloro-4-(octylthio)-1,3-butadiene (3b) and 1,2,3,4-tetrachloro-1,4-bis(octylthio)-1,3-butadiene (4b): Compounds 3b and 4b were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 1-octanethiol (2b) (1.68 g, 11.49 mmol) according to General Procedure I.

3b: Oil, yield 1.6 g (38%). R_f : 0.90 (hexane). IR (film) $\nu = 2900, 2920$ (CH), 1600 (C=C). ¹H NMR: $\delta = 0.85$ (t, J = 6.84 Hz, 3H, CH₃), 1.2–1.6 (m, 12H, 6 CH₂), 2.5 (t, J = 7.32 Hz, 2H, SCH₂). ¹³C NMR: $\delta = 14$ (CH₃), 23, 28.9, 29, 29.2, 29.4, 29.8, 30.2 (CH₂), 120.9, 124.9, 126, 134.6 (C_{butadiene}). MS (+ESI): m/z: 371 [M+H]⁺, 335 [M-Cl]⁺; C₁₂H₁₇Cl₅S (370.6). Calcd.%: C, 38.89; H, 4.62; S, 8.65. Found%: C, 38.95; H, 4.50; S, 8.70.

4b: Oil, yield 1 g (18%). R_f : 0.71 (hexane). IR (film) $\nu = 2920, 2970$ (CH), 1600 (C=C). ¹H NMR: $\delta = 0.85$ (t, J = 6.84 Hz, 6H, 2 CH₃), 1.2–1.4 (m, 24H, 12 CH₂), 2.7 (t, J = 7.32 Hz, 4H, 2 SCH₂). ¹³C NMR: $\delta = 13.5$ (CH₃), 21.6, 28.1, 28.5, 28.9, 29.4, 30.7, 30.9 (CH₂), 122, 134 (C_{butadiene}). MS (+ESI): m/z: 481 [M+H]⁺, 444 [M+H–Cl]⁺;

 $C_{20}H_{34}Cl_4S_2$ (480.4). Calcd.%: C, 50.0; H, 7.13; S, 13.35. Found%: C, 49.7; H, 7.22; S, 13.43.

1,1,2,3,4-Pentachloro-4-(nonylthio)-1,3-butadiene (3c) and 1,2,3,4-tetrachloro-1,4-bis(nonylthio)-1,3-butadiene (4c): Compounds 3c and 4c were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 1-nonanethiol (2c) (1.84 g, 11.49 mmol) according to General Procedure I.

3c: Oil, yield 1.4 g (32%). R_f : 0.90 (hexane). IR (film) $\nu = 2900, 2970$ (CH), 1600 (C=C). ¹H NMR: $\delta = 0.7$ (t, J = 6.84 Hz, 3H, CH₃), 1.06–1.61 (m, 14H, 7 CH₂), 2.85 (t, J = 7.32 Hz, 2H, SCH₂). ¹³C NMR: $\delta = 14.3$ (CH₃), 22.8, 28.6, 29.2, 29.4, 29.6, 29.9, 30, 32.2 (CH₂), 121, 125, 125.6, 134.5 (C_{butadiene}). MS (+ESI) *m/z*: 385 [M+H]⁺; C₁₃H₁₉Cl₅S (384.6). Calcd.%: C, 40.6; H, 4.98; S, 8.34. Found%: C, 40.5; H, 4.89; S, 8.3.

4c: Oil, yield 0.9 g (16%). R_f : 0.80 (hexane). IR (film) $\nu = 2900, 2930$ (CH), 1600 (C=C). ¹H NMR: $\delta = 0.85-0.88$ (m, 6H, 2 CH₃), 1.2–1.6 (m, 28H, 14 CH₂), 2.75–2.85 (m, 4H, 2 SCH₂). ¹³C NMR: $\delta = 13.5$ (CH₃), 21.6, 27.4, 28, 28.1, 28.3, 28.7, 30.8, 32.9 (CH₂), 119.9, 133.3 (C_{butadiene}). MS (+ESI) *m/z*: 509 [M+H]⁺, 473 [M+H–Cl]⁺; C₂₂H₃₈Cl₄S₂ (508.5). Calcd.%: C, 51.97; H, 7.53; S, 12.61. Found%: C, 52.11; H, 7.55; S, 12.59.

1,1,2,3,4-Pentachloro-4-(2-propylthio)-1,3-butadiene (3d) and 1,2,3,4-tetrachloro-1,4-bis(2-propylthio)-1,3-butadiene (4d): Compounds 3d and 4d were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 2-propanethiol (2d) (0.86 g, 11.49 mmol) according to General Procedure I.

3d: Oil, yield 1.14 g (33%). R_f : 0.82 (hexane). IR (film) $\nu = 2950, 2970$ (CH), 1610 (C=C). ¹H NMR: $\delta = 1.32$ (d, J = 6.84 Hz, 6H, 2 CH₃), 3.54–3.62 (m, J = 6.84 Hz, H, CH). ¹³C NMR: $\delta = 22.3$ (CH₃), 38.4 (CH), 121, 124, 125, 132.9 (C_{butadiene}). MS (+ESI) m/z: 301 [M+H]⁺, 265 [M+H–Cl]⁺; C₇H₇Cl₅S (300.5). Calcd.%: C, 27.98; H, 2.35; S, 10.67. Found%: C, 27.78; H, 2.19; S, 10.71.

4d: Oil, yield 0.78 g (20%). R_f : 0.62 (hexane). IR (film) $\nu = 2900, 2930$ (CH), 1600 (C=C). ¹H NMR: $\delta = 1.55$ (d, J = 6.84 Hz, 12H, 4 CH₃), 3.2–3.3 (m, J = 6.84 Hz, H, CH), 3.4–3.5 (m, J = 6.84 Hz, H, CH). ¹³C NMR: $\delta = 23.3$ (CH₃), 37.3 (CH), 123.8, 131.2 (C_{butadiene}). MS (+ESI) m/z: 341 [M+H]⁺, 305.3 [M+H–CI]⁺, 269 [M+H–2CI]⁺, 234 [M+H–3CI]⁺; C₁₀H₁₄Cl₄S₂ (340.2). Calcd.%: C, 35.31; H, 4.15; S, 18.85. Found%: C, 35.28; H, 4.11; S, 18.71.

1,1,2,3,4-Pentachloro-4-(tert-butylthio)-1,3-butadiene (*3e*)²³ and *1,2,3,4-tetrachloro-1,4-bis(tert-butylthio)-1,3-butadiene (4e)*: Compounds **3e** and **4e** were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 2-methylpropane-2-thiol (**2e**) (1.04 g, 11.49 mmol) according to **General Procedure I**.

3e: Oil, yield 1.5 g (42%). R_f : 0.68 (hexane). IR (film) $\nu = 2900$, 2920 (CH), 1600 (C=C). ¹H NMR: $\delta = 1.2-1.6$ (m, 9H, 3 CH₃). ¹³C NMR: $\delta = 31.7$ (CH₃), 52 (C_{tert}), 124, 125, 131, 134 (C_{butadiene}). MS (+ESI) *m/z*: 315 [M+H]⁺; C₈H₉Cl₅S (314.5). Calcd.%: C, 30.55; H, 2.88; S, 10.20. Found%: C, 30.45; H, 2.78; S, 10.3.

4e: Oil, yield 1 g (24%). R_f : 0.48 (hexane). IR (film) $\nu = 2900, 2920$ (CH), 1600 (C=C). ¹H NMR: $\delta = 1.3-1.4$ (m, 18H, 6 CH₃). ¹³C NMR: $\delta = 30.6$ (CH₃), 49 (C_{tert.}), 129, 132 (C_{butadiene}). MS (+ESI) m/z: 369 [M+H]⁺; C₁₂H₁₈Cl₄S₂ (368.2). Calcd.%: C, 39.19; H, 4.93; S, 17.42. Found%: C, 39.44; H, 4.87; S, 17.31.

1,1,2,3,4-Pentachloro-4-(4-tert-butylbenzylthio)-1,3-butadiene (3f) and 1,2,3,4tetrachloro-1,4-bis(4-tert-butylbenzylthio)-1,3-butadiene (4f): Compounds 3f and 4f were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 4-(tert-butylphenyl)methanethiol (2f) (2.1 g, 11.49 mmol) according to General Procedure I. **3f**: Oil, yield 1.47 g (32%). R_f : 0.58 (hexane). IR (film) $\nu = 3050$ (CH_{arom}), 2900, 2870 (CH), 1590 (C=C). ¹H NMR: $\delta = 1.0-1.3$ (m, 9H, 3 CH₃), 3.9–4.1 (m, 2H, SCH₂), 7.1–7.3 (m, J = 8.32 Hz, 4H, H_{arom}). ¹³C NMR: $\delta = 31.5$ (CH₃), 38 (CH₂), 38.9 (C_{tert}), 133.9, 151 (C_{arom}), 125, 127 (CH_{arom}), 120.9, 124.9, 126, 126.8 (C_{butadiene}). MS (+ESI) m/z: 405 [M+H]⁺, 369 [M+H–CI]⁺, 334 [M+H–2CI]⁺; C₁₅H₁₅Cl₅S (404.6). Calcd.%: C, 44.53; H, 3.74; S, 7.92. Found%: C, 44.50; H, 3.85; S, 7.44.

4f: Oil, yield 1 g (16%). R_f : 0.76 (CCl₄). IR (film) $\nu = 3050$ (CH_{arom}), 2900, 2890 (CH), 1600 (C=C). ¹H NMR: $\delta = 0.9$ –1.2 (m, J = 7.32 Hz, 18H, 6 CH₃), 3.4–4.1 (m, 4H, 2 SCH₂), 7.0–7.3 (m, J = 8.32 Hz, 8H, H_{arom}). ¹³C NMR: $\delta = 30.3$ (CH₃), 37 (CH₂), 38.9 (C_{tert}), 133.2, 149 (C_{arom}), 127.8, 128 (CH_{arom}), 119.9, 127 (C_{butadiene}). MS (+ESI) m/z: 549 [M+H]⁺, 514 [M+H–Cl]⁺, 478 [M+H–2Cl]⁺, 443 [M+H–3Cl]⁺; C₂₆H₃₀Cl₄S₂ (548.5). Calcd.%: C, 56.94; H, 5.51; S, 11.69. Found%: C, 56.95; H, 5.55; S, 11.73.

1,1,2,3,4-Pentachloro-4-(2-phenylethanethio)-1,3-butadiene (3g) and 1,2,3,4-tetrachloro-1,4-bis(2-phenylethanethio)-1,3-butadiene (4g): Compounds 3g and 4g were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 2-phenylethanethiol (2g) (1.59 g, 11.49 mmol) according to General Procedure I.

3g: Oil, yield 1.97 g (48%). R_f : 0.51 (hexane). IR (film) $\nu = 3040$ (CH_{arom}), 2900, 2960 (CH), 1600 (C=C). ¹H NMR: $\delta = 2.9$ (t, J = 7.32 Hz, 2H, SCH₂), 3.1–3.3 (m, 2H, CH₂), 7.1–7.3 (m, 5H, H_{arom}). ¹³C NMR: $\delta = 30$ (SCH₂), 38 (CH₂), 125, 127, 128 (CH_{arom}), 120.4, 124.1, 125.8, 132 (C_{butadiene}), 138.1 (C_{arom}). MS (+ESI) m/z: 363 [M+H]⁺, 327 [M–Cl]⁺, 290 [M–2Cl]⁺; C₁₂H₉Cl₅S (362.5). Calcd.%: C, 39.76; H, 2.50; S, 8.84. Found%: C, 39.89; H, 2.60; S, 8.50.

4g: Oil, yield 1.49 g (28%). R_f : 0.19 (hexane). IR (film) ν = 3020 (CH_{arom}), 2950, 2900 (CH), 1600 (C=C). ¹H NMR: δ = 2.7–2.9 (m, 4H, 2 SCH₂), 3.0–3.2 (m, 4H, 2 CH₂), 7.1–7.4 (m, 10H, H_{arom}). ¹³C NMR: δ = 32 (SCH₂), 39 (CH₂), 125.7, 127.6, 130.3 (CH_{arom}), 120.1, 138 (C_{butadiene}), 139 (C_{arom}). MS (+ESI) *m/z*: 465 [M+H]⁺, 430 [M+H–CI]⁺, 359 [M+H–3CI]⁺; C₂₀H₁₈Cl₄S₂ (464.3). Calcd.%: C, 51.74; H, 3.91; S, 13.81. Found%: C, 51.91; H, 3.37; S, 13.39.

1,1,2,3,4-Pentachloro-4-(cyclopentylthio)-1,3-butadiene (3h) and 1,2,3,4-tetrachloro-1,4-bis(cyclopentylthio)-1,3-butadiene (4h): Compounds 3h and 4h were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (2.0 g, 7.66 mmol) and cyclopentanethiol (2h) (0.78 g, 7.66 mmol) according to General Procedure I.

3h: Oil, yield 1.53 g (61%). R_f : 0.83 (hexane). IR (film) $\nu = 2900, 2950$ (CH), 1620 (C=C). ¹H NMR: $\delta = 1.53-1.77$ (m, 4H, 2 CH₂), 1.9–2.1 (m, 4H, 2 CH₂), 3.6–3.7 (m, H, CH). ¹³C NMR: $\delta = 23.8, 32.3$ (CH₂), 45 (CH), 120, 124, 125, 134 (C_{butadiene}). MS (+ESI) m/z: 325 [M–H]⁺, 289 [M–H–Cl]⁺, 183 [M–H–Cl]⁺; C₉H₉Cl₅S (326.5). Calcd.%: C, 33.11; H, 2.78; S, 9.82. Found%: C, 32.01; H, 2.79; S, 9.84.

4h: Oil, yield 0.9 g (30%). R_f : 0.6571 (hexane). IR (film) $\nu = 2900, 2930$ (CH), 1610 (C=C). ¹H NMR: $\delta = 1.4-1.7$ (m, 8H, 4 CH₂), 1.8–2.1 (m, 8H, 4 CH₂), 3.3–3.7 (m, 2H, 2 CH). ¹³C NMR: $\delta = 32, 34$ (CH₂), 46.1 (CH), 121.2, 131.9 (C_{butadiene}). MS (+ESI) *m/z*: 393 [M+H]⁺, 357 [M+H–Cl]⁺, 322 [M+H–2Cl]⁺; C₁₄H₁₈Cl₄S₂ (392.2). Calcd.%: C, 42.87; H, 4.63; S, 16.35. Found%: C, 42.58; H, 4.64; S, 16.50.

1,1,2,3,4-Pentachloro-4-(4-fluorophenylthio)-1,3-butadiene (3i): Compound **3i** was synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 4-fluorobenzenethiol (**2i**) (1.63 g, 11.49 mmol) according to **General Procedure I**.

3i: Oil, yield 1.27 g (31%). R_f : 0.75 (hexane). IR (film) $\nu = 3050$ (CH_{arom}), 1595 (C=C). ¹H NMR: $\delta = 6.9-7.8$ (m, 4H, H_{arom}). C₁₀H₄Cl₅FS (352.47). Calcd.%: C, 34.07; H, 1.14; S, 9.09. Found%: C 34.06; H 1.26; S 9.54.

1,1,2,3,4-Pentachloro-4-(4-bromophenylthio)-1,3-butadiene (3j and 1,2,3,4tetrachloro-1,4-bis(4-bromophenylthio)-1,3-butadiene (4j): Compounds 3j and 4j were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 4-bromobenzenethiol (2j) (2.33 g, 11.49 mmol) according to General Procedure I.

3j: Oil, yield 1.6 g (34%). R_f : 0.78 (hexane). IR (film) $\nu = 3050$ (CH_{arom}), 1600 (C=C). ¹H NMR: $\delta = 7.1-7.8$ (m, 4H, H_{arom}). C₁₀H₄Cl₅BrS (413.37). Calcd.%: C, 29.05; H, 0.97; S, 7.75. Found%: C, 29.07; H, 0.93; S, 7.38.

4j: Yellow crystals, mp: 95 °C–97 °C, yield 1.8 g (28%). R_f : 0.57 (hexane). IR (KBr) $\nu = 3020$ (CH_{arom}), 1600 (C=C). ¹H NMR: $\delta = 7.3-7.6$ (m, 8H, H_{arom}). C₁₆H₈Cl₄Br₂S₂ (565.99). Calcd.%: C, 33.95; H, 1.42; S, 11.33. Found%: C, 33.56; H, 1.58; S, 11.58.

1,1,2,3,4-Pentachloro-4-(4-aminophenylthio)-1,3-butadiene (3k): Compound **3k** was synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 4-aminobenzenethiol (**2k**) (1.44 g, 11.49 mmol) according to **General Procedure I**.

3k: Oil, yield 1.74 g (44%). R_f : 0.81 (hexane). IR (film) $\nu = 3000$ (CH_{arom}), 1595 (C=C). ¹H NMR: $\delta = 3.7$ –4.3 (m, 2H, NH₂), 6.5–7.6 (m, 4H, H_{arom}). C₁₀H₆Cl₅NS (349.49). Calcd.%: C, 34.36; H, 1.73; N, 4.0; S, 9.17. Found%: C, 34.14; H, 1.85; N, 3.9; S, 9.55.

1,1,2,3,4-Pentachloro-4-(2-furfurylthio)-1,3-butadiene (3l) and 1,2,3,4-tetrachloro-1,4-bis(2-furfurylthio)-1,3-butadiene (4l): Compounds 3l and 4l were synthesized from 1,1,2,3,4,4-hexachloro-1,3-butadiene (1) (3.0 g, 11.49 mmol) and 2-furfurylthiol (2l) (1.31 g, 11.49 mmol) according to General Procedure I.

31: Oil, yield 1.9 g (49%). R_f : 0.86 (hexane). IR (film) $\nu = 3020$ (CH_{arom.}), 2900, 2930 (CH), 1600 (C=C), 1080, 1160 (C–O–C). ¹H NMR: $\delta = 4.2$ (s, 2H, CH₂), 6.0–6.4 (m, 2H, 2 CH), 7.35 (s, H, CHO). C₉H₅Cl₅SO (338.47). Calcd.%: C, 31.94; H, 1.49; S, 9.47. Found%: C, 31.56; H, 1.43; S, 9.70.

41: Oil, yield 0.81 g (17%). R_f : 0.22 (hexane). IR (film) $\nu = 3050$ (CH_{arom}), 2900, 2930 (CH), 1600 (C=C), 1085, 1150 (C–O–C). ¹H NMR: $\delta = 3.5-4.4$ (m, 4H, 2 CH₂), 5.9–6.4 (m, 4H, 4 CH), 7.1–7.5 (m, 2H, 2 CHO). C₁₄H₁₀Cl₄S₂O₂ (416.18). Calcd.%: C, 40.4; H, 2.59; S, 15.4. Found%: C, 40.14; H, 2.30; S, 15.3.

1,1,2,3,4-Pentachloro-4-(pentylsulfinyl)-1,3-butadiene (5a): Compound 5a was synthesized from 1,1,2,3,4-pentachloro-4-pentylthio-1,3-butadiene (3a) (0.1 g, 0.304 mmol) and mcpba (0.21 g, 1.218 mmol) according to General Procedure II.

5a: Oil, yield 0.05 g (48%). R_f : 0.73 (CHCl₃). IR (film) $\nu = 2900, 2970$ (CH), 1610 (C=C), 1070 (S = O). MS (+ESI) *m*/*z*: 345 [M+H]⁺; C₉H₁₁Cl₅OS (344.5). Calcd.%: C, 31.38; H, 3.22; S, 9.31. Found%: C, 31.52; H, 3.42; S, 9.44.

1,1,2,3,4-Pentachloro-4-(2-propylsulfinyl)-1,3-butadiene (5d): Compound **5d** was synthesized from 1,1,2,3,4-pentachloro-4-(2-propylthio)-1,3-butadiene (**3d**) (0.3 g, 0.998 mmol) and mcpba (0.69 g, 3.992 mmol) according to **General Procedure II**.

5d: White crystals, mp: 67 °C–68 °C, yield 0.1 g (31%). R_f : 0.36 (CHCl₃). IR (KBr) $\nu = 2910, 2970$ (CH), 1610 (C=C), 1060, 1035 (S = O). MS (+ESI) *m/z*: 317 [M+H]⁺; C₇H₇Cl₅OS (316.5). Calcd.%: C, 26.57; H, 2.23; S, 10.13. Found%: C, 26.62; H, 2.40; S, 10.10.

1,1,2,3,4-Pentachloro-4-(4-tert-butylbenzylsulfinyl)-1,3-butadiene (5f) and 1,1,2,3, 4-pentachloro-4-(4-tert-butylbenzylsulfonyl)-1,3-butadiene (6f): Compounds 5f and 6f were synthesized from 1,1,2,3,4-pentachloro-4-(4-tert-butylbenzylthio)-1,3-butadiene (3f) (0.1 g, 0.247 mmol) and mcpba (0.17 g, 0.989 mmol) according to General Procedure II.

5f: Oil, yield 0.05 g (50%). R_f : 0.29 (CHCl₃). IR (film) $\nu = 3050$ (CH_{arom}), 2800, 2960 (CH), 1600 (C=C), 1060 (S = O). MS (+ESI) m/z 421.1 [M+H]⁺; C₁₅H₁₅Cl₅OS (420.6). Calcd.%: C, 42.83; H, 3.59; S, 7.62. Found%: C, 42.87; H, 3.61; S, 7.60.

6f: Oil, yield 0.05 g (45%). R_f : 0.64 (CHCl₃). IR (film) $\nu = 3020$ (CH_{arom}), 2800, 2960 (CH), 1600 (C=C), 1150, 1300 (SO₂). MS (+ESI) m/z: 436 [M+H]⁺; C₁₅H₁₅Cl₅O₂S (436.6). Calcd.%: C, 41.26; H, 3.46; S, 7.34. Found%: C, 41.52; H, 3.43; S, 7.40.

1,1,2,3,4-Pentachloro-4-(allylsulfinyl)-1,3-butadiene (8) and 1,1,2,3,4-pentachloro-4-(allylsulfonyl)-1,3-butadiene (9): Compounds 8 and 9 were synthesized from 1,1,2,3,4-pentachloro-4-allylthio-1,3-butadiene (7) (0.1 g, 0.335 mmol) and mcpba (0.23 g, 1.34 mmol) according to General Procedure II.

8: Oil, yield 0.05 g (48%). R_f : 0.40 (CCl₄). IR (film) $\nu = 2900, 2960$ (CH), 1600 (C=C), 1040, 1060 (S = O). MS (+ESI) *m*/*z*: 314.8 [M+H]⁺, 298.8 [M–O]⁺; C₇H₅Cl₅OS (314.4). Calcd.%: C, 26.74; H, 1.60; S, 10.20. Found%: C, 26.85; H, 1.51; S, 10.90.

9: Oil, yield 0.06 g (54%). R_f : 0.81 (CCl₄). IR (film) $\nu = 2900, 2960$ (CH), 1610 (C=C), 1150, 1350 (SO₂). MS (+ESI) m/z: 331 [M+H]⁺, 314 [M+H–O]⁺; C₇H₅Cl₅O₂S (330.4). Calcd.%: C, 25.44; H, 1.53; S, 9.70. Found%: C, 25.95; H, 1.72; S, 9.92.

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