

A convenient access to ring unsaturated cyclopentanecarbodithioates via hetero-Diels–Alder chemistry

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Dedicated to Professor Boris A. Trofimov on the occasion of his 65th birthday

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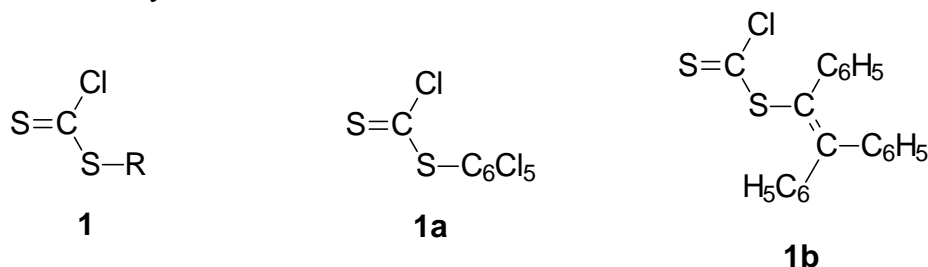
Abstract

Chlorodithioformates react with cyclopenta-1,3-dienes to give the corresponding hetero-Diels–Alder adducts which in turn eliminate HCl to form, depending on the substitution pattern, cyclopenta-2,4-dienecarbodithioates or cyclopent-2-enecarbodithioates with an additional exocyclic C=C double bond. The key structures **5b** and **5c** were determined by X-ray crystallography.

Keywords: Chlorodithioformates, cyclopenta-1,3-dienes, hetero-Diels–Alder reaction

Introduction

Our earlier review on chlorodithioformates, **1**, could not report any examples of **1** acting as dienophiles, as opposed to their well-documented 1,3-dipolarophilic properties,¹ and a somewhat earlier report from our laboratory explicitly stated that **1** (at ambient temperature) do not react with buta-1,3-diene.² An attempted hetero-Diels–Alder reaction between trichloromethyl chlorodithioformate, Cl-CSSCCl₃, and anthracene led only to Friedel–Crafts substitution with no observable intermediate cycloadduct.³

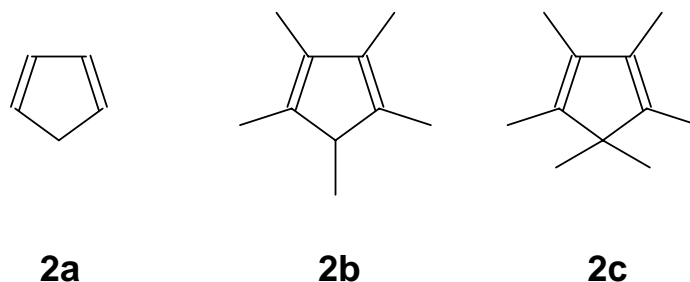


Scheme 1

On the other hand, several closely related thiocarbonyl compounds such as thiophosgene,⁴ cyanodithioformates NC-CSSR,⁵ C-sulfonyldithioformates R¹SO₂-CSSR,^{2,6} and phosphonyldithio-formates, (R¹O)₂PO-CSSR,^{2,7} do exhibit a rich hetero-Diels–Alder chemistry with 1,3-dienes.

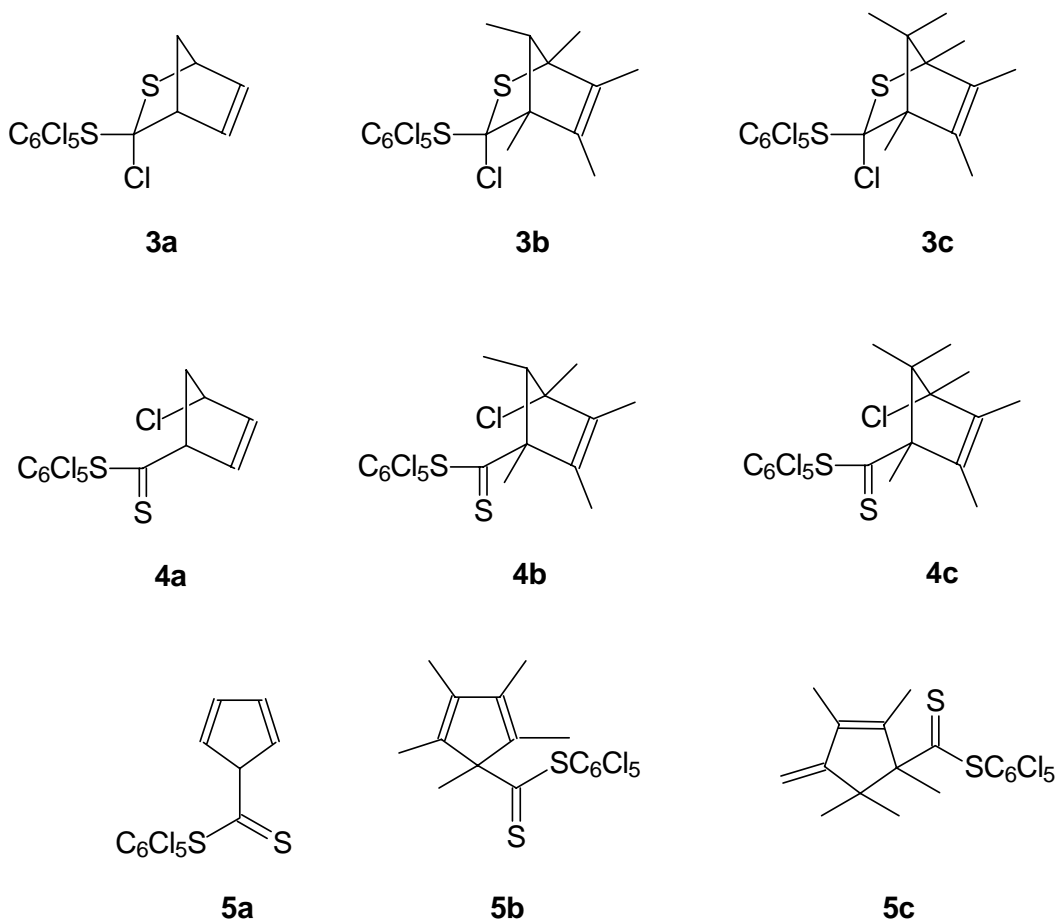
Results and Discussion

Following earlier work on hetero-Diels–Alder reactions of chlorodithioformates, including **1**, with acyclic 1,3-dienes⁸ we have now found that the corresponding reactions of **1a**^{9a} and **1b**^{9b} (*cf.* Scheme 1) with the cyclopenta-1,3-dienes **2a–c**¹⁰ (*cf.* Scheme 2) are even easier, *i.e.*, proceed at ambient temperature whereas the former required heating to 80 °C.

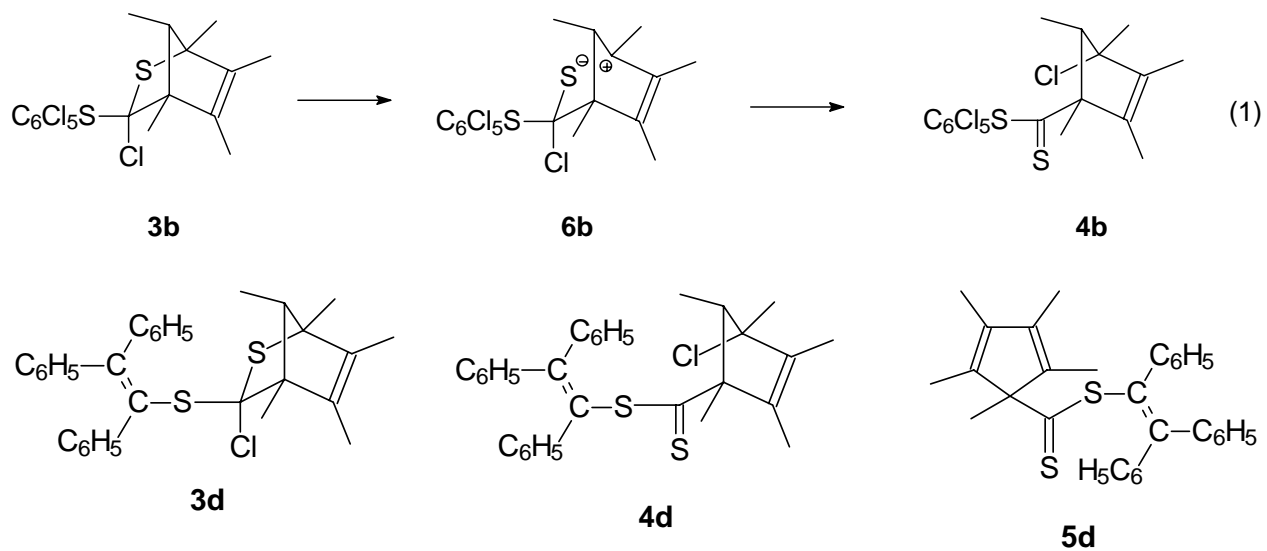


Scheme 2

In all cases, the primary Diels–Alder adduct **3** cannot be observed, but is apparently subject to easy rearrangement to the monocyclic dithioformate **4** which, in turn, more or less readily loses hydrogen chloride and gives the quasi-Friedel–Crafts product **5**, *cf.* Scheme 3. In the case of **4a** the spectroscopic data of the isolated product were satisfactory, while the results of the out-of-house elemental analysis showed extensive, but not quantitative, conversion to **5a** by loss of HCl. The driving force for the rearrangement **3** → **6** → **4** (which is not observed with the corresponding Diels–Alder adducts from acyclic 1,3-dienes,⁸ nor with the thiophosgene–cyclopenta-1,3-diene cycloadduct^{4a}) is in all likelihood the heterolytic cleavage of an endocyclic C–S bond with formation of a zwitterion with a highly stabilized tertiary allylic carbocationic positive pole and a negative pole well-suited for the expulsion of an incipient chloride ion, Eqn. (1). The products **4a** and/or **5a** derived from **2a** were difficult to purify and could not be fully characterized, while **5b** and **5c** were obtained in a high state of purity and characterized by the usual techniques, including single crystal X-ray crystallography.¹¹



Scheme 3



Scheme 4

Compound **5d** was obtained in the same way, *cf.* Scheme 4. In the molecular structures the alkene C=C bonds of **5b**, C3-C4 (1.344 Å) and C5-C6 (1.348 Å), and of **5c**, C3-C4 (1.330 Å) and C5-C10 (1.337 Å), are discernible as fully localized entities.

For recent work on the related Diels–Alder chemistry of spiro[2.4]hepta-4,6-diene and thiophosgene, see ref. 4b No Diels–Alder reactions between thiocarbonyl compounds and **4b** or **4c** appear to have been recorded.

Experimental Section

General Procedures. All syntheses were carried out under an atmosphere of dry nitrogen. All NMR experiments (solvent CDCl₃, TMS as internal standard) were carried out with a Varian Unity 400 MHz spectrometer (400 MHz for ¹H, 100 MHz for ¹³C). The mass spectra were obtained in the EI mode (70 eV, direct inlet) with a Finnigan MAT GCQ PLUS system. The infrared spectra (KBr disks) were run on a Perkin–Elmer FT/IR-1760 spectrometer. The melting points were taken with an SMP3 apparatus.

1,2,3,4,5,5-Hexamethylcyclopenta-1,3-diene, (2c). Compound **2c** was prepared by our improved version of an implied literature procedure.¹⁰ 1,2,3,4,5-Pentamethylcyclopenta-1,3-dienyl anion was generated at 0 °C by treatment of 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (1.50 mL, 1.30 g, 9.54 mmol), dissolved in THF, with 9.54 mL (14.3 mmol) of 1.50 M ethereal methyllithium/lithium bromide complex, and then treated with iodomethane (1.78 mL, 4.06 g, 28.6 mmol). The stirred reaction mixture was allowed to warm to room temperature (1 h), filtered, the solid residue extracted with ether, and the combined ether phases evaporated *in vacuo*. Subsequent Kugelrohr distillation of the oily residue at 32–34 °C/0.55 mm Hg afforded **2c** as a colorless oil, yield 1.27 g (89%). ¹H NMR (CDCl₃): δ 0.91 (s, 6H, 5,5-Me₂), 1.76 (s, 6H, 2,3-Me₂), 1.80 (s, 6H, 1,4-Me₂) ppm. ¹³C NMR (CDCl₃): δ 9.52 (q, 1,4-Me₂), 11.03 (q, 2,3-Me₂), 21.81 (q, 5,5-Me₂), 52.14 (s, C-5), 131.85 (s, C-2, C-3), 142.32 (s, C-1, C-4), the assignments, where there could be doubt, are in accord with an ACD simulation. Courtneidge *et al.*¹⁰ report a peak at 138.08 ppm in their ¹³C NMR spectrum instead of our 131.85 ppm peak—apparently a misprint in their paper. Our ACD/C-NMR simulation shows the corresponding peak at 131.89 ppm.

4-Chlorocyclopent-2-enecarbodithioic acid pentachlorophenyl ester, (4a). Chlorodithioformate **1a** (150 mg, 0.41 mmol) was dissolved in 3 mL trichloromethane and treated with 0.14 mL (2.05 mmol) of freshly distilled cyclopenta-1,3-diene. After 3 h all **1a** had been consumed and, after removal of the solvent and addition of ether (2 mL) and cooling to –10 °C a yellow solid precipitated which was washed three times with pentane to afford 139 mg (86%) of **4a** as yellow crystals, m.p. 119–122 °C. (Found: C, 35.95; H 1.71; Cl, 47.26; S, 14.51. Calculated for C₁₂H₆Cl₆S₂, *i.e.*, **4a**: C, 33.75; H, 1.42; Cl, 49.81; S, 15.02%: 427.02. Calculated for C₁₂H₅Cl₅S₂, *i.e.*, **5a**: C, 36.90; H, 1.29; Cl, 45.39; S, 16.42%: 390.56). Apparently, the analytical sample had

lost some HCl while in transit. IR (KBr): ν 3083, 2987, 2933, 1605, 1403, 1322, 1125, 833, 706, 687 cm^{-1} ; ^1H NMR (CDCl_3): δ 2.75 (m, 2H), 4.79 (m, 1H), 5.15 (m, 1H), 6.15 (m, 2H); ^{13}C NMR (CDCl_3): δ 43.68 (t), 63.44 (d), 63.48 (d), 132.80 (s), 133.88 (s), 135.44 (d), 135.98 (d), 136.78 (s), 138.34 (s), 230.61 (s); MS (EI): m/z (%) 388 (45, M-HCl), 353 (100, $\text{C}_{12}\text{H}_5\text{Cl}_4\text{S}_2$), 323 (16, $\text{C}_7\text{Cl}_5\text{S}_2$), 246 (18, C_6Cl_5), 212 (60, C_6Cl_4), 109 (40, $\text{C}_6\text{H}_5\text{S}$), 65 (23, C_5H_5).

1,2,3,4,5-Pentamethylcyclopenta-2,4-dienecarbodithioic acid pentachlorophenyl ester, (5b).

To a stirred solution of **1a** (0.30 g, 0.83 mmol) in 10 mL trichloromethane was added **2b** (0.26 mL, 0.23 g, 1.69 mmol). The reaction mixture was stirred at room temperature for 45 min. Evaporation *in vacuo* left crude **5b** as an orange solid. Recrystallization from ether/hexane (1:3) yielded 0.35 g (92%) of **5b** as orange crystals, m.p. 156–158 °C. (Found: C, 43.90; H, 3.00; S, 14.60. Calculated for $\text{C}_{17}\text{H}_{15}\text{Cl}_5\text{S}_2$: C, 44.32; H, 3.28; S, 13.92%: 460.704). IR (KBr): ν 2961, 2909, 2852, 1652, 1435, 1338, 1303, 1274 cm^{-1} . ^1H NMR (CDCl_3): δ 1.39 (s, 3H), 1.80 (s, 6H), 1.92 (s, 6H) ppm. ^{13}C NMR (CDCl_3): δ 10.15 (q), 11.63 (q), 21.30 (q), 75.03 (s), 132.24 (s), 132.55 (s), 135.67 (s), 138.83 (s), 139.50 (s), 139.68 (s), 234.22 (s). MS (EI): m/z (%) 458 (12, M, $\text{C}_{17}\text{H}_{15}\text{Cl}_5\text{S}_2$), 423 (100, $\text{C}_{17}\text{H}_{15}\text{Cl}_4\text{S}_2$), 291 (11, $\text{C}_7\text{Cl}_5\text{S}$), 134 (29, $\text{C}_{10}\text{H}_{14}$), 119 (24, C_9H_{11}), 91 (14, C_7H_7).

1,2,3,5,5-Pentamethyl-4-methylenecyclopent-2-enecarbodithioic acid pentachlorophenyl ester (5c).

To a stirred solution of **1a** (0.30 g, 0.83 mmol) in 10 mL trichloromethane was added 0.25 g (1.66 mmol) of **2c**. The reaction mixture was stirred at room temperature for 2 days. The solvent was then evaporated *in vacuo* and the residue purified by column chromatography (ether/pentane, 1:5) to afford an orange solid. Recrystallization from acetonitrile yielded **5c** (0.28 g, 72%) as orange crystals, m.p. 129–132 °C. (Found: C, 45.60; H 3.50; S, 13.30. Calculated for $\text{C}_{18}\text{H}_{17}\text{Cl}_5\text{S}_2$: C, 45.54; H, 3.60; S, 13.50%: 474.731). IR (KBr): ν 3082, 2976, 2937, 2914, 1627, 1516, 1449, 1380, 1339, 1307, 1121, 1100, 866, 773, 693 cm^{-1} ; ^1H NMR (CDCl_3 , NOESY): δ 1.08 (s, 3H, 5-Me_a), 1.14 (s, 3H, 5-Me_b), 1.44 (s, 3H, 1-Me), 1.84 (tq, 3H, 2-Me, $^6\text{J} = 0.66$ Hz, $^5\text{J} = 0.96$ Hz), 1.91 (q, 3H, 3-Me, $^5\text{J} = 0.96$ Hz), 4.75 (dq, 1H, =CH_a, $^2\text{J} = 0.40$ Hz, $^6\text{J} = 0.66$ Hz), 4.92 (dq, 1H, =CH_b, $^2\text{J} = 0.40$ Hz, $^6\text{J} = 0.66$ Hz) ppm; ^{13}C NMR (CDCl_3): δ 10.61 (q), 12.34 (q), 21.52 (q), 22.78 (q), 30.35 (q), 49.21 (s), 74.34 (s), 99.86 (dd), 132.29 (s), 132.47 (s), 133.43 (s), 135.67 (s), 138.33 (s), 144.15 (s), 162.28 (s), 238.73 (s) ppm; MS (EI): m/z 472 (71, M, $\text{C}_{18}\text{H}_{17}\text{Cl}_5\text{S}_2$), 323 (37, $\text{C}_7\text{Cl}_5\text{S}_2$), 279 (4, $\text{C}_6\text{Cl}_5\text{S}$), 149 (100, $\text{C}_{11}\text{H}_{17}$).

1,2,3,4,5-Pentamethylcyclopenta-2,4-dienecarbodithioic acid 1,2,2-triphenylethenyl ester (5d).

To a stirred solution of **1b** (0.20 g, 0.54 mmol) in 5 mL trichloromethane was added 0.15 g (1.10 mmol) of **2b**. The reaction mixture was stirred at room temperature for 1 h. It was then evaporated *in vacuo* and the orange residue recrystallized from hexane to yield **5d** (0.22 g, 87%) as orange crystals, m.p. 132–135 °C. (Found: C, 78.79; H 6.66; S, 13.13. Calculated for $\text{C}_{31}\text{H}_{30}\text{S}_2$: C, 79.78; H, 6.48; S, 13.74%: 466.712). IR (KBr): ν 2967, 2924, 2870, 1599, 1444, 1378, 1074, 926, 745, 698 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.24 (s, 3H), 1.41 (s, 6H), 1.78 (s, 6H), 6.96–7.27 (m, 15H) ppm; ^{13}C NMR (CDCl_3): δ 9.93 (q), 11.45 (q), 21.13 (q), 74.52 (s), 126.70 (d), 126.90 (d), 127.20 (d), 127.51 (d), 127.55 (d), 128.01 (d), 128.70 (d), 130.80 (d), 131.15 (d), 131.40 (s), 138.43 (s), 139.28 (s), 139.45 (s), 141.77 (s), 143.05 (s), 152.31 (s), 237.72 (s, C=S)

ppm; MS (EI): m/z (%) 466 (59, M, C₃₁H₃₀S₂), 255 (100, C₂₀H₁₅), 179 (31, C₁₁H₁₅S), 135 (83, C₁₀H₁₅).

X-Ray crystallographic study of 1,2,3,4,5-pentamethylcyclopenta-2,4-dienecarbodithioic acid pentachlorophenyl ester (5b). Crystal data: crystal system, monoclinic; space group, P2₁/c; $a = 8.6993(5)$ Å; $b = 29.353(2)$ Å; $c = 8.6614(5)$ Å; $\beta = 117.790(1)^\circ$; $V = 1956.6(2)$ Å³; $Z = 4$; crystal size $0.37 \times 0.26 \times 0.09$ mm; linear absorption coefficient 0.951 mm^{-1} ; transmission factors $0.919\text{--}0.678$; total number of unique reflections 5872; $[I > 2\sigma(I)] = 3738$; θ -range $2.7\text{--}30.3^\circ$; R (obs. data) = 0.075; $wR2$ (all data) = 0.062.

X-Ray crystallographic study of 1,2,3,5,5-pentamethyl-4-methylenecyclopent-2-enecarbodithioic acid pentachlorophenyl ester (5c). Crystal data: crystal system, monoclinic; space group, P2₁/c; $a = 10.761(1)$ Å; $b = 11.475(2)$ Å; $c = 16.846(2)$ Å; $\beta = 94.015(3)^\circ$; $V = 2075.1(5)$ Å³; $Z = 4$; crystal size $0.56 \times 0.23 \times 0.18$ mm; linear absorption coefficient 0.90 mm^{-1} ; transmission factors $0.893\text{--}0.662$; total number of unique reflections 6390; $[I > 2\sigma(I)] = 5025$; θ -range $2.4\text{--}30.5^\circ$; R (obs. data) = 0.050; $wR2$ (all data) = 0.056.

The two structures are not of high quality, despite being measured at 120 K, because of lack of strong packing forces.

Acknowledgments

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References and Notes

1. El-Sayed, I.; Abdel-Megeed, M. F.; Yassin, S. M.; Senning, A. *Sulfur Rep.* **1995**, *16*, 235.
2. Boerma, J. A.; Nilsson, N. H.; Senning, A. *Tetrahedron* **1974**, *30*, 2735.
3. Moltzen, K. E.; Senning, A.; Kramer, M. P.; Klabunde, K. J. *J. Org. Chem.* **1984**, *49*, 3854.
4. (a) Middleton, W. J. *J. Org. Chem.* **1965**, *30*, 1390. (b) Föhlisch, B.; Bakr, D. A.; Fischer, P. *J. Org. Chem.* **2002**, *67*, 3682.
5. Vyas, D. M.; Hay, W. *Can. J. Chem.* **1975**, *53*, 1362.
6. Yassin, S. M. *Sulfur Rep.* **1995**, *16*, 343.
7. Heuzé, B.; Gasparova, R.; Herras, M.; Masson, M. *Tetrahedron Lett.* **2000**, *41*, 7327.
8. El-Sayed, I.; Senning, A. *Sulfur Lett.* **2002**, *25*, 263.
9. (a) Hansen, H. C.; Jensen, B.; Senning, A. *Sulfur Lett.* **1985**, *3*, 61. (b) El-Sayed, I.; Abdel-Megeed, M. F.; Yassin, S. M.; Senning, A. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1994**, *86*, 239.
10. Courtneidge, J. L.; Davies, A. G.; Shields, C. J.; Yazdi, S. N. *J. Chem. Soc., Perkin Trans. 2* **1988**, 799 and references cited therein.

11. The full crystallographic data for **5b** and **5c** have been deposited with the Cambridge Crystallographic Data Centre, reference number CCDC 191808 (**5b**) and CCDC 191809 (**5c**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).