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Reactions of Cyclooctatetraene Dibromides with *N*-Morpholino-carbamodithioate, Ethyl Xanthogenate, and Dithioacetate

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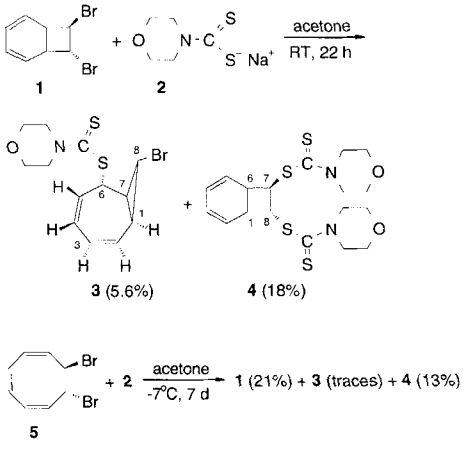
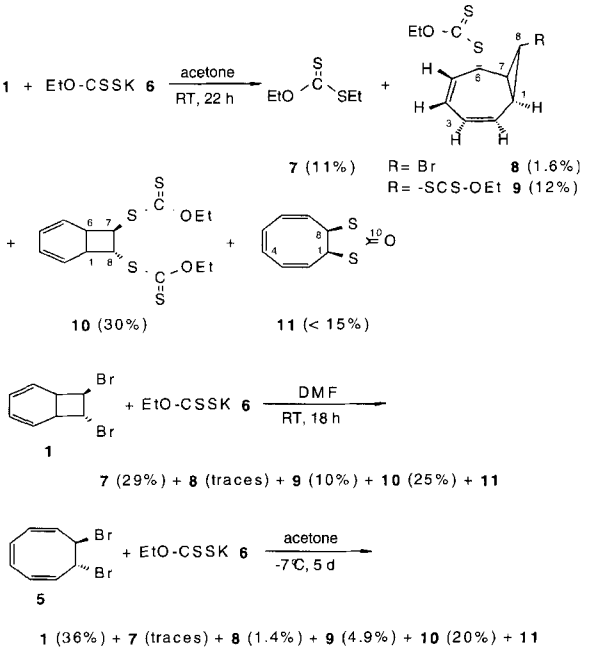
Condensation of valence tautomer **1** [1–3] with **2** [4] in acetone gives rise to (*exo*-8-bromo-1α,7α-bicyclo[5.1.0]octa-2,4-diene-6α-yl)-*N*-morpholinocarbamodithioate (**3**, 5.6%) and (*trans*-bicyclo[4.2.0]octa-2,4-diene-7,8-diyl)-bis-(*N*-morpholino-carbamodithioate) (**4**, 18%). In acetone at –7 °C, valence tautomer **5** is trans-formed to 13% of **4** and only traces of **3** while unreacted **5** undergoes valence tautomerism to **1** at about 0 °C during workup [3, 5]. Both condensations are accompanied by extensive decomposition which is generally observed with **1** and **5**.



Scheme 1

Reactions of potassium ethyl xanthogenate (**6**) with **1** and **5** lead to even more products. Among these, carbodithioic ester **7** and *cis*-9,11-dithiabicyclo[6.3.0]undeca-2,4,6-triene-10-one (**11**) are rather unexpected. The monocyclic dibromide **5** in acetone only yields small amounts of the bromo substituted bicyclo[5.1.0]octa-2,4-diene **8**; in DMF, formation of **8** is suppressed completely.

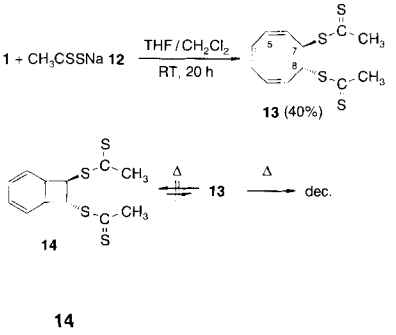


Scheme 2

NMR analysis of **3** together with force field computations [6] substantiate both constitution and conformation given by the formula. H,H coupling constants in the three-membered ring are similar to those of known cyclopropanes [7]. $^3J_{1'\text{-H},\,2'\text{-H}} = 7.2$ Hz and $^3J_{6'\text{-H},\,7'\text{-H}} = 5.3$ Hz are quite small, but related substances have coupling constants in the same range [8, 9]. Considering the δ value of C-1' (27.82 ppm in $CDCl_3$), C-7' shows a striking downfield shift ($\delta = 50.30$ ppm in $CDCl_3$); again, there are previous examples for this observation [9, 10]. The same arguments are valid for structures **8** and **9**.

Assignation of the bromo substituent to position 8' in **3** is suggested by the negligible differences between the chemical shifts of 8'-H (δ= 4.06 ppm in $CDCl_3$), C-8' (δ= 23.73 ppm in $CDCl_3$), and their equivalents in **8** (8-H, δ= 4.01 ppm; C-8, δ= 23.34 ppm; $CDCl_3$).

In contrast to the condensations discussed so far, the reaction of **1** with sodium dithioacetate (**12**) follows a pathway leading to disubstituted product **13** only. It is remarkable that *trans*-7,8-bis(dithioacetoxy)cycloocta-1,3,5-triene (**13**) persists in the monocyclic form while all other 7,8 disubstituted cycloocta-1,3,5-trienes (except if fused [1, 2, 3, 11]) experience valence tautomerism to 7,8 disubstituted bicyclo [4.2.0]octa-2,4-dienes [3, 5, 12, 13]. Attempted ^1H NMR observation of **13** tautomerizing to bicyclus **14** at elevated temperatures (50–90 °C; [D_5]bromobenzene) failed due to lacking thermal stability of **13**; when the sample had cooled down again, another run demonstrated that irreversible decomposition had taken place.



Scheme 3

trans Configuration of **13** is deduced easily from the ^{13}C NMR data because C-7 and C-8, 7-CH_3 and 8-CH_3 each display a signal of their own. Since the 400 MHz ^1H spectrum of **13** closely resembles the 60 MHz ^1H spectrum of its dibromo analogue **5** given by Huisgen and Boche [5], it appears very unlikely that this spectrum belongs to a mixture of **5** and its *cis* isomer as it was claimed by Huisgen and Boche.

Endo/*exo* assignations for protons in 7 and 8 positions in **4**, **10**, and **13** are based on the empirical rule that in 7,8 disubstituted cycloocta-1,3,5-trienes [5], bicyclo[4.2.0]octa-2,4-dienes [3], and bicyclo[4.2.0]oct-2-enes [14, 15] 7,8 *endo* protons will be found at higher field than the *exo* ones.

For a discussion of plausible reaction mechanisms leading to the products **3**, **4**, **7**, **8**–**11**, and **13**, see [3] and, in part, [1, 2].

We wish to express our gratitude to the Badische Anilin- und Soda-Fabrik for a generous gift of cyclooctatetraene and to the Fonds der Chemischen Industrie for financial support.

Experimental

Fourier transformed IR spectra: Nicolet 510 P spectrometer. ^1H and ^{13}C NMR spectra: Jeol JMN GX 400 (399.8 MHz for ^1H, 100.5 MHz for ^{13}C); the chemical shifts are given as δ values in ppm with TMS as the internal standard. Mass spectroscopy (MS): Micromass 7070H. Mass spectra were run at room temperature unless stated otherwise. Elemental analyses: carbon and hydrogen, Labormatic/Wösthoff CH analyzer; nitrogen, Hewlett-Packard CHN Autoanalyzer 185. **1** and **5** were prepared according to [1, 3], for **2** see [4]. Solvent ratios of eluents denote V/V mixtures.

Reaction of 1 with 2

trans-7,8-Dibromobicyclo[4.2.0]octa-2,4-diene (**1**) (1.32 g, 5 mmol) and sodium *N*-morpholinocarbamodithioate (**2**) (2.04 g, 11 mmol) are stirred in acetone (30 ml) at room temperature for 22 h. After addition of CH_2Cl_2 (30 ml), the precipitated salts are removed by filtration. The solvent mixture is distilled off, and the residue is separated by CC using pentane/CH_2Cl_2 = 1+3 until elution of **3** begins; then CH_2Cl_2 is employed, and acetone/CH_2Cl_2 = 1+9 follows as soon as **4** appears. Progress of CC is observed by TLC with CH_2Cl_2.

(Exo-8-bromo-1α,7α-bicyclo[5.1.0]octa-2,4-diene-6α-yl)-N-morpholinocarbamodithioate (**3**)

195 mg (6%) of a highly viscous yellow oil. Crystallization from acetone/pentane yields a small amount of white crystals, *m. p.* 160–163 °C (beginning dec. > 120 °C). ^1H NMR confirms identity of oil and crystals. – IR (film): ν (cm^{-1}) = 1462, 1420, 1268, 1228, 1215, 1114, 1029, 997, 731. – ^1H NMR ($CDCl_3$): 6.22 (dd, J = 11.7, 7.2 Hz, 1H, 2'-H), 5.95 (dd, J = 10.0, 8.0 Hz, 1H, 5'-H), 5.89 (dd, J = 10.0, 6.0 Hz, 1H, 4'-H), 5.61 (dd, J = 11.7, 6.0 Hz, 1H, 3'-H), 5.44 (dd, J = 8.0, 5.3 Hz, 1H, 6'-H), 4.18 (m, 2H, NC$\underline{H}_2$), 4.06 (pseudo t= dd, $J \approx$ 4.0, 4.0 Hz, 1H, 8'-H), 3.91 (m, 2H, NC$\underline{H}_2$), 3.76 (broad s, 4H, OC$\underline{H}_2$), 2.76 (dd, J = 5.3, ≈4.0 Hz, 1H, 7'-H), 1.78 (ddd, J = 10.2, 7.2, ≈4.0 Hz, 1H, 1'-H). – ^{13}C NMR ($CDCl_3$): 197.4 (C=S), 133.8 (C-2'), 131.2 (C-4'), 128.9 (C-5'), 125.3 (C-3'), 66.2 (O$\underline{C}H_2$), 50.8 (C-6'), 50.3 (C-7' and N$\underline{C}H_2$), 27.8 (C-1'), 23.7 (C-8'). All NMR assignations are confirmed by H,H and C,H COSY. – MS (chemical ionization, isobutane): *m/z* (%) = 348 (2; M^++1, ^{81}Br), 346 (3; M^++1, ^{79}Br), 266 (60), 132 (100). – HRMS: $^{12}C_{13}H_{16}{}^{79}BrNOS_2$+H, calcd. 345.9935, found 345.9944 ± 0.0100.

$C_{13}H_{16}BrNOS_2$	calcd.	C 45.09	H 4.66
(346.30)	found	C 45.68	H 4.68.

(trans-Bicyclo[4.2.0]octa-2,4-diene-7,8-diyl)-bis-(N-morpholinocarbamodithioate) (**4**)

789 mg (18%) of amorphous pale yellow flakes, *m.p.* 62–76 °C (without dec.). – IR (KBr): ν (cm^{-1}) = 1420, 1267, 1229, 1113, 996. – ^1H NMR ($CDCl_3$): 5.99 (dd, J = 10.2, 5.6 Hz, 1H, 3'-H), 5.84 (dd, J = 9.6, 5.6 Hz, 1H, 4'-H), 5.75 (dd, J = 9.6, 5.4 Hz, 1H, 5'-H), 5.61 (dd, 10.2, 3.7 Hz, 1H, 2'-H), 5.22 (pseudo t = dd, J= 8.5, 8.5 Hz, 1H, 7'-H *exo*), 5.09 (dd, J = 8.5, 8.5 Hz, 1H, 8'-H *endo*), ≈4.2 (m, 4H, NC$\underline{H}_2$), 3.93 (m, 5H, NC$\underline{H}_2$ and 1'-H), 3.75 (m, 8 H, OC$\underline{H}_2$), 3.23 (ddd, J = 11.2, 8.5, 5.4 Hz, 1H, 6'-H). – ^{13}C NMR ($CDCl_3$): 197.0 (C=S), 195.9 (C=S), 124.7 (C-2'), 124.5 (C-3'), 124.4 (C-5'), 122.9 (C-4'), 66.2 (broad, O$\underline{C}H_2$), 58.5 (C-7'), 54.2 (C-8'), 50.8 (broad, N$\underline{C}H_2$), 40.4 (C-6'), 37.5 (C-1'). Assignations are corroborated by H,H and C,H COSY. – MS (180 °C) *m/z* (%): 428 (5; M^+), 188 (28), 130 (92), 87 (21), 86 (54), 78 (21), 76

(100). HRMS: $^{12}C_{18}H_{24}N_2O_2S_4$, calcd. 428.0721, found 428.0722 ± 0.0100.

Reaction of 5 with 2

trans-7,8-Dibromocycloocta-1,3,5-triene (**5**) (1.32 g, 5 mmol) and **2** (2.04 g, 11 mmol) are allowed to condense in acetone at –7°C for 7 days. Workup is performed as described above, giving rise to **1** (21%), **3** (traces), and **4** (13%).

Reaction of 1 with 6

trans-7,8-Dibromobicyclo[4.2.0]octa-2,4-diene (**1**) (1.32 g, 5 mmol) and potassium ethyl xanthogenate (**6**) (1.76 g, 11 mmol) are mixed in acetone (30 ml). For reaction conditions and removal of salts see above (**3**, **4**). CC: After elution with pentane (150 ml), polarity is increased to pentane/CH_2Cl_2 = 19 + 1, and, as soon as **8** turns up, to 9 + 1. When elution of **8** is completed, pentane/CH_2Cl_2 = 4 + 1 is employed, and once **9** appears, a 7 + 3 mixture is used. Thin layer chromatography requires pentane/CH_2Cl_2 = 9 + 1 for **7**, **8**, **9**, **10** and 4 + 1 for **9**, **11**. Fractions **9** and **10** may overlap.

O-Ethyl S-ethyl carbodithioate (**7**)

86 mg (11%) of a yellow, pungently smelling oil which is volatile *in vacuo* at room temperature. – IR (film): ν (cm^{-1}) = 2980, 2929, 1470, 1212, 1112, 1063. – ^{1}H NMR ($CDCl_3$): 4.65 (q, J = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 3.12 (q, J = 7.4 Hz, 2H, $SC\underline{H}_2CH_3$), 1.42 (t, J = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$), 1.34 (t, J = 7.4 Hz, 3H, $SCH_2C\underline{H}_3$). – ^{13}C NMR ($CDCl_3$): 215.0 (C=S), 69.7 ($O\underline{C}H_2CH_3$), 30.1 ($S\underline{C}H_2CH_3$), 13.8 ($OCH_2\underline{C}H_3$), 13.5 ($SCH_2\underline{C}H_3$). – MS: *m/z* (%) = 150 (100; M^+), 122 (23), 77 (21), 62 (21), 61 (29). HRMS: $^{12}C_5H_{10}OS_2$, calcd. 150.0173, found 150.0173 ± 0.0100.

exo-8-Bromo-6α-ethoxythiocarbonylthio-1α,7α-bicyclo-[5.1.0]octa-2,4-diene (**8**)

25 mg (1.6%) of a yellowish oil. IR (film): ν (cm^{-1}) = 1651, 1219, 1147, 1111, 1047, 715. – ^{1}H NMR ($CDCl_3$): 6.21 (dd, J = 11.7, 7.2 Hz, 1H, 2-H), 5.87 (m, 2H, 4-, 5-H), 5.62 (m in which dd is recognizable, J = 11.7, 6.1 Hz, 1H, 3-H), 5.06 (m, 1H, 6-H), 4.67 (q, J = 7.1 Hz, 2H, $OC\underline{H}_2CH_3$), 4.01 (pseudo t = dd, $J \approx 4.0$, 4.0 Hz, 8-H), 2.66 (dd, $J \approx 5.5$,4.0 Hz, 7-H), 1.79 (ddd, J = 10.2, 7.2, ≈4.0 Hz, 1H, 1-H), 1.43 (t, J = 7.1 Hz, 3H, $OCH_2C\underline{H}_3$). – ^{13}C NMR ($CDCl_3$): 214.7 (C=S), 133.6 (C-2), 131.3 (C-4), 128.0 (C-5), 125.4 (C-3), 70.1 ($O\underline{C}H_2CH_3$), 50.0 (C-6), 48.9 (C-7), 27.6 (C-1), 23.3 (C-8), 13.83 ($OCH_2\underline{C}H_3$). Compare assignations for **3**. – MS (chemical ionization, isobutane): *m/z* (%) = 307 (3; M^++1, ^{81}Br), 305 (6; M^++1, ^{79}Br), 225 (21), 197 (40), 185 (96; ^{81}Br), 183 (100; ^{79}Br). – HRMS: $^{12}C_{11}H_{13}OS_2$, calcd. 225.0408, found 225.0410 ± 0.0100.

trans-7,8-Bis(ethoxythiocarbonylthio)bicyclo[4.2.0]octa-2,4-diene (**10**)

523 mg (30%) of a viscous yellow oil. – IR: ν (cm^{-1}) = 1212, 1146, 1112, 1059. – ^{1}H NMR ($CDCl_3$): 6.00 (dd, J = 9.8, 5.6 Hz, 1H, 4-H), 5.84 (dd, J = 9.6, 5.6 Hz, 1H, 3-H), 5.68 (dd, J = 9.6, 5.6 Hz, 1H, 2-H), 5.58 (dd, J = 9.8, 3.9 Hz, 1H, 5-H), 4.83 (pseudo t = dd, J= 9.3, 8.9 Hz, 1H, 7-H *exo*), 4.62 (m, 5H: 8-H *endo* and $OC\underline{H}_2CH_3$, the latter as 2 t with J = 7.1 Hz and $\Delta\delta$ = 2.4 Hz, 7-$OC\underline{H}_2CH_3$ *endo* being upfield), 3.78 (m, 1H, 6-H), 3.17 (ddd, J = 10.9, 8.7, 5.7 Hz, 1H, 1-H), 1.43 (t, J = 7.1 Hz, 3H, 8-$OCH_2C\underline{H}_3$ *exo*), 1.41 (t, J = 7.1 Hz, 3H, 7-$OCH_2C\underline{H}_3$ *endo*). Coupling between 1-H, 8-H and 7-H, 8-H respectively is proven by H,H-COSY. – ^{13}C NMR ($CDCl_3$): 213.3, 212.0 (C=S), 125.0, 123.2 (C-2, -5), 124.3 (C-4), 124.2 (C-3), 70.2, 70.1 ($O\underline{C}H_2CH_3$), 57.6 (C-7), 54.0 (C-8), 39.1 (C-6), 37.0 (C-1), 13.8 ($OCH_2\underline{C}H_3$). The NMR spectra are interpreted on the analogy of **1** [3]. – MS (100 °C): *m/z* (%)= 346 (2; M^+), 147 (100), 135 (48), 119 (70), 103 (21), 91 (45). – HRMS: $^{12}C_{14}H_{18}O_2S_4$, calcd. 346.0190, found 346.0179 ± 0.0100.

6α,exo-8-Bis(ethoxythiocarbonylthio)-1α,7α-bicyclo-[5.1.0]octa-2,4-diene (**9**)

209 mg (12%) of a viscous yellow oil. – IR: ν (cm^{-1}) = 2982, 1210, 1145, 1112, 1042. – ^{1}H NMR ($CDCl_3$): 6.22 (dd, J = 11.7, 7.1 Hz, 1H, 2-H), 5.94 (m, 2H, 4-, 5-H), 5.68 (m, 1H, 3-H), 5.05 (dd, J = 8.7, ≈ 5.4 Hz, 1H, 6-H), ≈4.6 (m, 4H, $OC\underline{H}_2CH_3$), 3.58 (pseudo t = dd, J = 4.8, ≈ 4.6 Hz, 1H, 8-H), 2.43 (dd, $J \approx 5.4$, ≈ 4.8 Hz, 1H, 7-H), 1.67 (ddd, J = 9.3, 7.1, ≈ 4.6 Hz, 1H, 1-H), ≈1.4 (m, 6H, $OCH_2C\underline{H}_3$). – ^{13}C NMR ($CDCl_3$): 214.7 (C=S), 133.7 (C-2), 131.1 (C-4), 128.8 (C-5), 125.5 (C-3), 69.9 ($O\underline{C}H_2CH_3$), 49.7, 48.4 (C-6, -7), 26.2, 25.4 (C-1, -8), 13.83($OCH_2\underline{C}H_3$). See **3**, **8**. – MS (80 °C): *m/z* (%)= 346 (3; M^+), 225 (71), 147 (100), 137 (53), 135 (97), 119 (53), 103 (56), 91 (85). – HRMS: $^{12}C_{14}H_{18}O_2S_4$, calcd. 346.0190, found 346.0182 ± 0.0100.

cis-9,11-Dithiabicyclo[6.3.0]undeca-2,4,6-triene-10-one (**11**)

147 mg of a brownish yellow oil which is still impure according to ^{1}H NMR. – IR: ν (cm^{-1})= 1685, 1653, 1221, 1146, 1047, 914, 872, 755, 651. – ^{1}H NMR ($CDCl_3$): 6.14 (m in which d can be identified, J= 11.5 Hz, 2H, 3-, 6-H), 6.01 (dd, J= 3.0, 1.7 Hz, probably part of a scarcely resolved AA'BB' system, 2H, 4-, 5-H), 5.95 (m in which d is recognizable, J= 11.5 Hz, 2H, 2-, 7-H), 5,21 (m, 2H, 1-, 8-H). – ^{13}C NMR ($CDCl_3$): 194.3 (C=O), 129.9, 128.6, 127.4 (C-2, -3, -4, -5, -6, -7), 55.5 (C-1, -8). – MS (70 °C): *m/z* (%)= 196 (7; M^+), 168 (21), 135 (29), 91 (100). – HRMS: $^{12}C_9H_8OS_2$, calcd. 196.0017, found 196.0041 ± 0.0100.

trans-7,8-Bis(dithioacetoxy)cycloocta-1,3,5-triene (**13**)

A solution of dithioacetic acid in THF (0.48 g of dithioacetic acid, 6 mmol) and sodium hydrogen carbonate (0.59 g, 7 mmol) are mixed and diluted with CH_2Cl_2 (4 ml). To this suspension of dithioacetate (**12**), *trans*-7,8-dibromobicyclo[4.2.0]octa-2,4-diene (**1**) (0.79g, 3 mmol) is added with vigorous stirring. Because of the stench of dithioacetic acid, it is advisable to close the flask loosely with a stopper. After 20 h at room temperature, the reaction mixture is poured into water containing a trace of potassium hydroxide, which then is extracted with CH_2Cl_2. The organic layer is washed with water, dried over $MgSO_4$, and evaporated *in vacuo* at room temperature. Pentane/CH_2Cl_2 = 4 + 1 is a suitable eluent for thin layer chromatography. Column chromatography using the

same mixture separates 346 mg (40%) of an extremely viscous reddish brown oil which smells very unpleasant and tends to decompose. – IR (film): ν (cm^{-1}) = 3008, 1431, 1366, 1193, 1067, 860, 826, 751, 734, 700, 647. – ^1H NMR ($CDCl_3$): δ (ppm) = 6.02 (m, 2H, 2-, 5-H), 5.86 (dd, J = 3.0, 1.7 Hz, 2H, 3-, 4-H), 5.81 (m, 2H, 1-, 6-H), 5.16 (ddd, J = 9.3, 6.9, 1.3 Hz, 1H, *exo*-7-H), 4.84 (ddd, J = 8.9, 5.4, 1.6 Hz, 1H, *endo*-8-H), 2.73 (s, 3H, *exo*-8-CH_3), 2.32 (s, 3H, *endo*-7-CH_3). Coupling constants of δ= 5.86 are probably just line distances of an ill resolved spin system; see **11**. – ^{13}C NMR ($CDCl_3$): δ (ppm)= 233.0 (C=S), 131.2, 129.5, 127.2, 127.1, 126.3 (5 signals for 6 olefinic carbon atoms C-2, -3, -4, -5, -6, -7), 57.5, 57.2 (C-1, -8), 38.6, 29.8 (CH_3). – MS (30 °C): *m/z* (%)= 286 (0.3; M^+), 194 (26), 135 (53), 116 (33), 104 (29), 91 (95), 78 (31), 59(100). – Analysis: $C_{12}H_{14}S_4$ (286.48), calcd. C 50.31 H 4.93, found C 50.38, H 4.68.

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