

HETEROCYCLES, Vol. 84, No. 2, 2012, pp. 1113 - 1122. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 1st August, 2011, Accepted, 5th September, 2011, Published online, 13th September, 2011
DOI: 10.3987/COM-11-S(P)93

SYNTHESIS OF NORBORNANE-FUSED 1,3-DITHIOLANES AND EVALUATION OF 1,3-DITHIOLANE-CONTAINING POLYMERS AS ABSORBANTS FOR MERCURY(II) SALTS

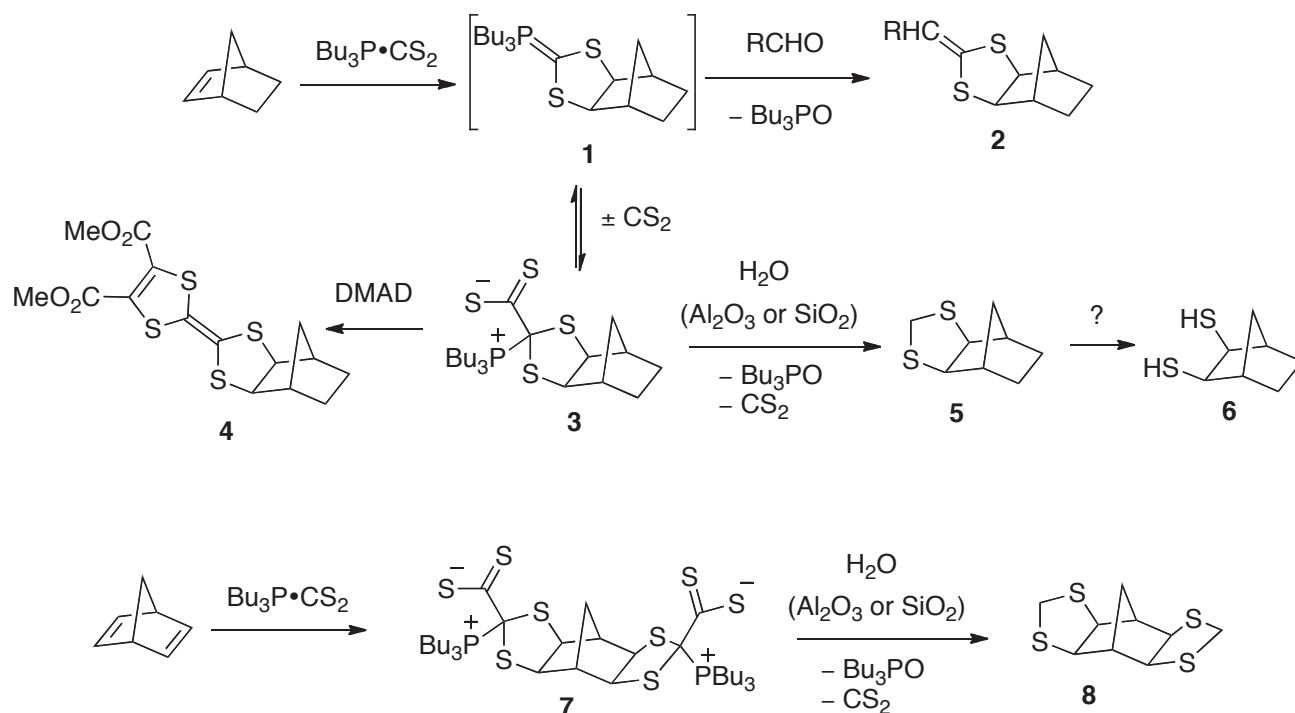
**R. Alan Aitken,* Kati M. Aitken, Stuart Lambert, Richard Playfair, and Neil
J. Wilson**

EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St
Andrews, Fife, KY16 9ST, UK; E-mail: raa@st-and.ac.uk

Abstract – Hydrolysis of the zwitterionic adducts formed from Bu_3P , CS_2 and norbornene or norbornadiene gives Bu_3PO and the corresponding norbornane-fused 1,3-dithiolanes. Oxidation of these gives *endo*-sulfoxides while attempted hydrolysis using HgCl_2 and CdCO_3 instead leads to formation of crystalline 1:1 HgCl_2 adducts. Based on this observation, a range of robust and readily accessible polymers containing norbornane-fused dithiolane units are evaluated for absorption of HgCl_2 from aqueous solution.

INTRODUCTION

Some time ago we reported that strained bicyclic alkenes such as norbornene (bicyclo[2.2.1]heptene) react with Bu_3P and CS_2 to generate the intermediate ylide **1** which, in the presence of an aldehyde, undergoes a Wittig reaction to form alkylidenedithiolanes **2**.¹ In the absence of an aldehyde, a pink solid adduct formulated as **3** can be isolated and this undergoes cycloaddition with acetylenic esters such as DMAD to give dihydrotetrathiafulvalene derivatives **4**.² With norbornadiene the corresponding adduct **7** was formed and could also be converted into bis(alkylidenedithiolanes)¹ and bis(dihydrotetrathiafulvalenes).² In the course of chromatographic purification of the products from these reactions we consistently isolated traces of stable byproducts which appeared to have the 2-unsubstituted dithiolane structures **5** and **8**. We report here their synthesis and characterisation as well as their remarkable affinity for mercuric chloride.

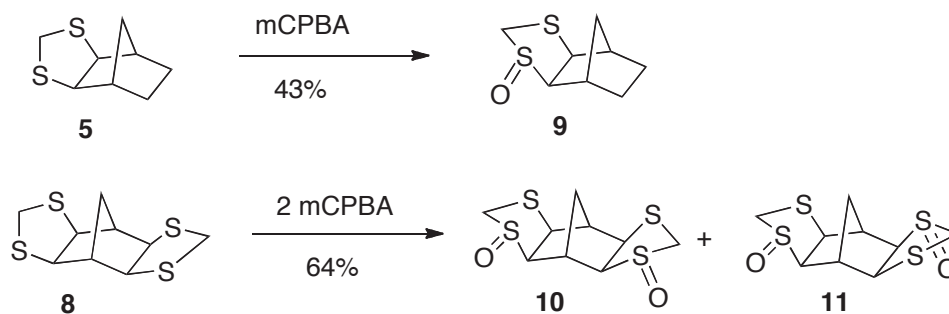


Scheme 1. Formation of dithiolanes **5** and **8**

RESULTS AND DISCUSSION

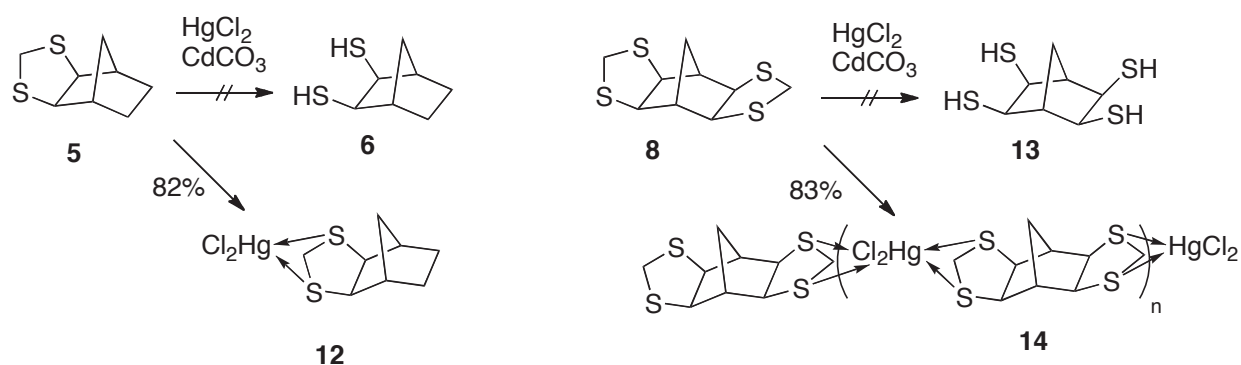
The structure of product **5** suggested its formation by hydrolysis of the ylide **1** which is in equilibrium with the CS_2 adduct **3** and this was supported by concomitant formation of Bu_3PO . After **3** was found to be inert towards aqueous acetic or hydrochloric acid, successful hydrolysis was achieved by stirring a CH_2Cl_2 solution of **3** with wet alumina for 18 h. Filtration, evaporation and chromatography of the residue on alumina gave dithiolane **5** as a colourless liquid in 30% yield. By changing to silica for both hydrolysis and chromatography, the same product was obtained but in only 6% yield. In the case of **7**, wet alumina hydrolysis followed by distillation to remove Bu_3PO and sublimation of the residue gave **8** as colourless crystals in 51% yield whereas use of silica gave only 8%.

In order to obtain a crystalline derivative of the liquid dithiolane **5**, it was subjected to oxidation with mCPBA and afforded the monosulfoxide **9** in moderate yield after recrystallisation. In the case of the bis(dithiolane) **8**, treatment with two equivalents of mCPBA afforded a mixture of regioisomeric disulfoxides **10** and **11** whose identity was clear from their ^1H and particularly ^{13}C NMR spectra. The differing symmetry of the two compounds results in the bridgehead CH groups being distinct in **10** but equivalent in **11**. It is notable that in each case there was no evidence of further oxidation, formation of two sulfoxide functions on the same ring, nor formation of stereoisomeric sulfoxides. All sulfoxide functions are believed to be *endo* as shown.



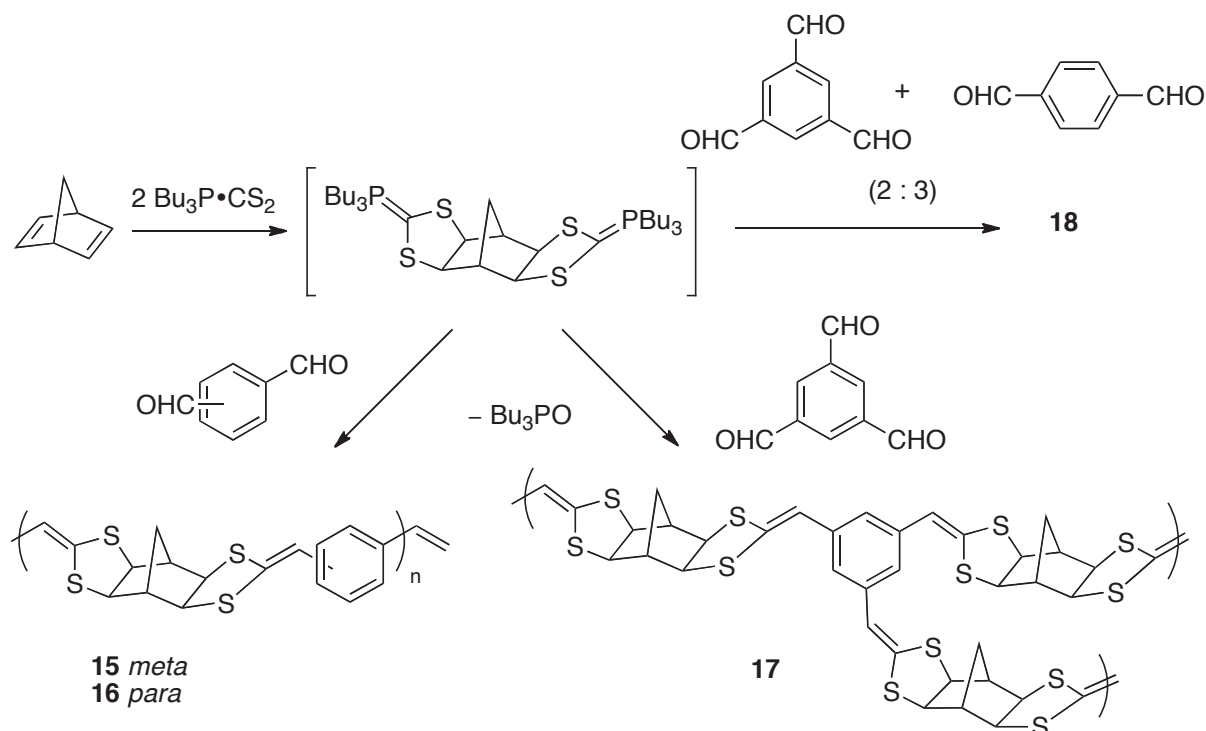
Scheme 2. Oxidation of compounds **5** and **8**

Given the ready availability of the reagents used to prepare **5**, we were interested to investigate its cleavage to the corresponding dithiol **6** which might thus provide a general method for overall conversion of strained alkenes into the corresponding 1,2-dithiols. This transformation is currently not easy to achieve and one of the few methods known involves reaction of norbornene with sulfur and ammonia in DMF to give the 1,2,3-trithiolane followed by reduction of this with sodium in liquid ammonia.³ The standard method to cleave 1,3-dithiolanes, first introduced by Hach in 1953⁴ and subsequently much used to cleave the homologous 1,3-dithianes, involves treatment with mercuric chloride and cadmium carbonate in hot ethanol. When this was applied to compounds **5** and **8**, however no trace of the expected thiols **6** and **13** was obtained. Instead the products were colourless solids which proved to be the 1:1 adducts **12** and **14** with mercuric chloride. These showed NMR data very little different from the starting dithiolanes and elemental analysis data in reasonable agreement with expectation. Such adducts from cyclic sulfides are in fact well known, with typical examples involving systems such as 1,3,5-trithiane,⁵ 1,4-oxathiane,⁶ tetrathiacyclotetradecane,⁷ dithiapropanes,⁸ and tetrahydrotetrathiafulvalene.⁹ In fact the ¹³C NMR data for **12** and **14** together with the 1:1 ratio observed in each case allow us to predict the precise mode of coordination of the HgCl₂, with equal coordination of HgCl₂ to both sulfurs in **12** giving a symmetrical structure with only 5 ¹³C NMR signals. In **14**, the 1:1 ratio as well as observation of only 4 ¹³C NMR signals is consistent with a polymeric structure with a repeat unit as shown involving one HgCl₂ coordinated between the four sulfurs of two adjacent molecules of **8**. These structures are in fact in good agreement with the previous HgCl₂ complexes mentioned above, where there are examples of one HgCl₂ linked to two sulfurs from the same ring in a monomeric structure as for **12**,⁷ and HgCl₂ shared between two sulfurs from different rings to form either a monomeric^{6,9} or polymeric^{5,8} structure, or shared between four sulfurs in a polymeric structure like **14**.⁸



Scheme 3. Formation of HgCl_2 adducts from **5** and **8**

The high affinity of these norbornane-fused dithiolanes for mercury prompted us to evaluate the mercury affinity of a series of polymers whose preparation we reported some time ago,¹⁰ by treatment of norbornadiene with tributylphosphine and carbon disulfide and an aromatic di- or trialdehyde. Using isophthalaldehyde and terephthalaldehyde respectively gave polymers **15** and **16** while mesitaldehyde gave the three dimensional structure **17**.¹⁰ In addition a copolymer **18** formed using a 2:3 mixture of mesitaldehyde and terephthalaldehyde with a hybrid structure between **16** and **17** was also prepared and evaluated. All the polymers are highly insoluble stable solids that are readily formed from low cost



Scheme 4. Polymers evaluated for mercury absorption

starting materials and contain a high proportion of sulfur (e.g. 37% by weight for **15** and **16**). They would thus seem to have considerable potential for removal of mercury ions from water, an area that has attracted considerable recent interest, with a range of sulfur-containing silica materials being among the most effective.¹¹ In a brief preliminary study, a sample of the *para* polymer **16** (1 g) was placed in a short glass column between layers of sand and covered with water. When a solution of HgCl₂ (100 mg) in water (10 cm³) was applied and eluted with water (50 cm³), evaporation of the water collected gave only 30 mg of HgCl₂. The absorbed mercury caused the initially yellow polymer to turn grey-green and could be partly recovered by washing through with 1 M NaCl solution. A more detailed quantitative study was therefore undertaken.

For this the polymers (1 g) were mixed with sand (2–2.5 g) and placed in a glass column between two layers of pure sand. The column was then wetted thoroughly with water and a solution of HgCl₂ in water (50 cm³) was passed through, followed by water (50 cm³). The mercury from the collected solutions was determined by gravimetric analysis after precipitation as [Cu(en)₂] [HgI₄].¹² The method was first validated by analysis of five samples containing between 5 mg and 110 mg of HgCl₂ in water (100 cm³). A calibration curve was constructed and showed a good correlation with R² = 0.9992 (see Experimental Section). This was then used to correct the weights obtained. The results are presented in Table 1.

Table 1. Mercury absorption results

Run	Polymer	column diameter (cm)	[Cu(en) ₂] [HgI ₄] obtained (g) ^a	equivalent of HgCl ₂ (mg)	HgCl ₂ absorbed(mg)
1	15	1.0	0.4118	92.6	7.4
2	16	1.0	0.2001	45.0	55.0
3	17	1.0	0.1572	35.4	64.6
4	18	1.0	0.1323	29.8	70.2
5	16	1.0	0.2268	51.0	49.0
6	16	2.5	0.3488	78.4	21.6
7 ^b	16	2.5	0.3652	82.1	17.9
8 ^c	16	2.5	0.3795	85.4	14.6

^a Corrected weight

^b Polymer column from run 6 reused after regeneration using aq. NaCl

^c Polymer column from run 7 reused after regeneration using aq. NaCl

After some experimentation, optimum conditions were established. The polymer, in the finely powdered form directly as obtained from the synthesis,¹⁰ (1 g) was mixed with sand (2.5 g) since this gave efficient absorption and a slow flow rate such that the mercury solution (50 cm³) passed through under gravity within 12 h. Using less sand resulted in much slower flow (up to 1 week) while using more gave faster

flow (3 h) but resulted in lower mercury absorption. Sand (1 g) was placed in the column, followed by the sand/polymer mixture and finally sand (7.5 g). Only then was the column thoroughly wetted from above (without applying external pressure) resulting in an evenly packed column with no visible air bubbles. Wetting at an earlier stage led to the light polymer floating up on top of the water. The four polymers were now compared (Table 1, entries 1–4) and it is clear that the *meta* polymer **15** behaved very poorly while the other three all gave good absorption. It might also be noted that **15** was white while the other three polymers were all yellow in colour. The determination of run 2 was repeated (run 5) and this gives an idea of the reproducibility of the results. Changing to a wider column with a thinner layer of polymer led to faster flow rate and consequently lower absorption of mercury (run 6). When the column from run 6 was washed thoroughly with aq NaCl then water and reused for another run, its absorption capacity was less but still significant (run 7), and this trend was continued when regenerating and reusing a third time led to a further fall to 2/3 of the original capacity.

These results are encouraging bearing in mind the inherently low cost of the polymers, particularly **16**, and their robust nature. The improvement in performance by **17** and the copolymer **18** is unexpected and merits further detailed studies.

EXPERIMENTAL

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. IR spectra were determined on a Perkin-Elmer 1710 spectrometer as Nujol mulls or thin films. All NMR spectra were obtained using a Varian Gemini 2000 spectrometer, at 300 MHz for ^1H and 75 MHz for ^{13}C , and are reported in ppm to high frequency of TMS as internal standard. Spectra were recorded in CDCl_3 unless otherwise stated. Mass spectra were recorded using an AEI Kratos MS-50 spectrometer using EI (70 eV) or, where noted, CI (isobutane). Elemental analysis was performed using a Carlo-Erba 1106 analyser. Alumina was Laporte Industries alumina Type H.

Starting Materials

Compounds **3** and **7**¹ as well as polymers **15**, **16** and **17**¹⁰ were prepared as described previously. Polymer **18** was prepared using the same method¹⁰ but with a mixture of mesitaldehyde and terephthalaldehyde in a 2:3 molar ratio.

Preparation of 2,6-*exo*-3,5-dithiatricyclo[5.2.1.0^{2,6}]decane **5**

4-Dithiocarboxylato-4-tri-*n*-butylphosphonio-3,5-dithiatricyclo[5.2.1.0^{2,6}]decane **3** (4.50 g, 10 mmol) was dissolved in CH_2Cl_2 (150 mL) and Al_2O_3 (2.00 g) preadsorbed with water (0.20 g, 11.11 mmol) was added. The mixture was stirred for 24 h, Al_2O_3 removed by filtration, and the CH_2Cl_2 removed *in vacuo*.

Flash column chromatography (Al_2O_3 , CH_2Cl_2 —petroleum, 1:1) of the residue followed by distillation (Kugelrohr) gave the product **5** (0.52 g, 30%) as a colourless oil; bp 95 °C/ 0.2 Torr; IR 1716, 1654, 1471, 1450, 1313, 1299, 1183 and 1043 cm^{-1} ; ^1H NMR δ 3.866 and 3.761 (AB pattern, $J = 11$ Hz, 2H, 4-H), 3.603 (d, $J = 2$ Hz, 2H, 2,6-H), 2.35 (s, 2H, 1,7-H), 1.908 (dt, 1H, $J = 10, 2$ Hz, 10-H), 1.617 (second order pattern*, $^2J = 8, ^3J = 2, ^3J = 1, ^4J = 2$ Hz, 2H, 8,9 $endo$ -H), 1.208 (second order pattern*, $^2J = 8, ^3J = 2, ^3J = 1$ Hz, 2H, 8,9 exo -H), 1.11 (dt, $J = 10, 2$ Hz, 1H, 10-H); ^{13}C NMR δ 62.0 (C-2, C-6), 43.6 (C-1, C-7), 37.3 (C-4), 32.7 (C-10), 27.7 (C-8, C-9); MS m/z 172 (M^+ , 100), 126 (33), 105 (44), 93 (52) and 66 (49). Anal. Calcd for $\text{C}_8\text{H}_{12}\text{S}_2$: C, 55.76; H, 7.02. Found: C, 55.44; H, 6.85.

(* Coupling constants derived by simulation)

Preparation of 2,6-*exo*-8,12-*exo*-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane **8**

2,6-*exo*-8,12-*exo*-4,10-Bis(dithiocarboxylato)-4,10-bis(tri-*n*-butylphosphonio)-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane **7** (6.00 g, 7.49 mmol) was suspended in CH_2Cl_2 (100 mL) and Al_2O_3 (2.00 g) preadsorbed with water (0.20 g, 11.1 mmol) was added. The mixture was stirred for 16 h, the Al_2O_3 removed by filtration, and the CH_2Cl_2 removed *in vacuo*. The residue was Kugelrohr distilled to remove tri-*n*-butylphosphine oxide (105 °C, 0.1 Torr) and the remaining material sublimed (160 °C, 0.1 Torr) to give the product **8** (0.94 g, 51%) as colourless crystals; mp 158–159 °C; IR 1448, 1420, 1312, 1292, 1264, 1220, 1188, 1169, 1079, 1029, 922, 858 cm^{-1} ; ^1H NMR δ 3.97 and 3.85 (AB pattern, $J = 11$ Hz, 4H, 4,10-H), 3.66 (s, 4H, 2,6,8,12-H), 2.45 (s, 2H, 1,7-H), 1.88 (s, 2H, 13-H); ^{13}C NMR δ 60.9 (C-2, C-6, C-8, C-12), 50.1 (C-1, C-7), 37.5 (C-4, C-10), 27.0 (C-13); MS m/z 248 (M^+ , 77), 157 (27), 104 (63), 57 (100). Anal. Calcd for $\text{C}_9\text{H}_{12}\text{S}_4$: C, 43.51; H, 4.87. Found: C, 43.77; H, 4.88.

Preparation of 2,6-*exo*-3,5-dithiatriacyclo[5.2.1.0^{2,6}]decane 3-*endo*-oxide **9**

A solution of *m*-chloroperoxybenzoic acid (70–75%, 0.265 g, 1.49–1.60 mmol) in CH_2Cl_2 (10 mL) was added to a solution of 2,6-*exo*-3,5-dithiatriacyclo[5.2.1.0^{2,6}]decane **5** (0.25 g, 1.45 mmol) in CH_2Cl_2 (50 mL). The solution was stirred for 16 h to afford a purple solution (λ_{max} 558 nm). This was washed with saturated aqueous NaHCO_3 solution (3 \times 30 mL), dried and the solvent removed by evaporation to give a pale yellow oil which crystallised upon standing. Recrystallisation from hexane/EtOAc gave the title compound **9** (0.12 g, 43%) as colourless crystals; mp 97–99 °C; IR 2796, 1452, 1314, 1300, 1254, 1076, 1042 cm^{-1} ; ^1H NMR δ 4.02 and 3.60 (AB pattern, $J = 10$ Hz, 2H, 4-H), 3.57 and 2.92 (AB pattern, $J = 6$ Hz, 2H, 2,6-H), 2.92 (br s, 1H, 1-H), 2.22 (br s, 1H, 7-H), 1.81 and 1.30 (AB pattern, $J = 10$ Hz, 2H, 10-H), 1.79–1.62 (m, 2H, 8,9-H), 1.28–1.14 (m, 2H, 8,9-H); ^{13}C NMR δ 76.9 (C-2), 52.5 (C-6), 50.1 and 41.0 (C-1, C-7), 38.9 (C-4), 34.2 (C-10), 27.3 (C-8, C-9); MS (CI) m/z 189 ($\text{M}+\text{H}^+$, 100), 126 (13), 93 (12), 66 (7), 56 (25). Anal. Calcd for $\text{C}_8\text{H}_{12}\text{OS}_2$: C, 51.03; H, 6.42. Found: C, 50.89; H, 6.36.

Preparation of 2,6-*exo*-8,12-*exo*-3,5,9,11-tetrathiatetracyclo [5.5.1.0^{2,6}.0^{8,12}]tridecane dioxide **10/11**

A solution of *m*-chloroperoxybenzoic acid (70–75%, 0.29 g, 1.17–1.25 mmol) in CH_2Cl_2 (10 mL) was

added to a solution of 2,6-*exo*-8,12-*exo*-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane **8** (0.25 g, 1.01 mmol) in CH₂Cl₂ (50 mL). The solution was stirred for 5 h, a second portion of *m*-chloroperoxybenzoic acid (0.29 g, 1.17–1.25 mmol) added and the solution stirred for a further 18 h after which time a white precipitate was observed to have formed. The mixture was washed with saturated aqueous NaHCO₃ solution (3 × 30 mL) and the solvent removed *in vacuo* to give the title compound **10/11** (0.18 g, 64%) as a white powder as a mixture of isomers; mp 240–242 °C; IR 1460, 1389, 1315, 1294, 1258, 1242, 1155, 1083, 1049, 1022, 930, 901 cm⁻¹; MS (CI) *m/z* 281 (M+H⁺, 100), 265 (7), 187 (26); HRMS: Calcd for C₉H₁₃O₂S₄ (M+H): 280.9798. Found: 280.9787.

2,6-*exo*-8,12-*exo*-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane 3,11-dioxide **10**; ¹H NMR (CD₃OD) δ 4.40 and 3.94 (AB pattern, *J* = 5.5 Hz, 4H, 4,10-H), 3.77 and 3.17 (AB pattern, *J* = 4 Hz, 4H, 2,6,8,12-H), 3.42 (s, 1H, 1-H), 2.23 (s, 1H, 7-H), 1.99 (s, 2H, 13-H); ¹³C NMR δ 76.6 (C-2, C-12), 52.1 (C-6, C-8), 52.0 (C-1), 47.1 (C-7), 45.0 (C-4, C-10), 32.1 (C-13).

2,6-*exo*-8,12-*exo*-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane 3,9-dioxide **11**; ¹H NMR (CD₃OD) δ 4.40 and 3.93 (AB pattern, *J* = 5.5 Hz, 4H, 4,10-H), 3.82 and 3.12 (AB pattern, *J* = 4 Hz, 4H, 2,6,8,12-H), 2.80 (s, 2H, 1,7-H) and 1.99 (s, 2H, 13-H); ¹³C NMR δ 76.4 (C-2, C-8), 52.5 (C-6, C-12), 50.1 (C-1, C-7), 44.8 (C-4, C-10), 30.8 (C-13).

Reaction of 2,6-*exo*-3,5-dithiatriacyclo[5.2.1.0^{2,6}]decane **5** with HgCl₂

To a solution of 2,6-*exo*-3,5-dithiatriacyclo[5.2.1.0^{2,6}]decane **5** (0.35 g, 2.03 mmol) in EtOH (10 mL) was added cadmium carbonate (0.38 g, 2.2 mmol). A solution of mercury(II) chloride (0.60 g, 2.2 mmol) in EtOH (10 mL) was added dropwise over a period of 2 h and the mixture stirred for 3 h at 50–60 °C. Unreacted CdCO₃ was removed by filtration, and the solid washed with hot water (20 mL) which resulted in a white precipitate being formed in the filtrate. This was removed by filtration and dried over P₂O₅ in a vacuum dessicator to give the product **12** (0.74 g, 82%) as a white powder; mp 116–118 °C; IR 1458, 1312, 1299, 1251, 1148, 1139, 947 cm⁻¹; ¹H NMR δ 4.17 and 4.05 (AB pattern, *J* = 11 Hz, 2H, 4-H), 3.93 (d, *J* = 2 Hz, 2H, 2,6-H), 2.49 (m, 2H, 1,7-H), 1.65–1.44 (m, 3H, 8,9,10-H *syn*), 1.33 (d, *J* = 8 Hz, 2H, 8,9-H), 1.20 (d, *J* = 10 Hz, 1H, 10-H *anti*); ¹³C NMR δ 62.9 (C-2, C-6), 45.1 (C-1, C-7), 39.6 (C-4), 34.5 (C-10), 28.0 (C-8, C-9); MS *m/z* 272 (HgCl₂⁺, 45), 237 (HgCl⁺, 3), 202 (Hg⁺, 17), 172 (dithiolane⁺, 100), 126 (27), 105 (35), 93 (42). Anal. Calcd for C₈H₁₂Cl₂HgS₂: C, 21.65; H, 2.73. Found: C, 20.87; H, 2.40.

Reaction of 2,6-*exo*-8,12-*exo*-3,5,9,11-tetrathiatetracyclo [5.5.1.0^{2,6}.0^{8,12}]tridecane **8** with HgCl₂

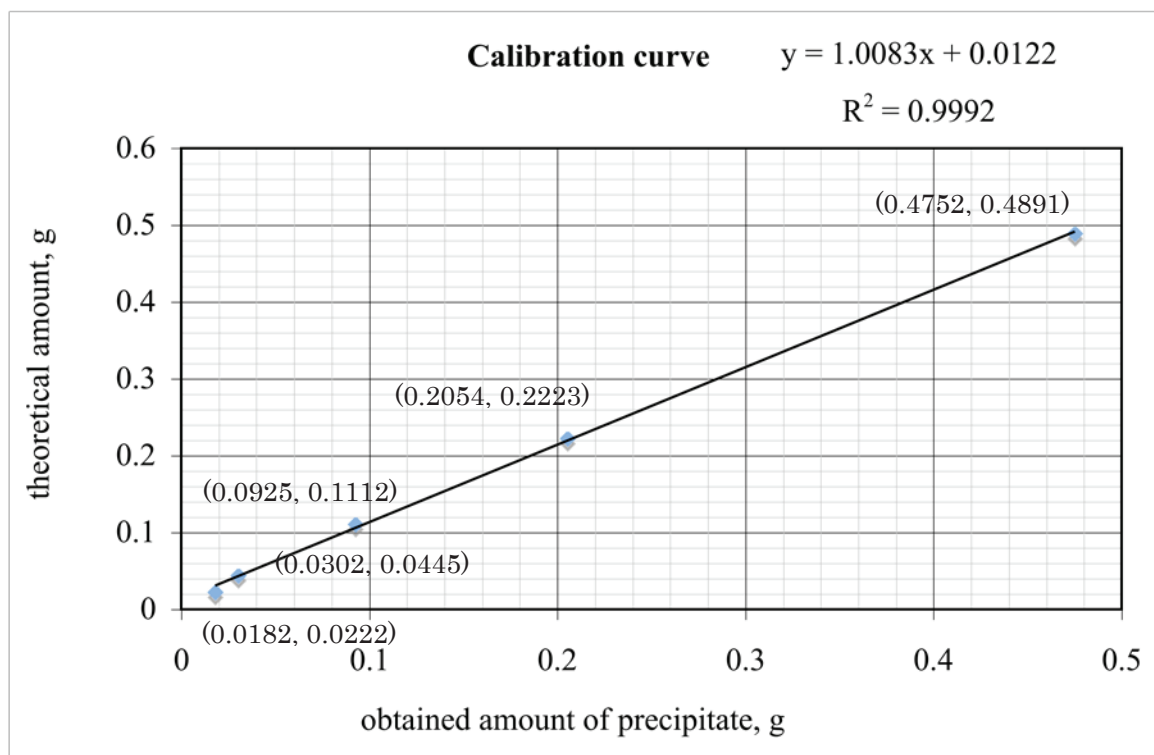
To a solution of 2,6-*exo*-8,12-*exo*-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane **8** (0.50 g, 2.01 mmol) in THF (25 mL) and water (2 mL) was added mercury(II) chloride (1.10 g, 4.05 mmol) and cadmium carbonate (0.70 g, 4.05 mmol). The mixture was heated under reflux for 52 h after which unreacted CdCO₃ was removed by filtration and hot water (25 mL) added to the filtrate. The resulting precipitate was isolated by filtration and dried over P₂O₅ in a vacuum dessicator to give the product **14**

(0.87 g, 83%) as colourless crystals; mp 189–191 °C; IR 1736, 1460, 1317, 1293, 1083, 921, 868 cm^{-1} ; ^1H NMR δ 4.00 and 3.89 (AB pattern, $J = 11$ Hz, 4H, 4,10-H), 3.70 (s, 4H, 2,6,8,12-H), 2.48 (s, 2H, 1,7-H), 1.86 (s, 2H, H-13); ^{13}C NMR δ 60.4 (C-2, C-6, C-8, C-12), 50.9 (C-1, C-7), 38.5 (C-4, C-10), 28.0 (C-13); MS m/z 272 (HgCl_2^+ , 9), 248 (dithiolane $^+$, 100), 202 (Hg^+ , 19), 169 (12), 143 (7), 123 (14), 104 (69). Anal. Calcd for $\text{C}_9\text{H}_{12}\text{Cl}_2\text{HgS}_4$: C, 20.79; H, 2.33. Found: C, 23.45; H, 2.47.

Mercury absorption studies

The columns used were standard small glass chromatography columns equipped with a sintered glass disc at the bottom and were of either 1 cm or 2.5 cm outside diameter, leading respectively to 3.5 cm and 1 cm deep layers of the polymer/sand mixtures. After filling as described earlier, the mercury solutions were allowed to run through under gravity and the collected eluates were analysed as follows:¹²

A neutral solution of HgCl_2 (0–0.50 mmol) in distilled water (100 cm^3) was treated with KI (2–3 g) and heated to 80 °C. It was then treated with a boiling solution of $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$ (0.16 g, 0.52 mmol) and the mixture was allowed to cool to room temperature overnight. The precipitate of $[\text{Cu}(\text{en})_2][\text{HgI}_4]$ was filtered off using a weighed crucible, washed with a small amount of an aqueous solution of KI (0.1%) and $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$ (0.1%), followed by EtOH (10 cm^3) and Et_2O (10 cm^3). The crucible was dried in a vacuum desiccator and weighed to get the yield of the complex.



REFERENCES

1. R. A. Aitken, T. Massil, and S. V. Raut, *J. Chem. Soc., Chem. Commun.*, 1994, 927; R. A. Aitken, K. Carcas, L. Hill, T. Massil, and S. V. Raut, *Tetrahedron*, 1997, **53**, 2261.
2. R. A. Aitken, L. Hill, and P. Lightfoot, *Tetrahedron Lett.*, 1997, **38**, 7927.
3. T. C. Shields and A. N. Kurtz, *J. Am. Chem. Soc.*, 1969, **91**, 5415.
4. V. Hach, *Chem. Listy*, 1953, **47**, 227 [*Chem. Abstr.*, 1955, **49**, 1021].
5. W. R. Costello, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (A)*, 1966, 1190.
6. R. S. McEwen and G. A. Sim, *J. Chem. Soc. (A)*, 1967, 271.
7. N. W. Alcock, N. Herron, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1978, 394.
8. F. H. Herbstein, P. A. Ashkenazi, M. Kaftory, M. Kapon, G. M. Reisner, and D. Ginsburg, *Acta Cryst., Sect. B*, 1986, **42**, 575.
9. M. D. Glick, W. H. Isley, and A. R. Siedle, *Inorg. Chem.*, 1981, **20**, 3819.
10. R. A. Aitken, L. Hill, T. Massil, M. B. Hursthouse, and K. M. Abdul Malik, *Tetrahedron*, 1997, **53**, 10441.
11. J. Brown, L. Mercier, and M. Jaroniec, *Chem. Commun.*, 1999, 69; A. M. Liu, K. Hidajat, S. Kawi, and D. Y. Zhao, *Chem. Commun.*, 2000, 1145; V. Antochshuk and M. Jaroniec, *Chem. Commun.*, 2002, 258; L. Zhang, W. Zhang, J. Shi, Z. Hua, Y. Li, and J. Yan, *Chem. Commun.*, 2003, 210.
12. A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis', Longmans, London, 3rd Edition, 1961, p. 488.