Cycloaddition of Bu$^n_3$P•CS$_2$: Direct One-pot Conversion of Strained Double Bonds to 2-Alkylidene-1,3-dithiolanes

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Abstract: Reaction of the adduct between tri-*n*-butylphosphine and carbon disulfide **1** with norbornene gives the novel zwitterionic structure **9**. In solution this dissociates to the ylide **8** which undergoes Wittig reaction with aldehydes. Using the same method, the overall conversion of the strained double bond in a variety of bicyclo[2.2.1]alkenes into 2-benzylidene-1,3-dithioles **15-24** has been achieved and the reaction is also applicable to norbornadiene. affording bis-dithiolanes **29-31**. © 1997, Elsevier Science Ltd. All rights reserved.

Although the red crystalline adducts formed between trialkylphosphines and CS$_2$ have been known for well over 100 years,[1] their chemistry has been little investigated. Their 1,3-dipolar structure, established by X-ray crystallography,[2] suggests a rich cycloaddition chemistry but this has so far only been studied in a few cases. Reaction of the tri-*n*-butylphosphine adduct **1** with electron-deficient alkynes such as DMAD leads to cycloaddition across the two sulfur atoms to give 2-tri-*n*-butylphosphoranylidene-1,3-dithioles **2** which can be trapped by protonation to give **4**,[3] or by *in situ* Wittig reaction with an added aldehyde to give **3**.[4] In the absence of any trap, we have shown that 2:1 adducts with the stabilised ylide structure **5** are formed.[5]
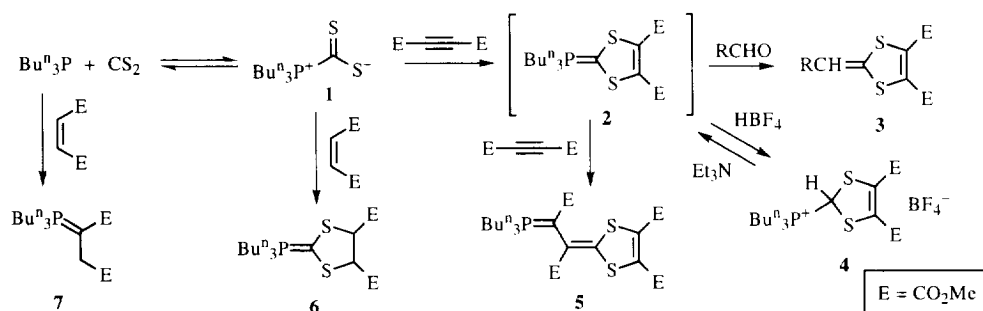
The reactivity of **1** with double bonds has only been examined for electron-deficient alkenes such as dimethyl maleate which, in methanol, produced dimethyl succinate, Bu$^n_3$PO, CS$_2$ and dimethyl ether.[4] The situation here is complicated by the fact that, in solutions of adducts such as **1**, there is an appreciable equilibrium concentration of the starting phosphine and CS$_2$. The former undergoes ready conjugate addition to dimethyl maleate to give the stabilised ylide **7** whose methanolysis accounts for the observed products. For some electron-deficient alkenes, such as maleic anhydride and *N*-phenylmaleimide, cycloaddition does occur and we have

reported briefly that mixtures of **6** and **7** are obtained in these cases.[6] The equilibrium constants for formation of **1**[7] and related adducts[8] have been determined in a wide variety of solvents of different polarity and this has allowed some degree of control over the ratio of **6** to **7**.[7] In this paper we describe the first examples of cycloaddition of **1** to unactivated alkene double bonds.[9]

While **1** was unreactive towards a wide variety of alkenes including styrene, stilbene, hex-1-ene, cyclohexene and cyclopentene, it reacted rapidly at room temperature with norbornene in ether to give a pink precipitate. On the basis of analytical and spectroscopic properties, particularly the observation of ^{13}C NMR signals at δ 240.1 ($^2J_{CP}$ 8 Hz) and 90.9 ($^1J_{CP}$ 39 Hz), this appears to be a 1:1 adduct + CS_2 with the novel zwitterionic structure **9**. The *exo* configuration of the dithiolane ring follows from the configuration of the Wittig products described below, but the *exo/endo* configuration of the $Bu^n_3P^+$ and CS_2^- groups and indeed the state of bonding within this part of the molecule remains uncertain. The thiaphosphetane structure can not be ruled out although the ^{31}P NMR value of δ_P +41.7 is in good agreement with expectation for a tri-*n*-butylphosphonium salt. The formation of **9** is readily understood as resulting from initial formation of the expected 1:1 adduct **8** which is then stabilised by reaction with CS_2 present in solution from dissociation of **1**. This results in formation of Bu^n_3P, which was indeed found in the filtrate from the reaction. It is notable that **9** is formed even with a 1:1 ratio of norbornene to **1**, the precipitation of **9** obviously providing the driving force for the reaction.
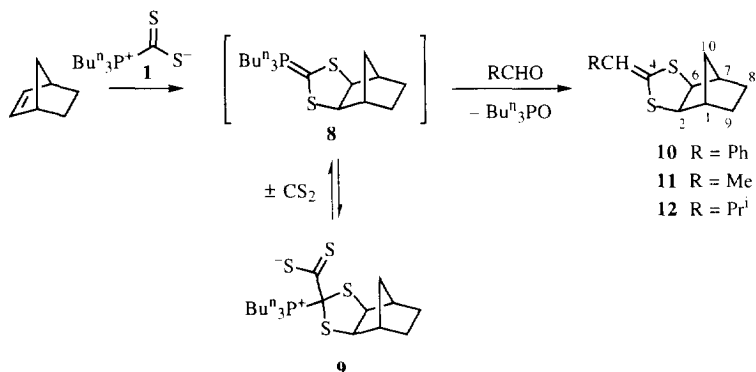
Although **9** is essentially insoluble in ether, it dissolves readily in CH_2Cl_2 and in this solvent dissociates significantly to regenerate **8**. Thus, addition of benzaldehyde to a solution of **9** in CH_2Cl_2 affords the expected Wittig product **10** in moderate yield. The same product can be obtained by directly reacting norbornene, **1** and PhCHO in CH_2Cl_2, and indeed it is not even necessary to preform **1**: interaction of Bu^n_3P, CS_2, norbornene and PhCHO in CH_2Cl_2 at room temperature directly affords **10**. The small value of 2 Hz observed for the coupling between C*H*S and the bridgehead CH in **10** indicates the *exo* configuration shown. The corresponding products are also formed from aliphatic aldehydes as illustrated by the formation of **11** and **12** with acetaldehyde and isobutyraldehyde, respectively. The ^{13}C NMR spectra of these products are presented in Table 1 and provide ready confirmation of the structures.

The direct transformation of the double bond of norbornene to the 2-alkylidene-1,3-dithiolane of **10** in a one-pot procedure represents a valuable synthetic transformation. The scope of the reaction was then examined using a variety of strained double bond compounds **13**, readily available from the Diels-Alder reaction of cyclopentadiene, to give the products **14** in moderate to good yield. In most cases the products could be directly

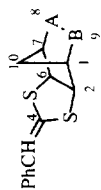Table 1: ^{13}C NMR spectra of tricyclic dithiolanes 10-12 and tetracyclic bis-dithiolanes 29-31, δ_C (CDCl$_3$)

							R signals			
10-12	C-1,7	C-2,6	C-4	C-8,9	C-10	=CHR	C-1	C-2	C-3	C-4
21-23	C-1,7	C-2,6,8,12	C-4,10	—	C-13	=CHR	C-1	C-2	C-3	C-4
10	45.4, 45.2	63.6, 57.3	139.7*	27.8, 27.5	32.1	115.1	137.3*	127.5	128.1	125.7
11	45.5, 45.3	61.1, 59.5	137.1	27.9, 27.8	32.3	111.9	18.2			
12	45.5, 45.4	61.2, 59.2	134.5	28.0, 27.8	32.3	124.9	33.2	22.6, 22.55		
29(E)	53.9	61.4, 55.2	139.7*	—	27.0	117.0	137.1*	127.9	128.3	126.4
29(Z)	54.1, 53.6	61.2, 55.4	138.2*	—	27.0	117.0	137.1*	127.9	128.3	126.4
30(E)	53.6	58.4, 57.0	136.0	—	26.5	112.8	17.8			
30(Z)	53.9, 53.4	58.3, 56.9	136.0	—	26.5	112.8	17.8			
31(E)	54.2	59.0, 57.2	133.7	—	27.0	126.6	33.3	22.5		
31(Z)	54.4, 54.0	58.9, 57.0	133.7	—	27.0	126.5	33.3	22.5		

* Assignments may be interchanged

filtered off in pure form after stirring a solution of the reactants in CH$_2$Cl$_2$ at room temperature for 24 h. The ^{13}C NMR spectra of the resulting products 15–24 shown in Table 2 again form a highly consistent pattern and show that, as expected, the unsymmetrical examples 20,21 and 24 are formed as essentially 1 : 1 mixtures of E and Z isomers. The reaction at only one double bond in dicyclopentadiene to afford 20 provides further evidence of the selectivity for strained double bonds. Even the two carbon bridged cyclohexa-1,3-diene – maleic anhydride adduct did not react with 1 and the system seems to be very sensitive to the degree of ring strain present. Compound 22 was obtained by methanolysis of 15 and further esterification gave 23 whose spectroscopic data were clearly distinct from the isomer 24 formed by direct addition to the cyclopentadiene – dimethyl fumarate adduct.
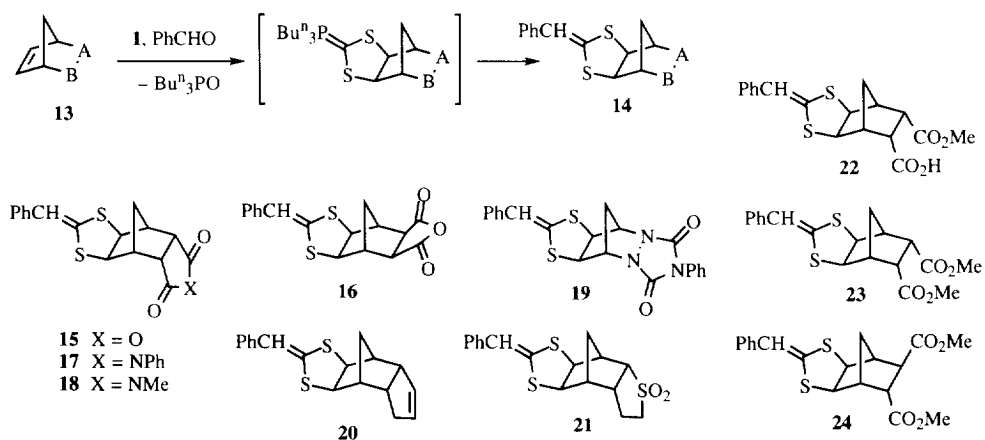

The sulfone 21 was of particular interest since it was hoped that, upon flash vacuum pyrolysis (FVP), the compound would undergo extrusion of SO$_2$ and ethylene as shown to give an intermediate which could readily

Table 2: ^{13}C NMR Spectra of tri- and tetracyclic dithiolanes **15-24**, δ_C (CDCl$_3$, numbering as shown)

	C-1,7	C-2,6	C-4	C-8,9	C-10	=CHPh	Ph signals C-1	C-2,6	C-3,5	C-4	Other signals
15	49.3, 48.9	59.0, 53.1	137.2*	49.1	37.2	118.9	137.1*	128.5	128.9	127.3	170.8 (CO)
16a	48.5, 48.3*	60.4, 54.2	138.6	47.9, 47.6*	28.3	115.6	136.7	127.4	128.3	126.1	172.4 (CO)
17	48.2, 48.0*	58.5, 52.5	137.2¶	47.6, 47.4*	36.3	117.8	136.8¶	127.9	128.3	126.6	175.5, 175.4 (CO), N<u>Ph</u>: 131.2 (C-1), 129.3 (2 C), 129.0 (C-4), 126.5 (2 C)
18	47.9, 47.7*	58.5, 52.5	137.3¶	47.6, 47.5*	36.3	117.8	136.9¶	127.9	128.4	126.5	176.5 (CO), 24.7 (N<u>Me</u>)
19	65.02, 65.07	59.7, 54.2	b	—	32.7	120.7	136.4	128.1	128.5	127.2	156.0 (CO), N<u>Ph</u>: 130.0 (C-1), 129.3 (2 C), 128.6 (C-4), 125.3 (2 C)
20	50.3/50.1, 47.9/47.6	60.3/56.6, 53.6/52.4	140.0	52.1/50.3	31.7, 35.2	115.7	137.2	127.5	128.0	125.6	131.7, 131.0/130.9, 41.7/ 41.5
21maj	49.0, 50.9	56.9, 51.0	137.85	63.4, 41.3	35.8	117.4	136.9	127.9	128.3	126.5	52.3, 20.9
21min	48.8, 50.8	57.1, 51.1	137.9	63.7, 41.1	35.8	117.5	137.0	127.9	128.3	126.5	52.3, 20.9
22maj	48.7, 48.5	58.2, 51.1	138.2	45.9, 45.6	33.3	115.8	136.8	127.3	127.9	125.7	173.0, 171.7, 51.3
22min	48.6, 48.4	57.7, 51.4	138.2	46.2, 45.4	33.3	115.9	136.8	127.3	127.9	125.7	173.0, 171.7, 51.5
23	49.1, 48.8	58.1, 51.8	139.2	46.3, 46.1	33.8	116.6	137.3	127.8	128.3	126.1	171.8, 51.9
24	50.0, 48.5*	58.4, 56.4¶	138.2	47.9, 47.7*	32.2	116.9	137.0	127.6	128.2	126.2	173.3, 172.5 (CO), 52.35, 52.3¶

a: in CD$_3$SOCD$_3$ b: signal could not be detected due to extremely low intensity.   Assignments of signals marked * or ¶ may be interchanged.

lose cyclopentadiene to afford the benzylidenedithiole **25**. The behaviour of **26** as an acetylene synthon in this way,[10] which would allow the overall transformation of benzaldehyde into **25** in two steps should potentially be applicable to any aldehyde. Unfortunately FVP of **21** at 650–750 °C did not take the expected course and the only products were CS$_2$, the alkene **26** from which **21** was formed, cyclopentadiene and 2-sulfolene from its decomposition,[10] and a tar presumably derived from phenylcarbene. It is clear that the alkylidenedithiole moiety is more thermally labile than the sulfone.
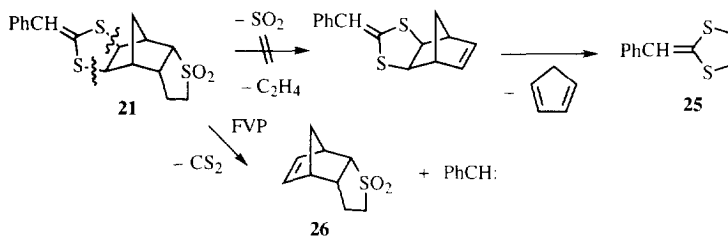
With norbornadiene, **1** also reacts rapidly in ether to form a pink precipitate **28**. Elemental analysis of this indicates a gross composition corresponding to the expected **27** + 2CS$_2$ but it is insoluble in any common solvent and has an unknown, possibly polymeric structure. If the reaction of **1** with norbornadiene is instead performed in CH$_2$Cl$_2$ in the presence of an aldehyde, the expected bis-dithiolanes **29–31** are formed in good yield as a mixture of E and Z isomers as clearly shown by the ^{13}C NMR data presented in Table 2.

29 R = Ph
30 R = Me
31 R = Pr^i
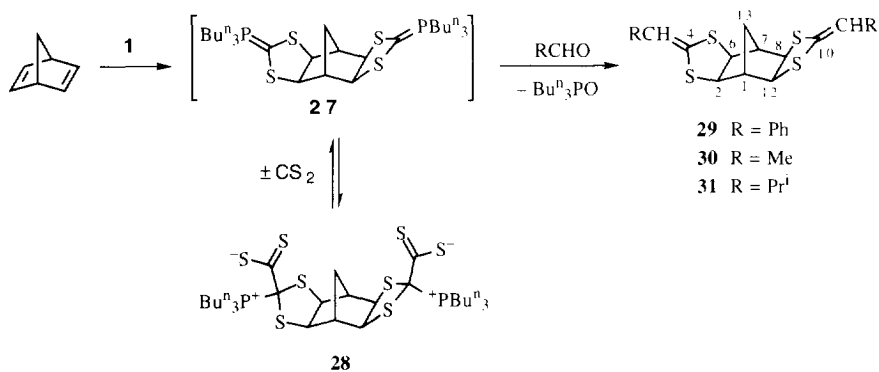
The extension of this convenient new method of heterocyclic synthesis to other types of strained double bond and other modes of reaction of the novel functional group present in **9** and **28** are currently under investigation.

Experimental

General

All NMR spectra were recorded on solutions in deuteriochloroform unless otherwise stated. ^{1}H spectra were recorded at 300 MHz and ^{13}C spectra at 75 MHz on a Bruker AM300 instrument with tetramethylsilane as internal reference. ^{31}P spectra were recorded at 32 MHz on a Varian CFT20 instrument and are referenced to external H$_3$PO$_4$. Low and high resolution mass spectra were obtained on a Finnegan Incos 50 mass spectrometer using electron impact at 70 eV. Elemental analyses for C and H were performed on a Carlo-Erba 1106 analyser and analyses for P and S were carried out by the Department of Chemistry, University of Durham. Melting points

were determined on a Reichert hot-stage microscope and are uncorrected. Column chromatography was performed using BDH silica gel for flash chromatography (particle size 40-63 μm).

1. Preparation of tri-n-butylphosphoniodithioformate 1

Tri-*n*-butylphosphine (20 g, 0.10 mol) in dry petroleum ether (b.p. 40-60°C, 50 ml) was added dropwise to a mixture of carbon disulphide (7.5 g, 0.10 mol) and dry petroleum ether (100 ml) at 0–5 °C. After complete addition the mixture was stirred at R.T. for a further 4–5 h. The product was filtered off and washed with petroleum ether to give **1** as dark red needles (19.7 g, 74%), m.p. 65–66 °C (lit.[11], m.p. 65.5 °C).

2. Reaction of 1 with norbornene

4-Dithiocarboxylato-4-tri-n-butylphosphonio-3,5-dithiatricyclo[5.2.1.0²,⁶]decane 9

A solution of tri-*n*-butylphosphoniodithioformate (2.0 g, 7.2 mmol) and norbornene (0.34 g, 3.6 mmol) in dry ether (50 ml) was stirred at room temperature for 4 h. The resulting precipitate was filtered off and dried to give *the title adduct* **9** (0.68 g, 42%) as a pink powder, m.p. 106–108 °C (Found: C, 56.3; H, 8.6; P, 7.15; S, 27.8. $C_{21}H_{37}PS_4$ requires C, 56.2; H, 8.3; P, 6.9; S, 28.6%); v_{max} /cm⁻¹ 1305, 1195, 1152, 1098, 1050 (s), 987, 914, 868 and 728; δ_H 4.30 and 3.72 (2 H, m), 2.62 (2 H, m), 2.45–2.25 (6 H, m), 1.80 (2 H, m), 1.7–1.4 (14 H, m) and 1.05–0.9 (11 H, m); δ_P +41.7; δ_C 240.1 (d, *J* 8, CS_2^-), 90.9 (d, *J* 39, C-4), 67.4 (C-2,6), 43.4 (C-1,7), 32.6 (C-10), 27.3 (C-8,9), 25.8 (d, *J* 5, C-2'), 24.9 (d, *J* 14, C-3'), 21.1 (d, *J* 43, C-1') and 14.0 (C-4'); *m/z* 416 (M⁺–S, 4%), 383 (1), 372 (M⁺–CS_2, 2), 360 (2), 304 (7), 248 (7), 234 (16), 225 (8), 214 (26), 202 (17), 178 (30), 173 (20) and 122 (100).

3. Wittig reaction of 8 with aldehydes

a. 2,6-exo-4-Phenylmethylene-3,5-dithiatricyclo[5.2.1.0²,⁶]decane 10

A solution of tri-n-butylphosphoniodithioformate (10.0 g, 36 mmol), norbornene (3.5 g, 36 mmol) and benzaldehyde (3.85 g, 36 mmol) in dry dichloromethane (200 ml) was stirred at RT for 24 h. The resulting yellow solution was evaporated and the residue Kugelrohr distilled to remove Bu^n_3PO. The residual solid was recrystallised from methanol to give the *title compound* **10** (4.1 g, 44%) as colourless crystals, m.p. 77–78 °C (Found: C, 68.8; H, 6.3. $C_{15}H_{16}S_2$ requires C, 69.2; H, 6.2%); v_{max} /cm⁻¹ 1570, 1550, 1440, 1304, 1290, 1226, 1178, 928, 899, 814, 745 and 685; δ_H 7.4–7.25 (4 H, m), 7.14 (1 H, m), 6.50 (1 H, s), 3.99 and 3.70 (2 H, AB pattern of d, *J* 8, 2), 2.32 (2 H, m), 1.95 (1 H, m), 1.6–1.5 (2 H, m) and 1.25–1.1 (3 H, m); δ_C see Table 1; *m/z* 260 (M⁺, 10%), 218 (7), 189 (38), 176 (8), 163 (20), 147 (24), 119 (36) and 92 (100).

b. 2,6-exo-4-ethylidene-3,5-dithiatricyclo[5.2.1.0²,⁶]decane 11

A solution of tri-n-butylphosphoniodithioformate (2.1 g, 7.4 mmol), norbornene (0.70 g, 7.4 mmol) and acetaldehyde (0.33 g, 7.5 mmol) in dichloromethane (10 ml) was stirred at RT for 72 h. The resulting yellow solution was evaporated and the residual red oil was purified by flash-column chromatography (SiO_2, light petroleum) yielding the *title compound* **11** (1.04 g, 71%) as a colourless oil (b.p. not determined due to decomposition on heating) (Found: C, 60.3; H, 7.3. $C_{10}H_{14}S_2$ requires C, 60.6; H, 7.1%); v_{max} /cm⁻¹ 2960, 2870, 1600, 1553, 1450, 1375, 1314, 1300, 1187, 1025, 940, 885, 766 and 690; δ_H 5.43 (1 H, q, *J* 7), 3.83 and 3.74 (2 H, AB pattern of doublets, *J* 8 and 2), 2.34 (2 H, m), 1.97 (1 H, d of m, *J* 12,), 1.75 (3 H, d, *J* 7), 1.61 (2 H, m) and 1.21 (3 H, m); δ_C see Table 1; *m/z* 198 (M⁺, 100%), 171 (30), 131 (46), 126 (32), 104 (25), 93 (51), 72 (46), and 66 (47).

c. *2,6-exo-4-(2-methylpropylidene)-3,5-dithiatricyclo[5.2.1.0^{2,6}]decane* **12**

The method above was followed but using isobutyraldehyde (7.4 mmol) in place of acetaldehyde. Evaporation followed by flash-column chromatography (SiO$_2$, light petroleum) yielded the *title compound* **12** (0.83 g, 50%) as a colourless oil (b.p. not determined due to decomposition on heating) (Found: M$^+$, 226.0859. C$_{12}$H$_{18}$S$_2$ requires *M*, 226.0850); v_{max} /cm^{-1} 2940, 2855, 1583, 1452, 1445, 1373, 1351, 1308, 1290, 1163, 947, 818, 799 and 682; δ_H 5.28 (1 H, d, *J* 9), 3.87 and 3.66 (2 H, AB pattern of d, *J* 8 and 2), 2.43 (1 H, d of septets, *J* 9 and 7), 2.32 (2 H, m), 1.97 (1 H, d of quintets, *J* 10 and 2), 1.6 (2 H, m), 1.2 (3 H, m), 1.01 (3 H, d, *J* 7) and 0.98 (3 H, d, *J* 7); δ_C see Table 1; *m/z* 226 (M$^+$, 48%), 211(100), 159 (6), 143 (7), 127 (24), 126 (25), 117 (9), 93 (23) and 85 (68).

4. Formation of 2-benzylidene-1,3-dithiolanes **15–24**

a. *2,6-endo-8,12-exo-3,5-Dioxo-10-phenylmethylene-4-oxa-9,11-dithiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane* **15**

Reaction was carried out as in 3a. using *endo*-norbornene-5,6-dicarboxylic acid anhydride in place of norbornene. After stirring at RT for 24 h the resulting white solid was filtered off and washed with ether to give the *title compound* **15** (80%) as colourless crystals, m.p. 185–186 °C (Found: C, 61.6; H, 4.4. C$_{17}$H$_{14}$O$_3$S$_2$ requires C, 61.8; H, 4.3%); v_{max} /cm^{-1} 1825, 1740, 1570, 1554, 1308, 1218, 1138, 1078, 947, 920, 840, 815, 790, 748 and 692; δ_H 7.4–7.2 (5 H, m), 6.62 (1 H, s), 4.20 and 3.93 (2 H, AB pattern of d, *J* 8, 2), 3.6–3.5 (2 H, m), 3.0–2.9 (2 H, m) and 2.38 and 1.67 (2 H, AB pattern, *J* 12); δ_C see Table 2; *m/z* 330 (M$^+$, 100%), 304 (2), 192 (9), 168 (18) and 134 (22).

b. *2,6-exo-8,12-exo-3,5-Dioxo-10-phenylmethylene-4-oxa-9,11-dithiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane* **16**

Reaction was carried out as in 3a. using *exo*-norbornene-5,6-dicarboxylic acid anhydride in place of norbornene. After stirring at RT for 24 h the resulting white solid was filtered off and washed with ether to give the *title compound* **16** (74%) as colourless crystals, m.p. 264–265 °C (Found: C, 61.8; H, 4.7. C$_{17}$H$_{14}$O$_3$S$_2$ requires C, 61.8; H, 4.3%); v_{max} /cm^{-1} 1842, 1760, 1550, 1312, 1240, 1216, 1150, 1078, 918, 896, 812, 793, 743 and 687; δ_H (CD$_3$SOCD$_3$) 7.4–7.2 (5 H, m), 6.42 (1 H, s), 4.45 and 4.15 (2 H, AB pattern, *J* 8), 3.35 (2 H, s), 2.72 (2 H, s) and 1.82 and 1.22 (2 H, AB pattern, *J* 12); δ_C see Table 2; *m/z* 330 (M$^+$, 8%), 241 (4), 189 (10), 104 (10), 91 (66), 76 (64) and 66 (100).

c. *2,6-endo-8,12-exo-3,5-Dioxo-4-phenyl-10-phenylmethylene-9,11-dithia-4-azatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tri-
-decane* **17**

Reaction was carried out as in 3a. using *endo*-norbornene-5,6-dicarboxylic acid *N*-phenylimide in place of norbornene. After stirring at RT for 24 h the solution was evaporated and the Bu$^n_3$PO removed by Kugelrohr distillation. The residue was triturated with ether to give a pale brown solid which was purified by chromatography on silica (ether–hexane, 1:1) to give the *title compound* **17** (43%) as colourless crystals, m.p. 157–159 °C (Found: M$^+$, 405.0828. C$_{23}$H$_{19}$NO$_2$S$_2$ requires *M*, 405.0857); v_{max} /cm^{-1} 1767, 1692, 1490, 1280, 1195, 1180, 900, 788, 732 and 688; δ_H 7.55–7.2 (10 H, m), 6.60 (1 H, s), 4.22 and 3.93 (2 H, AB pattern of d, *J* 8, 2), 3.4–3.3 (2 H, m), 3.03–2.95 (2 H, m) and 2.37 and 1.67 (2 H, AB pattern, *J* 12); δ_C see Table 2; *m/z* 405 (M$^+$, 2%), 239 (20), 173 (55), 129 (20), 119 (17), 91 (67) and 66 (100).

d. *2,6-endo-8,12-exo-3,5-Dioxo-4-methyl-10-phenylmethylene-9,11-dithia-4-azatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tri-
-decane* **18**

Reaction was carried out as in 3a. using *endo*-norbornene-5,6-dicarboxylic acid *N*-methylimide in place of norbornene. After stirring at RT for 24 h the resulting white solid was filtered off and washed with ether to give the *title compound* **18** (46%) as colourless crystals, m.p. 246–247 °C (Found: C, 62.7; H, 5.3; N, 3.9.

$C_{18}H_{17}NO_2S_2$ requires C, 62.9; H, 5.0; N, 4.1%); ν_{max} /cm^{-1} 1770, 1675, 1272, 1250, 1130, 1110, 1078, 972, 842, 821, 794, 750, 738 and 690; δ_H 7.4–7.27 (4 H, m), 7.25–7.15 (1 H, m), 6.57 (1 H, s), 3.98 and 3.68 (2 H, AB pattern of d, *J* 8, 2), 3.22–3.17 (2 H, m), 2.99 (3 H, s), 2.92–2.85 (2 H, m) and 2.29 and 1.60 (2 H, AB pattern, *J* 12); δ_C see Table 2; *m/z* 343 (M$^+$, 100%), 192 (14), 166 (33), 134 (100) and 66 (90).

e. 2,6-exo-9,11-Dioxo-10-phenyl-4-phenylmethylene-3,5-dithia-8,10,12-triazatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tri--decane **19**

Reaction was carried out as in 3a. using the Diels–Alder adduct of cyclopentadiene and *N*-phenyltriazolinedione in place of norbornene. After stirring at RT for 15 min the resulting white solid was filtered off and washed with ether to give the *title compound* **19** (91%) as colourless crystals, m.p. 313–314 °C (Found: C, 61.2; H, 4.75; N, 9.6; M$^+$, 407.0747. $C_{21}H_{17}N_3O_2S_2$ requires C, 61.9; H, 4.2; N, 10.3%; *M*, 407.0762); ν_{max} /cm^{-1} 1780, 1700, 1490, 1410, 1235, 1138, 1070, 1053, 933, 845, 770, 745 and 685; δ_H 7.5–7.4 (2 H, m), 7.4–7.3 (3 H, m), 7.26 (5 H, s), 6.72 (1 H, s), 4.68 (1 H, s), 4.62 (1 H, s), 4.58 and 4.30 (2 H, AB pattern, *J* 10) and 2.30 and 1.93 (2 H, AB pattern, *J* 14); δ_C see Table 2; *m/z* 407 (M$^+$, 65%), 214 (48), 205 (10), 192 (16), 134 (100) and 119 (24).

f. 2,6-exo-8,12-endo-4-Phenylmethylene-3,5-dithiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-9-ene **20**

Reaction was carried out as in 3a. using dicyclopentadiene in place of norbornene. After stirring at RT for 24 h the solution was evaporated and the residue Kugelrohr distilled to give Bu$^n_3$PO followed by the *title compound* **20** (39%) as a yellow oil which crystallised on standing, m.p. 65–67 °C (Found: C, 70.7; H, 6.4; M$^+$, 298.0858. $C_{18}H_{18}S_2$•0.4 H$_2$O requires C, 70.7; H, 6.2%; $C_{18}H_{18}S_2$ requires *M*, 298.0850); ν_{max} /cm^{-1} (CH$_2$Cl$_2$) 1653, 1521, 1466, 1381, 1262, 1219, 1021, 910 and 809; δ_H 7.45–7.3 (4 H, m), 7.25–7.15 (1 H, m), 6.59 (1 H, s), 5.8–5.7 (1 H, m), 5.65–5.55 (1 H, m), 4.20 and 3.92, and 4.08 and 3.78 (2 H, AB pattern of d for *E* and *Z* isomers, *J* 8, 2), 3.25–3.13 (1 H, m), 2.65 (1 H, m), 2.52 (1 H, m), 2.4–2.12 (4 H, m) and 1.55–1.45 (1 H, m); δ_C see Table 2; *m/z* 298 (M$^+$, 16%), 218 (4), 209 (5), 189 (32), 134 (40) and 92 (100).

g. 2,6-exo-8,12-endo-4-Phenylmethylene-3,5,9-trithiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane 9,9-dioxide **21**

Reaction was carried out as in 3a. using *endo*-3-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 3,3-dioxide[10] in place of norbornene. After stirring at RT for 3 days the solution was evaporated and the residue triturated with ether to remove Bu$^n_3$PO. The resulting yellow solid (48%) was subjected to Kugelrohr distillation (120-150 °C/0.05 mm Hg) to remove residual Bu$^n_3$PO which left as the residue the *title compound* **21** (40%) as colourless crystals, m.p. 180–184 °C (Found: C, 58.2; H, 5.2. $C_{17}H_{18}O_2S_3$ requires C, 58.3; H, 5.2%); ν_{max} /cm^{-1} 1595, 1577, 1555, 1310, 1292, 1263, 1128, 1220, 1185, 1172, 1142, 1118, 1100, 1080, 973, 941, 898, 845, 830, 810, 750, 725, 692, and 650; δ_H 7.1–7.4 (5 H, m), 6.61 (0.2 H, s), 6.58 (0.8 H, s), 4.98 (0.8 H, d, *J* 8), 4.72 (0.2 H, d, *J* 8), 4.32 (0.2 H, d, *J* 8), 4.03 (0.8 H, d, *J* 8), 3.39 (1 H, m), 3.17 (1 H, m), 3.00 (2 H, m), 2.86 (1 H, m), 2.57 (1 H, m), 2.29 (2 H, m), 2.15 (1 H, m) and 1.49 (1 H, d, *J* 10); δ_C see Table 2; *m/z* 350 (M$^+$, 100%), 261 (9), 192 (9), 166 (15) and 134 (92).

h. 2,6-exo-8,9-endo-bis(Methoxycarbonyl)-4-phenylmethylene-3,5-dithiatricyclo[5.2.1.0^{2,6}]decane 23

A solution of **15** (2.0 g) in dry methanol (20 ml) containing conc. H$_2$SO$_4$ (0.2 ml) was heated under reflux for 2 h. Water (5 ml) was added and the methanol evaporated. Extraction of the residue with CH$_2$Cl$_2$, drying and evaporation gave a solid (1.95 g, 89%) which proved to be a mixture of *E*- and *Z*-isomers of the diacid monoester **22**; δ_H 7.4–7.3 (4 H, m), 7.25–7.1 (1 H, m), 6.55 (1 H, s, C*H*Ph), 4.82 and 4.39 (2 H, AB pattern, *J* 8, minor isomer), 4.67 and 4.54 (2 H, AB pattern, *J* 8, major isomer), 3.65 (3 H, s), 3.18 and 3.00 (each 1 H, d, *J* 2,

minor isomer), 3.13 and 3.06 (each 1 H, d, J 2, major isomer), 2.70–2.60 (2 H, m) and 2.18 and 1.39 (2 H, AB pattern, J 13, C10-H$_2$); δ_C see Table 2.

Complete conversion to the diester was achieved by heating this product under reflux with dry methanol (50 ml) and conc. H$_2$SO$_4$ (0.5 ml) for 18 h. Work-up as above then gave the *title compound* **23** (1.13 g, 56%) as a pale green powder, m.p. 120–121 °C (Found: M$^+$, 376.0812. C$_{19}$H$_{20}$O$_4$S$_2$ requires M, 376.0803); ν_{max} /cm^{-1} 1743, 1344, 1202, 1169, 1098, 1056, 929, 826, 758 and 700; δ_H 7.40–7.30 (4 H, m), 7.25–7.15 (1 H, m), 6.55 (1 H, s), 4.69 and 4.41 (2 H, AB pattern, J 9), 3.70 (6 H, s), 3.10 (2 H, s), 2.70 (2 H, s) and 2.21 and 1.38 (2 H, AB pattern, J 12); δ_C see Table 2; m/z 376 (M$^+$, 72%), 345 (5), 271 (3), 242 (6), 231 (5), 210 (12), 192 (6), 182 (8), 151 (10) and 134 (100).

i. 2,6-exo-8,9-trans-bis(Methoxycarbonyl)-4-phenylmethylene-3,5-dithiatricyclo[5.2.1.0^{2,6}]decane **24**

Reaction was carried out as in 3a. using dimethyl *trans*-norbornene-5,6-dicarboxylate in place of norbornene. After stirring at RT for 24 h the solution was evaporated and the residue triturated with ether to remove Bu$^n_3$PO. Chromatography of the residue on silica (ether–hexane, 1:1) gave the *title compound* **24** (16%) as colourless crystals, m.p. 105–107 °C (Found: M$^+$, 376.0815. C$_{19}$H$_{20}$O$_4$S$_2$ requires M, 376.0803); ν_{max} /cm^{-1} 1715, 1580, 1556, 1320, 1285, 1260, 1221, 1185, 1170, 1114, 1018, 813 and 753; δ_H 7.4–7.3 (4 H, m), 7.25–7.1 (1 H, m), 6.55 (1 H, s), 4.17 and 3.89, and 4.09 and 3.82 (2 H, AB pattern of d for E and Z isomers, J 8, 2), 3.73 and 3.72 (3 H, s for E and Z isomers), 3.70 and 3.69 (3 H, s for E and Z isomers), 3.4–3.3 (1 H, m), 2.95–2.90 (1 H, m), 2.8–2.7 (2 H, m) and 2.08 and 1.53 (2 H, AB pattern, J 12); δ_C see Table 2; m/z 376 (M$^+$, 10%), 218 (5), 189 (37), 162 (20), 147 (22), 134 (32), 120 (36) and 92 (100).

5. Flash vacuum pyrolysis of 21

A sample of **21** (200 mg) was subjected to FVP at 650 °C and 10^{-2} mmHg using the apparatus previously described.[12] A solid obtained at the furnace exit proved to be the unchanged starting material (55%) while the cold trap contained a mixture of the tricyclic sulfone **25**, cyclopentadiene and 2-sulfolene as shown by ^{1}H NMR.

Repeat pyrolysis at 750 °C resulted in complete reaction to give a mixture of cyclopentadiene and 2-sulfolene in the cold trap. In both cases a tar, presumably derived from the benzylidene group, remained in the inlet tube.

6. Reaction of 1 with norbornadiene

A solution of tri-n-butylphosphoniodithioformate (5.5 g, 20 mmol) and carbon disulfide (1.52 g, 20 mmol) in dry ether (100 ml) was stirred at RT while norbornadiene (0.96 g, 10 mmol) was added. After the addition the mixture was stirred for a further 3 h and the resulting solution filtered to give *the product* **28** as a pink solid insoluble in any common solvent (5.2 g, 65%), m.p. 86–88 °C (Found: C, 52.1; H, 7.6. (C$_{35}$H$_{62}$P$_2$S$_8$)$_n$ requires C, 52.5; H, 7.8%); ν_{max} /cm^{-1} 1732, 1156, 1047, 972 and 730.

7. Wittig reaction of 27 with aldehydes

a. 4,10-bis(Phenylmethylene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane **29**

A solution of tri-n-butylphosphoniodithioformate (9.5 g, 34 mmol), norbornadiene (1.58 g, 17 mmol) and benzaldehyde (3.6 g, 34 mmol) in dry dichloromethane (200 ml) was stirred at RT for 24 h. The resulting white solid was filtered off and washed with ether to give a mixture of the *E*- and *Z*- isomers of the *title compound* **29** (5.15 g, 71%) as colourless crystals, m.p. 214–216 °C (Found: C, 65.3; H, 4.5. C$_{23}$H$_{20}$S$_4$ requires C, 65.1; H, 4.7%); ν_{max} /cm^{-1} 1580, 1561, 1488, 1443, 1315, 938, 754 and 692; δ_H 7.4–7.25 (8 H, m), 7.18 (2 H, m), 6.53 (2 H, s), 4.05 and 3.77, and 4.03 and 3.74 (2 H, AB pattern for E and Z isomers, J 8), 2.52 (2 H, m) and

1.99 (2 H, m); δ_C see Table 1; *m/z* 424 (M$^+$, 75%), 256 (3), 218 (12), 192 (95), 189 (24), 166 (20), 147 (18), 134 (100) and 92 (72).

b. 4,10-bis(Ethylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane **30**

A solution of tri-n-butylphosphoniodithioformate (5.0 g, 18 mmol), norbornadiene (0.83 g, 9 mmol) and acetaldehyde (0.80 g, 18 mmol) in dry dichloromethane (25 ml) was stirred at RT for 24 h. The solution was evaporated and the residual orange oil was purified by flash-column chromatography (SiO$_2$, CH$_2$Cl$_2$-light petroleum, 1:4) yielding a mixture of the *E*- and *Z*- isomers of the *title compound* **30** (2.01 g, 75%) as colourless crystals, m.p. 85–91 °C (Found: M$^+$, 300.0152. C$_{13}$H$_{16}$S$_4$ requires *M*, 300.0135); ν_{max} /cm^{-1} 1630, 1403, 1302, 1226, 1142, 1090, 1000, 965, 900 and 803; δ_H 5.43 (2 H, q, *J* 7), 3.83 and 3.73 (4 H, AB pattern, *J* 8), 2.40 (2 H, m) 1.88 (2 H, s) and 1.71 (6 H, d, *J* 7); δ_C see Table 1; *m/z* 300 (M$^+$, 65%), 228 (6), 195 (12), 189 (25), 130 (90), 92 (65) and 84 (100).

c. 4,10-bis(2-Methylpropylidene)-3,5,9,11-tetrathiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridecane **31**

The above procedure was followed using isobutyraldehyde in place of acetaldehyde. The solution was evaporated and the residual orange oil was purified by flash-column chromatography (SiO$_2$, CH$_2$Cl$_2$-light petroleum, 1:4) yielding a mixture of the *E*- and *Z*- isomers of the *title compound* **31** (0.80 g, 31%) as colourless crystals, m.p. 117–123 °C (Found: C, 57.7; H, 6.9. C$_{17}$H$_{24}$S$_4$ requires C, 57.3; H, 6.8%); ν_{max} /cm^{-1} 1594, 1313, 1162, 1096, 950, 923 and 811; δ_H 5.32 (2 H, d, *J* 9), 3.90 and 3.68 (4 H, AB pattern, *J* 8), 2.45 (4 H, m), 1.94 (2 H, s), 1.00 (6 H, d, *J* 7) and 0.93 (6 H, d, *J* 7); δ_C see Table 1; *m/z* 356 (M$^+$, 8%), 341 (19), 199 (100), 143 (9), 127 (83) and 109 (16).

Acknowledgements

References and Notes

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