Organic Heterocyclothiazenes. Part 16.[1] Reactions of Trithiadiazepyne with Cyclopentadienones. Some Stable Norbornadienones

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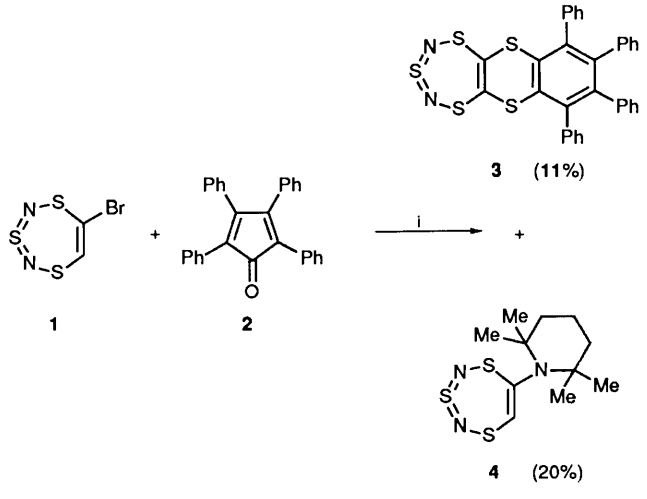
Trithiadiazepyne reacts with 2,5-dimethyl-**11a** and 2,5-diethyl-3,4-diphenylcyclopentadienone **11b** in hot acetonitrile to give the initial Diels–Alder cycloadducts, **12a** and **12b**, which are remarkably stable norbornadienones. It reacts similarly with 2-methyl-3,4,5-triphenylcyclopentadienone **15** in cold acetonitrile to give the less stable carbonyl-bridged adduct **28**. These initial cycloadducts readily lose carbon monoxide when heated to give the aromatic benzotrithiadiazepines, **13** and **29**. In the reaction of trithiadiazepyne with phencyclone **8** the decarbonylated product **9** is the first to be isolated. With tetracyclone **2**, and with the methyltriphenyl analogue **15** in hot acetonitrile, two molecules of the aryne are involved and more extensive reactions result in formation of the dithiins, **3** and **16**, respectively. Stronger heating of the benzotrithiadiazepines induces a molecular arrangement with loss of nitrogen to give benzo-1,2,3-trithioles, **10**, **14a,b** and **17**. A reaction sequence is proposed (Scheme 6) to explain the formation of all of these products.

In the two preceding Parts of this series we described the generation[2] of 6,7-didehydrotrithiadiazepine (trithiadiazepyne) from 6-bromotrithiadiazepine **1** and its reactions with nucleophiles,[2] conjugated dienes,[2] and diazoalkanes.[1] We now describe its reactions with cyclopentadienones and some novel chemistry of the resulting cycloadducts.

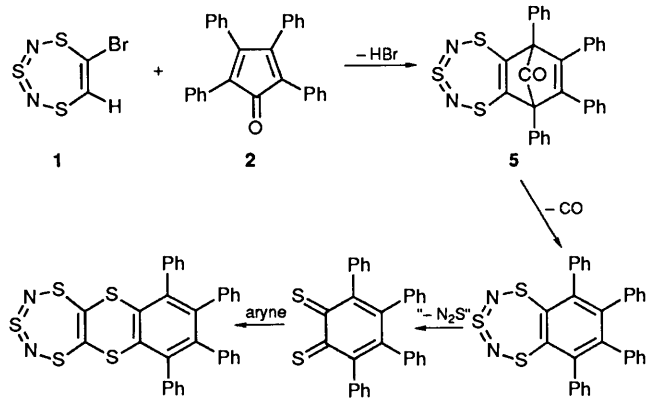
Reactions of Trithiadiazepine with Cyclopentadienones.—In keeping with its relatively high stability, trithiadiazepyne is not intercepted by dienes whose Diels–Alder reactivity is diminished for steric or electronic reasons. Even 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) **2**, normally an excellent trap for arynes, did not react with trithiadiazepyne generated in methanol. However in tetrahydrofuran (THF), with 2,2,6,6-tetramethylpiperidine as base, it did react with the hetaryne to give the dithiin **3** and the amine **4**, the product of addition of the highly hindered base to the aryne (Scheme 1).



1 2

Scheme 1 *Reagents*: i, 2,2,6,6-Tetramethylpiperidine, THF, 20 °C

The dithiin **3** is an unusual and unexpected product in which the aryne appears to have been incorporated twice, once intact and once with the loss of N_2S. A possible pathway for its formation is shown in Scheme 2. Normal aryne cycloaddition would give the carbonyl-bridged intermediate **5** which would readily extrude carbon monoxide to form 6,7,8,9-tetraphenylbenzotrithiadiazepine **6**. If this were unstable, unlike the parent benzotrithiadiazepine,[3] and lost the elements of N_2S to give the *o*-dithioquinone **7**, or its dithiete valence tautomer,[4] another cycloaddition of the aryne to this would give the observed dithiin **3**. Possibly steric compression between the four buttressed phenyl groups and the *peri* related sulphur atoms in the benzotrithiadiazepine **6** could destabilise it sufficiently to cause disruption of the heterocyclic ring. It was decided to explore this possibility further by treating the aryne with other cyclopentadienones with differing steric requirements, starting with phencyclone **8**. Refluxing acetonitrile was found to be a good medium for the formation and interception of the aryne with this diene.

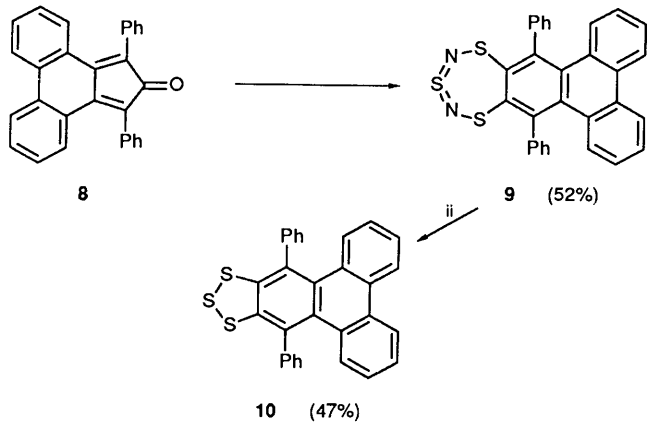


1 2 5 3 7 6

Scheme 2

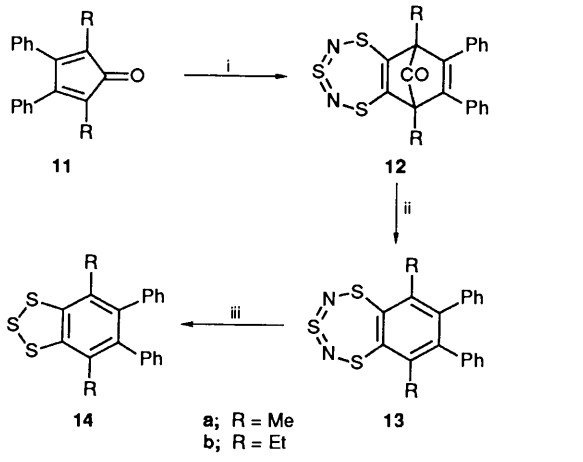
The reaction was rapid (20 min) and a reasonable yield of the benzotrithiadiazepine **9** was now isolated (Scheme 3), thus providing good support for the first two steps of the above mechanism (Scheme 2). Steric compression between the phenyl rings is possibly less in **9** than **6**, thus allowing the isolation of the former. Evidently the aryne does not react with trithiadiazepine **9** to give a dithiin and a control experiment showed that **9** was not decomposed by the aryne. On brief heating at its melting point (220 °C), compound **9** decomposed with loss of nitrogen to give the trithiole **10**, with all the sulphur atoms retained.

We then turned to 2,5-dimethyl-3,4-diphenylcyclopentadi-



Scheme 3 *Reagents:* i, **1**, $EtNPr^i_2$, MeCN, 82 °C; ii, 220 °C, 30 s

enone **11a** as a more reactive diene in the hope that we might be able to isolate an earlier intermediate in the reaction sequence. The cyclopentadienone[5] exists as a dimer but equilibrates with the monomer **11a** when heated. To our surprise, generation and interception of the aryne now gave the proposed initial cycloadduct **12a** (56%) with the carbon monoxide bridge still retained (Scheme 4). This is a stable



Scheme 4 *Reagents:* i, **1**, $EtNPr^i_2$, MeCN, 82 °C; ii, 140 °C, 15 min; iii, 210 °C, 30 s

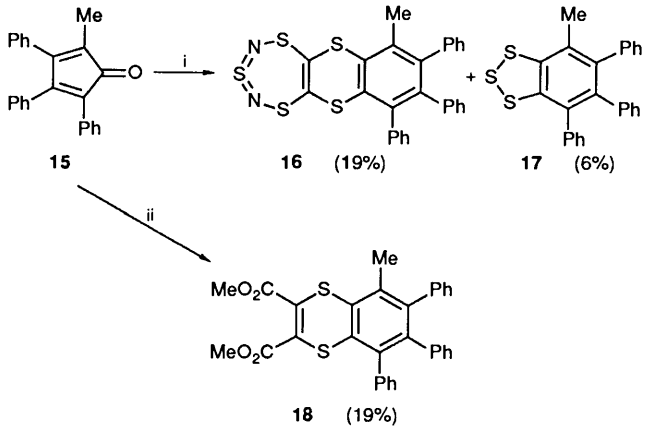
crystalline compound which when heated at 140 °C in the solid state extruded carbon monoxide to give the dimethyldiphenylbenzotrithiadiazepine **13a** almost quantitatively. On stronger heating, at 210 °C, this in turn lost nitrogen to give the trithiole **14a** (44%). The yield of this trithiole could be increased somewhat (to 60%) by carrying out the thermolysis in the presence of sulphur, though the product obtained in this way was difficult to purify from the higher polysulphides formed; benzotrithioles are known to equilibrate with benzopentathiepines on being heated with sulphur.[6]

The hetaryne was also generated from 6-bromotrithiadiazepine **1** and Hünig's base in refluxing acetonitrile in the presence of 2,5-diethyl-3,4-diphenylcyclopentadienone **11b**[7] and again gave the stable carbon monoxide bridge cycloadduct **12b** in better yield (65%). On neat pyrolysis at 200 °C for 30 s this adduct lost both carbon monoxide and nitrogen to give the corresponding trithiole **14b** (54%) directly.

The ready formation of trithioles in these reactions suggest that the dithiin **3** isolated from the tetracyclone reaction (Schemes 1 and 2) could have been derived from a reaction between the aryne and the trithiole rather than the dithioquinone **7**. However generation of the aryne in the presence of the trithioles **10** and **14** in THF or refluxing acetonitrile gave no dithiins; these sterically protected trithioles are thermally stable and are inert under the aryne-forming conditions.

To probe the formation of the dithiin **3** and the ease with which the tetraphenylbenzotrithiadiazepine **6** appears to lose nitrogen, we turned to 2-methyl-3,4,5-triphenylcyclopentadienone **15**[8] of intermediate reactivity between the tetraphenyl and dimethyldiphenyl analogues. In refluxing acetonitrile this cyclopentadienone **15** gave both a dithiin **16** and a trithiole **17**, though in low yields (Scheme 5). The intermediate benzotrithiadiazepine was not detected and again the trithiole **17** was shown not to react with the aryne, under the same conditions, to give the dithiin **16**. When the aryne trapping reaction with methyltriphenylcyclopentadienone **15** was run in the presence of sulphur, the yield of trithiole was much increased (to 38%) and that of the dithiin **16** much reduced (to 2%). When the same reaction was run in the presence of dimethyl acetylenedicarboxylate the new dithiin **18** was formed to the exclusion of products **16** and **17**. The hetaryne and the acetylenic ester are presumably undergoing the same type of cycloaddition, though the less reactive ester is present in much higher concentration.

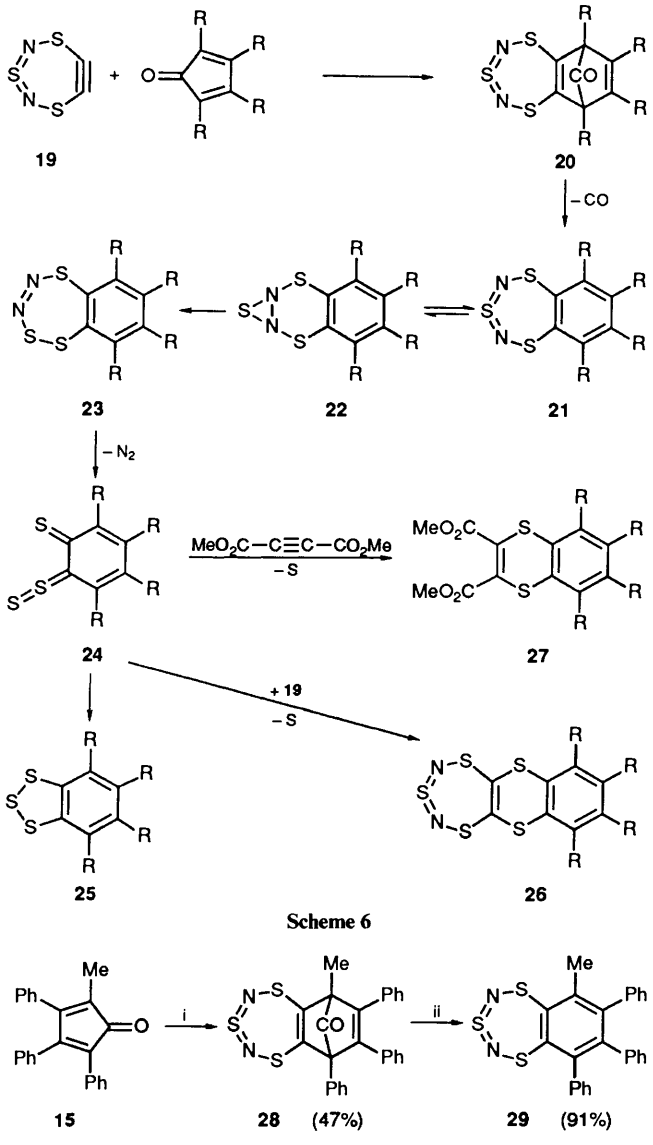
Overall Reaction Scheme.—We consider that the simplest reaction scheme that will explain all the above results is that shown in Scheme 6. Examples of compounds **20**, **21**, **25**, **26** and



Scheme 5 *Reagents:* i, **1**, $EtNPr^i_2$, MeCN, 82 °C; ii, as for i, plus $MeO_2C{-}C{\equiv}C{-}CO_2Me$.

27 have all been isolated. Contraction of the seven-membered ring in **21** with N–N bond formation to give **22** could be facilitated by the steric compression mentioned earlier. This could be followed by rearrangement to the isomeric trithiadiazepine **23** (possibly *via* an *N*-sulphide) which could extrude nitrogen to form the reactive thiocarbonyl *S*-sulphide ('thiosulphine') **24**;[9] this could then close to the much more stable trithiole **25** or be intercepted by aryne or alkyne to give the dithiin **26** or **27**, with accompanying loss of sulphur.

We saw above (Scheme 5) that reaction of the hetaryne **19** and methyltriphenylcyclopentadienone **15** in boiling acetonitrile gave the dithiin **16** and the trithiole **17** only. When this reaction is run in acetonitrile at room temperature, the hetaryne being generated for this purpose from the bromo compound **1** and silver acetate, the initial carbon monoxide bridged cycloadduct **28** could be isolated in reasonable yield (47%). This product is stable in the solid state and its structure was confirmed by X-ray crystallography.[10] It can be readily aromatised in high yield to give 6-methyl-7,8,9-triphenylbenzotrithiadiazepine **29** by refluxing in acetonitrile for 8 min or dichloromethane for 5 h (Scheme 7). This ready loss of carbon monoxide explains why the initial adduct **28** was not observed from interception of trithiadiazepyne **19** in refluxing acetonitrile. However the stability of the benzotrithiadiazepine **29** in refluxing acetonitrile was initially surprising in view of

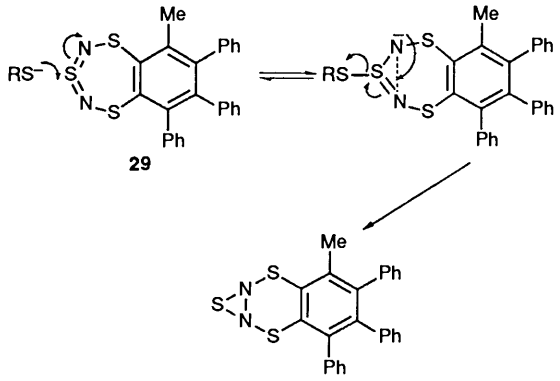


Scheme 6

Scheme 7 *Reagents:* i, **1**, AgOAc, MeCN, 20 °C; ii, MeCN, 82 °C, 8 min

the decomposition products **16** and **17** obtained when it had been generated in boiling acetonitrile (Scheme 5). A pure solution of compound **29** in refluxing acetonitrile is stable, so something is required to initiate its decomposition. This was confirmed by subjecting **29** to the aryne-generating conditions (bromo compound **1** and Hünig's base in boiling acetonitrile) when it was smoothly converted into the dithiin **16** (25%) and trithiole **17** (57%); the yields are higher than in Scheme 5 since prior formation of benzo compound **29** from the aryne has been by-passed.

Thus the decomposition of the benzo compound **29** could have been initiated by the aryne itself, possibly by cycloaddition to the sulphur diimide unit of **29**; but it could also have been initiated by any strongly thiophilic nucleophile generated in the medium, such as sulphur plus Hünig's base, as the following experiments show. When compound **29** was heated in acetonitrile with sulphur or with Hünig's base no decomposition occurred, but when heated with a mixture of the two it gave the trithiole **17** in high yield (76%). The activation of elementary sulphur by tertiary bases is well known;[11] presumably Hünig's base opens the S_8 cage structure to form an equilibrium amount of a highly thiophilic polysulphide anion. This could reversibly attack S(3) of compound **29**, as shown in Scheme 8, catalysing its ring contraction and rearrangement[12] to an intermediate of type **22** in Scheme 6.



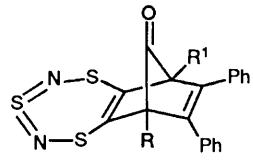
Scheme 8

If this proposal is correct other thiophilic nucleophiles should decompose the benzotrithiadiazepine **29**, and this was demonstrated with potassium thiocyanate. Five equivalents of KSCN in refluxing acetonitrile for 2.5 h converted compound **29** into the trithiole **17** in high yield (81%); 1 equiv. gave the trithiole **17** in 87% yield in 12 h. These high yields, and the absence of elementary sulphur (TLC monitoring), provide good support for the sulphur walk mechanism, **22** ⟶ **23**, of Scheme 6. The ring contraction step, **21** ⟶ **22** of Scheme 6 may, in general, require initiation by some such attack on the heterocyclic ring.

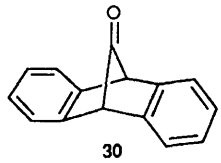
Thermolysis of methyltriphenylbenzotrithiadiazepine **29** in the solid state at a higher temperature, 220 °C for 30 s, gave the trithiole **17** (57%) in agreement with the earlier results (Schemes 3 and 4). Thus, starting from methyltriphenylcyclopentadienone **15** we have been able, under appropriate conditions, to isolate and characterise all four of the stable compounds proposed in Scheme 6 (*i.e.* **20**, **21**, **25** and **26**).

Stable Norbornadienones.—One remarkable feature of the above results is the stability of the three hetaryne–cyclopentadienone adducts, **12a**, **12b** and **28**, which were readily isolated. These adducts were characterised by a carbonyl stretch in the IR region near 1780 cm^{-1} (*cf.* 1790–1795 cm^{-1} for norbornadienone and its benzo derivatives in frozen matrices) and an NS stretch at 1160 cm^{-1}. Weak molecular ions are observed in the mass spectra, with fragments for the loss of 28 (CO) followed by 46 (NS) or 28 (N_2). Accurate microanalytical data were obtained for the more stable compounds **12a** and **b**, but not for the less stable methyltriphenyl compound **28**, which was characterised by X-ray crystallography.[10]

Such norbornadienones are very rare because of their great tendency to extrude carbon monoxide to form an aromatic species, usually well below room temperature. In spite of many attempts to prepare them, only very few authentic norbornadienones have been isolated,[13] such as the dibenzo derivative **30** which rapidly decarbonylates to anthracene in boiling benzene.[14] In contrast with our compounds, the analogous monobenzo derivative **31** is not stable at room temperature.



12a; R = R^1 = Me
12b; R = R^1 = Et
28; R = Me, R^1 = Ph



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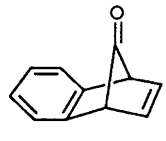

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The greater stability of compounds **12a**, **12b** and **28** presumably results from a combination of steric effects of the carbocyclic ring substituents, and differences in bond lengths and angles associated with the larger heterocyclic ring, together with electronic effects. It has been shown[15] that aromatic nitro groups in **30** increase the rate of decarbonylation, and our electron-rich heterocyclic ring certainly has the opposite effect. However, as we have seen above, the relatively modest change of structure of the methyltriphenyl adduct **28** to the tetraphenyl adduct **5** and the analogous phenanthrenodiphenyl adduct gave compounds which decarbonylated too fast to be isolated at room temperature.

Experimental

For general points see earlier Parts of this series.

7,8,9,10-*Tetraphenyl*[1,4]*benzodithiin*[2,3-*f*]-1,3λ^{4}δ^2,5,2,4-*trithiadiazepine* **3**.—6-Bromotrithiadiazepine **1** (100 mg, 0.44 mmol) and tetracyclone **2** (168 mg, 0.44 mmol) in THF (20 ml) were treated with 2,2,6,6-tetramethylpiperidine (60 mg, 0.47 mmol). The mixture was stirred at room temperature for 10 h after which the solvent was removed under reduced pressure and the residue chromatographed on silica. Light petroleum eluted 6-(2,2,6,6-tetramethylpiperidino)trithiadiazepine **4** (25 mg, 20%) identical with that previously described.[2] Light petroleum–dichloromethane (75:25) eluted the *title compound* (28 mg, 11%) as a yellow solid, m.p. 276–277 °C (from light petroleum–dichloromethane) (Found: C, 64.8; H, 3.6; N, 4.6. $C_{23}H_{20}N_2S_5$ requires C, 64.9; H, 3.4; N, 4.7%); λ_{max}(EtOH)/nm 248 (log ε 3.80) and 358 (3.66); $\nu_{max}(CCl_4)/cm^{-1}$ 1145 vs; δ_H(250 MHz; $CDCl_3$) 6.60–7.30 (m); *m/z* (240 °C) 592 (M^+, 100%), 546 (M^+ − NS, 44) and 514 (M^+ − NS_2, 35).

6,15-*Diphenyltriphenyleno*[2,3-*f*]-1,3λ^{4}δ^2,5,2,4-*trithiadiazepine* **9**.—6-Bromotrithiadiazepine (320 mg, 1.40 mmol) and phencyclone **8** (198) (570 mg, 1.5 mmol) in acetonitrile (30 ml) were treated with Hünig's base (300 mg, 2.3 mmol) and refluxed for 40 min. The solvent was then removed under reduced pressure and the residue chromatographed on silica. Light petroleum–dichloromethane (80:20) eluted the *title compound* (393 mg, 56%), m.p. 220–221 °C (decomp.) (from light petroleum–dichloromethane) (Found: C, 71.7; H, 3.4; N, 5.4. $C_{30}H_{18}N_2S_3$ requires C, 71.7; H, 3.6; N, 5.6); λ_{max}(EtOH)/nm 348 (log ε 3.90); $\nu_{max}(CCl_4)/cm^{-1}$ 1265s; δ_H(250 MHz; $CDCl_3$) 7.4 (2 H, t, *J*/Hz 9 and 8), 7.48 (10 H, m, ArH), 7.6 (2 H, t, *J*/Hz 9 and 8), 7.93 (2 H, d, *J*/Hz 8) and 8.7 (2 H, d, *J*/Hz 8); *m/z* (220 °C) 502 (M^+, 9%), 474 (M^+ − N_2, 9) and 456 (M^+ − NS, 74).

4,13-*Diphenyltriphenyleno*-1,2,3-*trithiole* **10**.—6,15-Diphenyltriphenyleno[2,3-*f*]-trithiadiazepine **9** (100 mg, 0.20 mmol) was heated neat at 220 °C for 30 s. The melt was then allowed to cool and chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted the *title compound* (45 mg, 47%) as a yellow solid, m.p. 268–269 °C (from light petroleum–dichloromethane) (Found: C, 75.9; H, 3.7. $C_{30}H_{18}S_3$ requires C, 75.95; H, 3.8%); λ_{max}(EtOH)/nm 272 (log ε 3.94) and 325 (3.81); $\nu_{max}(CCl_4)/cm^{-1}$ 1495s, 1442w and 1390s; δ_H(250 MHz; $CDCl_3$) 7.01 (2 H, t), 7.36 (2 H, t), 7.58 (2 H, d), 8.40 (2 H, d) and 7.40–7.50 (10 H, m, 2 × Ph); *m/z* (220 °C) 474 (M^+, 100%) and 442 (M^+ − S, 0.2).

6,9-*Dimethyl*-7,8-*diphenyl*-6,9-*methano*-1,3λ^{4}δ^2,5,2,4-*benzotrithiadiazepin*-10-*one* **12a**.—A solution of 2,5-dimethyl-3,5-diphenylcyclopentadienone dimer (160 mg, 0.31 mmol) in acetonitrile was refluxed for 0.5 h. 6-Bromotrithiadiazepine (50 mg, 0.22 mmol) in acetonitrile (3 ml) was added to the refluxing solution followed by Hünig's base (67 mg, 0.52 mmol). The reaction was refluxed for 0.5 h and then allowed to cool. The solvent was removed under reduced pressure and the residue chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted the *title compound* (51 mg, 56%) as a pale yellow solid, m.p. 188–189 °C (decomp.) (Found: C, 61.5; H, 3.9; N, 6.8. $C_{21}H_{16}N_2OS_3$ requires C, 61.8; H, 3.9; N, 6.9%); λ_{max}(EtOH)/nm 335 (log ε 3.45); $\nu_{max}(CCl_4)/cm^{-1}$ 1786s and 1160s; δ_H(250 MHz; $CDCl_3$): 1.80 (6 H, s, 2 × Me), 7.0–7.10 (4 H, m) and 7.20–7.31 (6 H, m); δ_C(62.9 MHz; $CDCl_3$) 9.6, 64.6, 127.8, 128.2, 129.3, 133.4, 145.7, 148.3 and 184.2; *m/z* (190 °C) 408 (M^+, 0.6%), 380 (M^+ − CO, 12), 352 (M^+ − CO, $-N_2$, 6) and 334 (M^+ − CO, −NS, 100).

6,9-*Dimethyl*-7,8-*diphenyl*-1,3λ^{4}δ^2,5,2,4-*benzotrithiadiazepine* **13a**.—6,9-Dimethyl-7,8-diphenyl-6,9-methanobenzotrithiadiazepinone **12a** (50 mg, 0.12 mmol) was heated neat at 140 °C for 15 min. Crystallisation from light petroleum–dichloromethane gave the *title compound* (44 mg, 95%), m.p. 195–196 °C (Found: C, 63.1; H, 4.5; N, 7.1. $C_{20}H_{16}N_2S_3$ requires C, 63.2; H, 4.2; N, 7.4%); λ_{max}(EtOH)/nm 293 (log ε 4.07) and 358 (3.72); $\nu_{max}(CCl_4)/cm^{-1}$ 1181s; δ_H(250 MHz; $CDCl_3$) 2.0 (6 H, s, 2 × Me), 6.9 (4 H, m) and 7.1 (6 H, m); *m/z* (190 °C) 380 (M^+, 17%), 352 (M^+ − N_2, 9) and 334 (M^+ − NS, 100).

4,7-*Dimethyl*-5,6-*diphenyl*-1,2,3-*benzotrithiole* **14a**.—6,9-Dimethyl-7,8-diphenylbenzotrithiadiazepine **13a** (50 mg, 0.13 mmol) was heated at 210 °C for 30 s. The product was then chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted the *title compound* (20 mg, 44%) as a yellow solid, m.p. 218–220 °C (from light petroleum–dichloromethane) (Found: C, 68.2; H, 4.4. $C_{20}H_{16}S_3$ requires C, 68.2; H, 4.6%); λ_{max}(EtOH)/nm 275 (log ε 3.81); $\nu_{max}(CCl_4)/cm^{-1}$ 1444s, 1381s and 1073w; δ_H(250 MHz; $CDCl_3$) 2.10 (6 H, s, 2 × Me), 6.78–7.00 (4 H, m) and 7.00–7.19 (6 H, m); *m/z* (160 °C) 352 (M^+, 100%) and 320 (M^+ − S, 4).

6,9-*Diethyl*-7,8-*diphenyl*-6,9-*methano*-1,3λ^{4}δ^2,5,2,4-*benzotrithiadiazepin*-10-*one* **12b**.—6-Bromotrithiadiazepine (100 mg, 0.44 mmol) and 2,5-diethyl-3,4-diphenylcyclopentadienone **11b** (126 mg, 0.48 mmol) in refluxing acetonitrile (15 ml) were treated with Hünig's base (100 mg, 0.78 mmol). The mixture was refluxed for 20 min after which it was cooled, and the solvent removed under reduced pressure. Chromatography on silica of the residue with light petroleum–dichloromethane as eluent gave the *title compound* (124 mg, 65%), m.p. 133–135 °C (decomp.) (from light petroleum–dichloromethane) (Found: C, 63.3; H, 4.6; N, 6.4. $C_{23}H_{20}N_2OS_3$ requires C, 63.3; H, 4.6; N, 6.4%); λ_{max}(EtOH)/nm 250 (log ε 3.82) and 358 (3.38); $\nu_{max}(CCl_4)/cm^{-1}$ 1781vs and 1160w; δ_H(250 MHz; $CDCl_3$) 1.13 (6 H, t, 2 × Me), 2.30 (4 H, q, 2 × CH_2), 7.12 (4 H, m) and 7.24 (6 H, m); *m/z* (150 °C) 436 (M^+, 6%), 408 (M^+ − CO, 26), 380 (M^+ − CO, $-N_2$, 25) and 362 (M^+ − 28, − NS, 100%).

4,7-*Diethyl*-5,6-*diphenyl*-1,2,3-*benzotrithiole* **14b**.—6,9-Diethyl-7,8-diphenylmethanobenzotrithiadiazepin-10-one **12b** (90 mg, 0.21 mmol) was heated neat at 200 °C for 30 s. The product was then chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted the *title compound* (43 mg, 54%) as a yellow solid, m.p. 166–168 °C (from light petroleum–dichloromethane) (Found: C, 69.3; H, 5.35. $C_{22}H_{20}S_3$ requires C, 69.5; H, 5.3%); λ_{max}(EtOH)/nm 280 (log ε 3.84) and 325 (3.73); $\nu_{max}(CCl_4)/cm^{-1}$ 1494vs and 1392 vs; δ_H(250 MHz; $CDCl_3$) 0.92 (6 H, t, 2 × Me), 2.43 (4 H, q, 2 × CH_2), 6.90 (4 H, m) and 7.11 (6 H, m); *m/z* (160 °C): 380 (M^+, 100%) and 348 (M^+ − S, 4).

7-*Methyl*-8,9,10-*triphenyl*[1,4]*benzodithiin*[2,3-*f*]-1,3λ^{4}δ^2,5,2,4-*trithiadiazepine* **16**.—6-Bromotrithiadiazepine (115 mg,

0.5 mmol) and 2-methyl-3,4,5-triphenylcyclopentadienone **15** (162 mg, 0.50 mmol) in refluxing acetonitrile (20 ml) were treated with Hünig's base (120 mg, 0.93 mmol). After 20 min at reflux the mixture was allowed to cool and the solvent removed under reduced pressure. The residue was chromatographed on silica by dry flash chromatography. Light petroleum–dichloromethane (90:10) eluted 4-*methyl*-5,6,7-*triphenylbenzotrithiole* **17** (14 mg, 6%) as a yellow solid, m.p. 188–190 °C (from light petroleum–dichloromethane) (Found: C, 72.2; H, 4.3. $C_{25}H_{18}S_3$ requires C, 72.5; H, 4.35%); λ_{max}(EtOH)/nm 280 (log ε 3.79); $\nu_{max}(CCl_4)/cm^{-1}$ 1444vs, 1378s and 1074w; δ_H(250 MHz; $CDCl_3$): 2.20 (3 H, s, Me) and 6.68–7.27 (15 H, m, 3 × Ph); *m/z* (180 °C) 414 (M^+, 100%), 382 (M^+ − S, 5) and 350 (M^+ − 2S, 55). This was followed by the *title compound* (50 mg, 19%) as a yellow solid, m.p. 218–219 °C (from light petroleum–dichloromethane) (Found: C, 61.2; H, 3.3; N, 5.25. $C_{27}H_{18}N_2S_5$ requires C, 61.2; H, 3.4; N, 5.3%); λ_{max}(EtOH)/nm 360 (log ε 3.98); $\nu_{max}(CCl_4)/cm^{-1}$ 1145s; δ_H(250 MHz; $CDCl_3$) 2.37 (3 H, s, Me) and 6.62–7.24 (15 H, m, 3 × Ph); *m/z* (180 °C) 530 (M^+, 100%), 484 (M^+ − NS, 42) and 452 (M^+ − NS_2, 46).

4-*Methyl*-5,6,7-*triphenylbenzo*-1,2,3-*trithiole* **17**.—6-Bromotrithiadiazepine (100 mg, 0.44 mmol), 2-methyl-3,4,5-triphenylcyclopentadienone **15** (140 mg, 0.44 mmol) and sulphur (200 mg) were treated with Hünig's base (100 mg, 0.78 mmol) in refluxing acetonitrile (20 ml). After being refluxed for 20 min the mixture was allowed to cool and the solvent was removed under reduced pressure. Chromatography of the residue on silica by dry flash chromatography with light petroleum–dichloromethane (90:10) as eluent gave the title compound (70 mg, 38%) identical with that described above. This was followed by 7-methyl-8,9,10-triphenyl[1,4]benzodithiin[2,3-*f*]-1,3λ^{4}δ^2,5,-2,4-trithiadiazepine **16** (3 mg, 2%) identical with that described above.

Dimethyl 5-*Dimethyl*-6,7,8-*triphenyl*-1,4-*benzodithiin*-2,3-*dicarboxylate* **18**.—6-Bromotrithiadiazepine (30 mg, 0.13 mmol), 2-methyl-3,4,5-triphenylcyclopentadienone **15** (50 mg, 0.16 mmol) and dimethyl acetylenedicarboxylate (50 mg, 0.35 mmol) were treated with Hünig's base (85 mg, 0.66 mmol) in refluxing acetonitrile (10 ml). After 10 min the mixture was allowed to cool, and the solvent removed under reduced pressure. Chromatography of the residue on silica with dichloromethane as the eluent gave the *title compound* (13 mg, 19%) as a yellow solid, m.p. 175–179 °C (from light petroleum–dichloromethane) (Found: C, 71.0; H, 4.7. $C_{31}H_{24}O_4S_2$ requires C, 71.0; H, 4.6%); $\nu_{max}(CCl_4)/cm^{-1}$ 1733vs and 1264vs; δ_H(250 MHz; $CDCl_3$) 2.29 (3 H, s, Me), 3.72 (3 H, s, OMe), 3.85 (3 H, s, OMe) and 6.6–7.2 (15 H, m); *m/z* (150 °C) 524 (M^+, 100%) and 493 (4).

6-*Methyl*-7,8,9-*triphenyl*-6,9-*methano*-1,3λ^{4}δ^2,5,2,4-*benzotrithiadiazepin*-10-*one* **28**.—6-Bromotrithiadiazepine (300 mg, 1.31 mmol) and 2-methyl-3,4,5-triphenylcyclopentadienone **15** (425 mg, 1.32 mmol) in acetonitrile (20 ml) were treated with silver acetate (22 mg, 1.33 mmol). The reaction mixture was stirred at room temperature for 3 h after which the solvent was removed under reduced pressure. The residue was chromatographed by dry flash chromatography on silica. Light petroleum–dichloromethane (75:25) eluted the *title compound* (290 mg, 47%) as a crystalline solid (from light petroleum–dichloromethane) which decomposed when heated (Found: C, 65.5; H, 4.35; N, 5.4. $C_{26}H_{18}N_2OS_3$ requires C, 66.4; H, 3.8; N, 6.0%); microanalysis data were consistently poor; λ_{max} (EtOH)/nm 356 (log ε 3.9); $\nu_{max}(CCl_4)/cm^{-1}$ 1783vs and 1161w; δ_H(250 MHz; $CDCl_3$): 1.8 (3 H, s, Me) and 6.8–7.6 (15 H, m, 3 × Ph); *m/z* (160 °C): 442 (M^+ − CO, 12%), 414 (M^+ −CO, $-N_2$, 3) and 396 (M^+ − CO, −NS, 100).

6-*Methyl*-7,8,9-*triphenyl*-1,3λ^{4}δ^2,5,2,4-*benzotrithiadiazepine* **29**.—6-Methyl-7,8,9-triphenyl-6,9-methanobenzotrithiadiazepineone **28** (50 mg, 0.11 mmol) in dry acetonitrile (10 ml) was refluxed for 8 min. The solvent was removed under reduced pressure to give the *title compound* (43 mg, 91%) as a yellow solid, m.p. 201–202 °C (from light petroleum–dichloromethane) (Found: C, 67.7; H, 3.9; N, 6.3. $C_{25}H_{18}N_2S_3$ requires C, 67.9; H, 4.1; N, 6.3%); λ_{max}(EtOH)/nm 380 (log ε 3.61); $\nu_{max}(CCl_4)/cm^{-1}$ 1178s; δ_H(250 MHz; $CDCl_3$) 2.48 (3 H, s, Me), 6.70–6.90 (5 H, m, Ph) and 7.00–7.30 (10 H, m, 2 × Ph); *m/z* (140 °C) 442 (M^+, 13%), 414 (M^+ − 56, 3) and 396 (M^+ − CO, −NS, 100).

4-*Methyl*-5,6,7-*triphenyl*-1,3λ^{4}δ^2,5,2,4-*benzotrithiole* **17**.—(i) 6-Methyl-7,8,9-triphenylbenzotrithiadiazepine **29** (50 mg, 0.11 mmol) was heated neat at 220 °C for 30 s. The product was chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted the title compound (26 mg, 57%) identical with that described above.

(ii) 6-Methyl-7,8,9-triphenylbenzotrithiadiazepine **29** (80 mg, 0.18 mmol), sulphur (50 mg, 1.56 mmol), and Hünig's base (70 mg, 0.54 mmol) were refluxed in acetonitrile (6 ml) for 6 min. The solvent was then removed under reduced pressure and the residue chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted the title compound (57 mg, 76%) identical with that described above.

(iii) 6-Methyl-7,8,9-triphenylbenzotrithiadiazepine **29** (100 mg, 0.23 mmol) and potassium thiocyanate (112 mg, 1.15 mmol) were refluxed in acetonitrile (15 ml) for 2.5 h. The solvent was then removed under reduced pressure and the residue chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted the title compound (76 mg, 81%) identical with that described.

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