Organic Heterocyclothiazenes. Part 15.[1] Pyrazolotrithiadiazepines and Their Rearrangement to 1,2,3-Dithiazoles

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Treatment of 6-bromotrithiadiazepine **1** with Hünig's base in the presence of diphenyldiazomethane **2a** gives the hetaryne cycloadduct **3a**. Neat thermolysis of this at 210 °C results in very rapid loss of N_2 and 'HNS' in a deep-seated rearrangement to give the new indeno-1,2,3-dithiazole ring system **4a**. A mechanism proposed for this rearrangement (Schemes 2 and 5) is supported by the isolation of a key intermediate **12** when the cycloadduct **3a** is thermolysed in dilute solution at lower temperatures. The intermediate **12** dimerises reversibly to give **13**, possibly by a 8-electron ene-type reaction. Other diaryldiazomethanes **2** give analogous hetaryne cycloadducts **3** (70–80%) which rearrange similarly when heated to give more complex 1,2,3-dithiazoles **4** (20–40%) (Scheme 1).

We have described the generation of trithiadiazepyne and its reactions with nucleophiles and dienes.[1] We now show that it can also be intercepted by diaryldiazomethanes, and the resulting 1,3-dipolar cycloadducts undergo a deep-seated molecular rearrangement when heated.

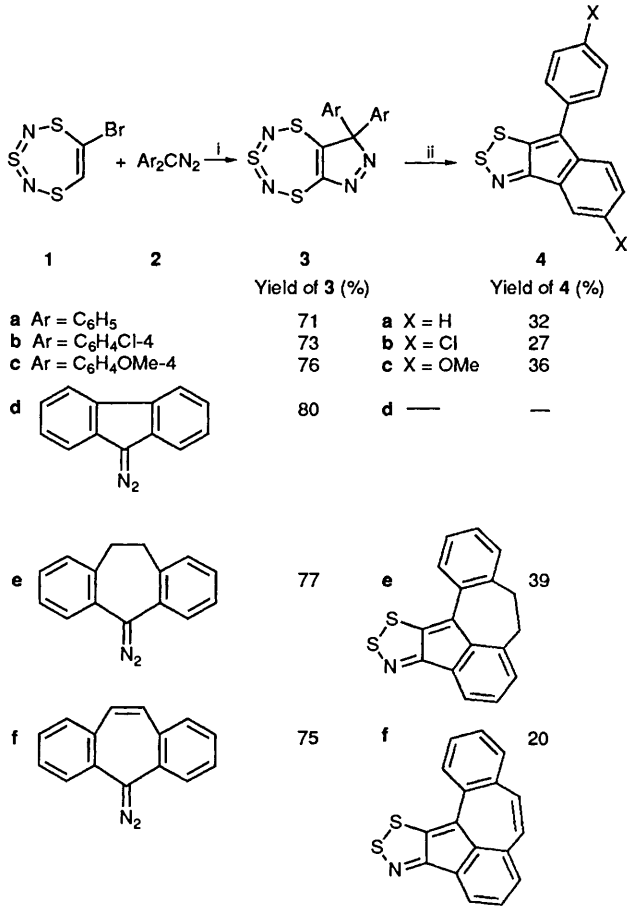
When 6-bromotrithiadiazepine **1** and the diazo compounds **2** were treated with *N*-ethyldi-isopropylamine (Hünig's base) in methanol at room temperature the expected cycloadducts **3** were formed rapidly in high yield, as stable, colourless, crystalline compounds (Scheme 1). Their mass spectra did not show molecular ions because of the ready loss of N_2 (28) followed by NS (46). Their IR absorptions near 1165 cm^{-1} and long wavelength UV absorptions at about 335 nm are typical of trithiadiazepines; their ^{13}C NMR spectra and microanalyses also agreed with the proposed structures **3**. 2-Diazopropane gave a similar cycloadduct in lower yield (48%).

Solid State Thermolysis of the Pyrazolotrithiadiazepines **3**.— Since the adducts **3** are cyclic azo compounds they could, on pyrolysis, lose nitrogen to form other fused trithiadiazepine derivatives. We assumed that in compound **3a**, for example, either a phenyl group would migrate to give a more stable pyrazole or nitrogen would be lost, followed by collapse to a cyclopropane or an analogue of fluorene. Compound **3a** decomposed above its m.p. to form a new deep red product; gas evolution was very rapid and vigorous at 210 °C. The mass spectrum of the product showed a strong peak at *m/z* 267 and a weak peak for loss of 64(S_2). The IR showed a stretch at 1120 cm^{-1} (NS) and the UV spectrum was too complex for a simple trithiadiazepine ring, showing peaks at 520, 350, 315, 280 and 255 nm. ^{13}C Spectroscopy indicated one monosubstituted and one disubstituted benzene ring. Microanalysis indicated the formula $C_{15}H_9NS_2$ consistent with the molecular ion in the mass spectrum. We deduced two possible structures, **4a** and **5**, but could not distinguish between them on the evidence available.

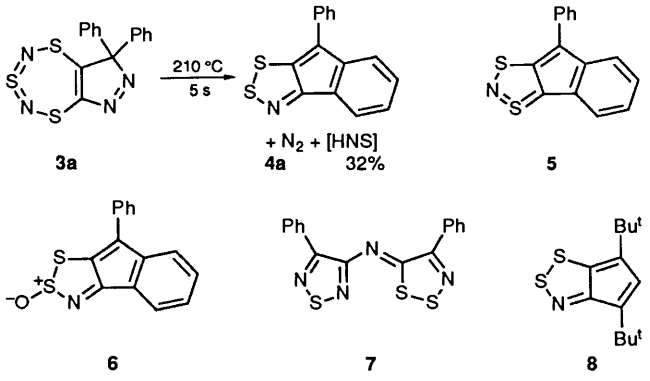
Mechanistically, the SNS isomer **5** seemed the more likely structure although the absence of a fragment for loss of 46(NS) in the mass spectrum and the presence of a fragment for loss of 64(S_2) suggested the NSS isomer **4a**. Clearly the trithiadiazepine ring, which is normally so thermally stable, has not survived the extrusion of nitrogen from the 3*H*-pyrazole ring and the resulting molecular rearrangement; the elements of HNS have also been extruded. Some sulphur was formed in the reaction and since hydrogen sulphide could be smelt the HNS fragment may appear as nitrogen, hydrogen sulphide and sulphur.

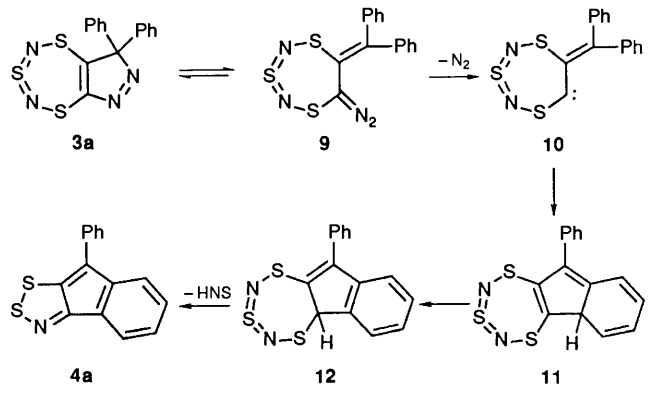
Crystals of the red pyrolysis product suitable for X-ray crystallography could not be obtained. We have previously found that oxidation to an *S*-oxide may give a more crystalline derivative, and indeed this product reacted smoothly with N_2O_4 in dichloromethane to give a crystalline *S*-oxide (74%) for which an X-ray diffraction analysis proved structure **6**.[2] This strongly suggested that the coloured rearrangement product was the SSN isomer **4a**.

The site of oxidation of **4a** was consistent with the earlier observation that the bicyclic imine **7** was oxidised by N_2O_4 exclusively on S(2) of the dithiazole ring;[3] S(1) of this ring is less



Scheme 1 *Reagents and conditions:* i, Et NPr^i_2, MeOH, 20 °C, 20 min; ii, 210 °C, 5 s.





Scheme 2

nucleophilic than S(2) because of electron delocalisation onto the exocyclic imine nitrogen. Similarly, for the dithiazole **4a** S(1) will be less nucleophilic than S(2) owing to its electron release onto the imine nitrogen around the 5,5-fused ring system.

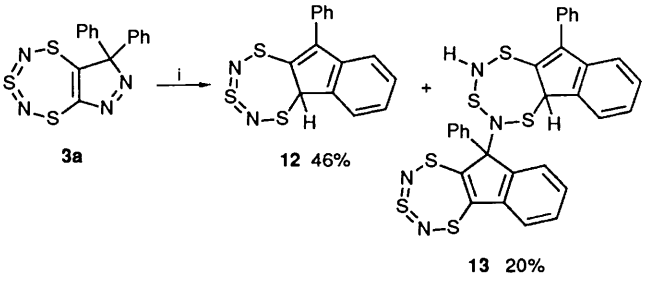
The other diaryldiazomethane cycloadducts were thermolysed in the hope of producing further derivatives of the unusual compound **4a**; the aryl substituents should influence the ease with which nitrogen is extruded, and a more crystalline derivative suitable for X-ray crystallography might be obtained.

The pyrazolotrithiadiazepines **3b**, **3c**, **3e** and **3f** gave analogous deeply coloured rearrangement products on neat thermolysis at 210 °C for *ca.* 5 s (Scheme 1). The diazofluorene adduct **3d** decomposed violently but the analogous coloured product was not formed and no other compounds were isolated; presumably the greater strain that would be present in the product prevented formation of the new carbon–carbon bond. The cycloheptadiene adduct **3e**, where the aryl rings have a greater degree of flexibility, gave the expected product **4e** and a small amount of the dehydrogenated derivative **4f**. At some stage the bismethylene bridge of **4e** must be dehydrogenated, possibly by a carbene or radical species generated in the reaction. Since the cyclic azo derivative **3f** rearranges to compound **4f** the dehydrogenation step could have occurred in the starting material **3e** before rearrangement.

Compounds **3e** and **3f** lose nitrogen more violently than the diphenyl compound **3a**. This probably results from the greater degree of coplanarity of the aryl rings in **3e** and **3f** and their orthogonality to the carbon–nitrogen bond being broken on opening of the azo ring. Fortunately the cycloheptadiene product **4e** gave crystals suitable for X-ray crystallography which again showed the order of heteroatoms to be SSN.[2] Since all the products have similar spectroscopic properties they undoubtedly have the same ring structure. This benzo 5,5-fused ring system is a new, potentially 14 π aromatic structure; one example of the 5,5-fused system, the violet oil **8**, has been reported.[4]

A possible mechanism for this molecular rearrangement is shown in Scheme 2. The cyclic azo compound **3a** could well undergo reversible electrocyclic ring opening to the diazo compound **9**, which is stabilised by extensive conjugation.[5] The diazo intermediate **9** could then lose nitrogen to form a carbene **10**, also stabilised by delocalisation, which would cyclise onto one of the phenyl rings. Intermediate **11** has a stable trithiadiazepine ring which could be disrupted by a 1,5 hydrogen shift to give an aromatic benzene ring and the more reactive array of heteroatoms in **12**. Exactly how the heteroatoms rearrange and extrude HNS is more speculative and is discussed later.

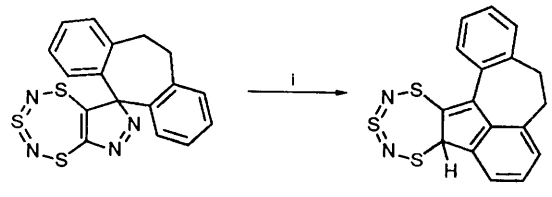
Solution Thermolysis of the Pyrazolotrithiadiazepines **3**.—In the neat, high temperature pyrolysis conditions above no intermediates were isolated. A careful study of the thermolyses was therefore carried out under milder conditions in solution in the hope of isolating intermediates that might throw light on the reaction mechanism. The thermolysis of the diphenyldiazomethane adduct **3a** was studied in boiling xylene (140 °C for 20 min), bromobenzene (156 °C for 6 min) and *o*-dichlorobenzene (180 °C for 3 min). The red product **4a** was again obtained but in lower yield (20, 16 and 15% respectively) than in the solid state pyrolysis. However TLC monitoring showed that an orange coloured product was also present in solution and that this could be an intermediate on the reaction pathway. It was however difficult to isolate pure and appeared to decompose on silica. The solute concentration was found to be critical to the outcome of the reaction. Thermolysis of the adduct **3a** in a *dilute, deoxygenated* xylene solution (0.75 mg ml^{-1}) for 25 min allowed the isolation of two products (Scheme 3). The first was an orange coloured product isolated as a crude



Scheme 3 *Conditions:* i, Xylene, reflux, N_2, 25 min

oil. It showed a strong IR stretch at 1137 cm^{-1} and a molecular ion peak at *m/z* 314 in the mass spectrum. Microanalysis supported the molecular formula $C_{15}H_{10}N_2S_3$, with all the heteroatoms retained, and ^{13}C NMR spectroscopy showed the presence of an aliphatic CH group, one monosubstituted and one disubstituted benzene ring. Structure **12** was assigned to this product. A singlet for the proton on the tetrahedral carbon was not observed and is presumbly masked by the complex aromatic multiplets. 6,7-Dihydrotrithiadiazepine, with the same arrangement of heteroatoms, is also orange. An orange solution of compound **12** left in the air turned red at the top owing to the formation of some dithiazole **4a**. This indicated the ease of oxidation of **12** and explained the need for rigorous deoxygenation in the solution thermolysis. A sealed solution of **12** was stable and did not rearrange to the red dithiazole **4a**.

The second product was a more polar, pale yellow compound; its IR spectrum showed an NS stretch at 1164 cm^{-1} and a broad absorption at 3329 cm^{-1} possibly from an NH group. The UV spectrum had an absorption at 352 nm characteristic of a trithiadiazepine ring and the mass spectrum showed a weak molecular ion at *m/z* 314. The ^1H NMR was complex and difficult to interpret. Eventually the structure was

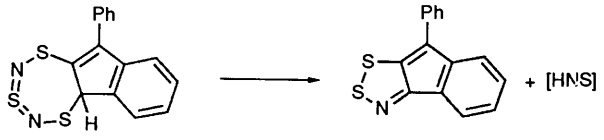


Scheme 4 *Conditions:* i, Xylene, reflux, N_2, 4 min

solved by X-ray crystallography and it proved to be a dimer **13**.[2] This is presumably formed by dimerisation of the monomer **12** and it probably dissociates readily to the monomer, explaining the absence of a peak at *m/z* 628 in the mass spectrum. A mechanism for the dimerisation is discussed later.

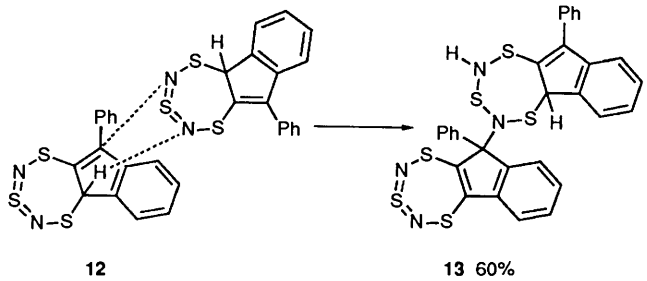
Similar thermolysis of the cycloheptadiene adduct **3e**, in xylene for 4 min, gave the corresponding orange product **14** (Scheme 4). This adduct **3e** decomposes more rapidly than the diphenyldiazomethane adduct **3a** and the length of time of heating is critical. Thermolysis of adducts **3b** and **3c** was studied in dilute xylene solution but the orange intermediates formed were difficult to isolate and purify.

Thermolysis of 6-*Phenyl*-10b*H*-*indenotrithiadiazepine* **12**.—Isolation of the orange intermediates **12** and **14** lent support to our proposed mechanism where the key carbon–carbon bond is formed before the array of heteroatoms is disrupted. The orange product **12** is also on the reaction pathway and can be converted into the red product **4a** by further thermolysis in a more concentrated xylene solution. The yield of product **4a** (36%) was higher than that (20%) obtained by thermolysis of the diphenyldiazomethane adduct **3a** in solution; this is reasonable since compound **12** is further along the reaction pathway.



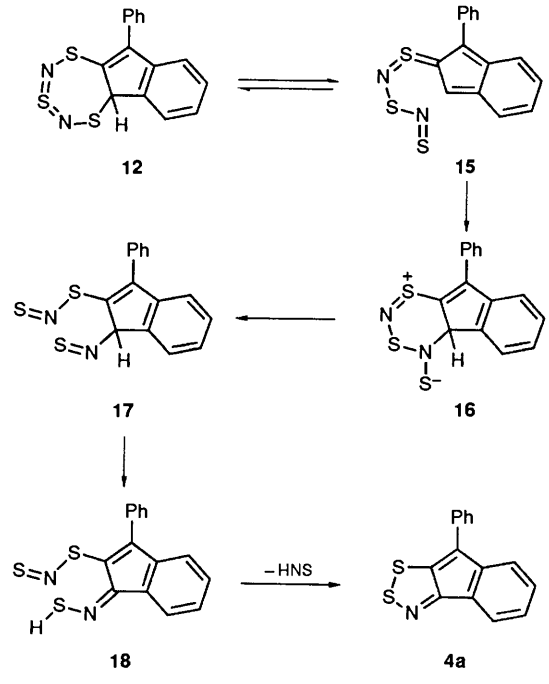
However the yield is still not high and this suggests that the low yielding steps are associated with the rearrangement and loss of heteroatoms and not with formation of the new carbon–carbon bond.

The isolation and structure determination of the dimer **13** provided strong evidence that the order of heteroatoms in compound **12** is correct. We attempted to convert the orange compound **12** into the dimer **13** in order to confirm its structure. We observed that when compound **12** was adsorbed on a dry flash silica plate it slowly formed a colourless product with the same R_F as the dimer **13**. A ground mixture of the orange compound **12** and dry flash silica from a silica plate, heated at 60 °C for 30 min, gave dimer **13** in 60% yield. This dimerisation also occurred on heating on Florisil and so it is not necessarily acid catalysed.



The dimer **13** could be formed directly, as shown, by an 8-electron ene-type reaction between two molecules of the monomer **12**, though this is formally disallowed as a suprafacial process by the Woodward Hoffmann rules. However a strong driving force for the reaction may come from the aromatisation of one trithiadiazepine ring and the reduction of S^{IV} to S^{II} in the other. It could also be formed in a more conventional 6-electron ene reaction if the hydrogen atom is initially transferred to sulphur, followed by a 1,2-shift to nitrogen.

From Indenotrithiadiazepine **12** *to Indenodithiazole* **4a**.—Now that the structure of the orange compound **12** has been firmly established a mechanism for its rearrangement to the red dithiazole **4a** is proposed (Scheme 5). Compound **12** could undergo reversible ring-opening to the intermediate **15**; breaking of the relatively weak carbon–sulphur bond will be assisted by electron donation from the electron-rich sulphur diimide group, and electron withdrawal by the indene ring which can stabilise a negative charge. The process is formally a 12 π electrocyclic ring opening. The indene ring of **15**, which is nucleophilic, could now react with the terminal thionitroso group to form **16**, rapidly followed by opening of the new heterocyclic ring to give **17** and proton transfer to give the thio-oxime **18**. The thio-oxime would be highly reactive and could cyclise to the observed product **4a** with loss of HNS.



Scheme 5

This mechanism involves intramolecular transfer of a thionitroso group, **15** ⟶ **17**. The best yields of the red products **4** were obtained from solid state thermolyses, and the orange intermediate **12** rearranged faster in more concentrated solution. Also rearrangement yields were always < 50%. These facts all suggest that transfer of the thionitroso group could possibly be an intermolecular process.

The high thermal stability and deep colour of the indenodithiazoles **4** suggest that they may be delocalised 14 π systems in spite of the presence of a formal S–S single bond.

Experimental

For general points see earlier Parts of the series.

3,3-*Diphenyl*-3H-*pyrazolo*[6,7-c]-1,3λ⁴δ²,5,2,4-*trithiadiazepine* **3a**.—6-Bromotrithiadiazepine (500 mg, 2.18 mmol) and diphenyldiazomethane (508 mg, 2.62 mmol) in methanol (35 ml) were treated with Hünig's base (563 mg, 4.37 mmol) at room temperature. The mixture was stirred for 20 min after which the precipitated product was filtered off and washed with methanol to give the *title compound* (529 mg, 71%), m.p. 110–111 °C (from light petroleum–dichloromethane) (Found: C, 52.5; H, 2.8; N, 16.5. $C_{15}H_{10}N_4S_3$ requires C, 52.6; H, 2.9; N, 16.4%); λ_{max}(EtOH)/nm 305 (log ε 4.32) and 335 (3.79); ν_{max}(CCl_4)/cm^{-1} 1490vs, 1448vs, 1011s and 1164vs; δ_H(250 MHz; $CDCl_3$) 7.20–7.30 (4 H, m, ArH) and 7.30–7.41 (6 H, m, ArH); *m/z* (120 °C) 314 ($M^+ - N_2$, 12%), 268 ($M^+ - N_2 - NS$, 69), 236 ($M^+ - N_2 - NS_2$, 24) and 222 ($M^+ - N_2 - N_2S_2$, 56).

3,3-*Bis*(4-*chlorophenyl*)-3H-*pyrazolo*[6,7-c]-1,3λ⁴δ²,5,2,4-*trithiadiazepine* **3b**.—6-Bromotrithiadiazepine (320 mg, 1.40 mmol) and bis-(4-chlorophenyl)diazomethane (380 mg, 1.44 mmol) in methanol (30 ml) were treated with Hünig's base (320 mg, 2.48 mmol) at room temperature. The mixture was stirred for 20 min after which the precipitated product was filtered off and washed with methanol to give the *title compound* (442 mg, 77%), m.p. 162–165 °C (decomp.) (from light petroleum–dichloromethane) (Found: C, 43.7; H, 1.9; N, 13.6. $C_{15}H_8Cl_2N_4S_3$ requires C, 43.8; H, 2.0; N, 13.6%); λ_{max}(EtOH)/nm 304 (log ε 4.10) and 335 nm (3.73); ν_{max}(CCl_4)/cm^{-1} 1458s, 1166s and 1097s; δ_H(250 MHz; $CDCl_3$) 7.16 (4 H, d, *J*/H_2 8) and 7.35 (4 H, d, *J*/H_2 8); *m/z* (150 °C) 382 ($M^+ - N_2$, 8%), and 336 ($M^+ - N_2 - NS$, 43).

3,3-*Bis*(4-*methoxyphenyl*)-3H-*pyrazolo*[6,7-c]-1,3λ⁴δ²,5,2,4-*trithiadiazepine* **3c**.—6-Bromotrithiadiazepine (120 mg, 0.52 mmol) and bis(4-methoxyphenyl)diazomethane (173 mg, 0.68 mmol) in methanol (15 ml) were treated with Hünig's base (150 mg, 1.16 mmol). The mixture was stirred at room temperature for 20 min after which the precipitated product was filtered off and washed with methanol to give the *title compound* (160 mg, 76%), m.p. 106–107 °C (decomp.) (from light petroleum–dichloromethane) (Found: C, 50.7; H, 3.3; N, 13.9. $C_{17}H_{14}N_4O_2S_3$ requires C, 50.8; H, 3.5; N, 14.0%); λ_{max}(EtOH)/nm 297 (log ε 4.21) and 332 (3.81); ν_{max}(CCl_4)/cm^{-1} 1510vs, 1255vs and 1179s; δ_H(250 MHz; $CDCl_3$) 3.79 (6 H), 6.85 (4 H, d, *J*/Hz 9) and 7.13 (4 H, d, *J*/Hz 9); δ_C(62.9 MHz; $CDCl_3$) 55.4, 108.2, 114.0, 129.1, 130.3, 153.1, 156.0 and 160.0; *m/z* (170 °C) 374 ($M^+ - N_2$, 41%) and 328 ($M^+ - N_2 - NS$, 41).

Spiro[*fluorene*-9,3′-*pyrazolo*[6,7-c]-1,3λ⁴δ²,5,2,4-*trithiadiazepine*] **3d**.—6-Bromotrithiadiazepine (100 mg, 0.44 mmol) and diazofluorenone (100 mg, 0.52 mmol) in methanol (20 ml) were treated with Hünig's base (120 mg, 0.93 mmol) at room temperature. The mixture was stirred for 20 min after which the precipitated product was filtered off and washed with methanol to give the *title compound* (119 mg, 80%), m.p. 152–156 °C (decomp.) (from light petroleum–dichloromethane) (Found: C, 53.1; H, 2.3; N, 16.3. $C_{15}H_8N_4S_3$ requires C, 52.9; H, 2.4; N, 16.5%); λ_{max}(EtOH)/nm 295 (log ε 3.85) and 338 (4.20); ν_{max}/cm^{-1} 1476s, 1164s and 1007s; δ_H(250 MHz; $CDCl_3$) 6.79 (2 H, d, *J*/Hz 7), 7.25 (2 H, t, *J*/Hz 8 and 7), 7.50 (2 H, t, *J*/Hz 8 and 7) and 7.86 (2 H, d, *J*/Hz 8 and 7); δ_C(62.9 MHz; $CDCl_3$) 109.4, 126.5, 128.1, 129.0, 129.1, 131.0, 138.5, 152.6 and 156.5; *m/z* (150 °C) 340 (M^+, 0.3%), 312 ($M^+ - N_2$, 18) and 266 ($M^+ - N_2 - NS$, 48).

Spiro[*dibenzocycloheptene*-5,3′-*pyrazolo*[6,7-c]-1,3λ⁴δ²,5,2,4-*trithiadiazepine*] **3e**.—6-Bromotrithiadiazepine (100 mg, 0.44 mmol) and 5-diazo-10,11-dihydrodibenzo[*a,d*]cycloheptene (125 mg, 0.57 mmol) in methanol (20 ml) were treated with Hünig's base (115 mg, 0.88 mmol) at room temperature. The mixture was stirred for 20 min after which the precipitated product was filtered off and washed with methanol to give the *title compound* (125 mg, 77%), m.p. 135–137 °C (decomp.) (from light petroleum–dichloromethane) (Found: C, 55.7; H, 3.2; N, 15.0. $C_{17}H_{12}N_4S_3$ requires C, 55.4; H, 3.3; N, 15.2%); λ_{max}(EtOH)/nm 332 (log ε 3.80); ν_{max}(CCl_4)/cm^{-1} 1455s, 1165s and 1017s; δ_H(250 MHz; $CDCl_3$) 3.35 (2 H, dd, *J*/Hz 15 and 10), 3.60 (2 H, dd, *J*/Hz 15 and 10), 6.49 (2 H, d, *J*/Hz 8), 6.96 (2 H, t, *J*/Hz 8 and 7.5) and 7.19–7.26 (4 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 36.0, 111.1, 126.8, 128.7, 130.0, 131.0, 132.9, 144.2, 156.1 and 158.2; *m/z* (120 °C) 340 ($M^+ - 28$, 18%), 294 ($M^+ - N_2 - NS$, 87) and 293 ($M^+ - 28, -NSH$, 50).

Spiro[*dibenzocycloheptene*-5,3′-*pyrazolo*[6,7-c]-1,3λ⁴δ²,5,2,4-*trithiadiazepine*] **3f**.—6-Bromotrithiadiazepine (200 mg, 0.87 mmol) and 5-diazodibenzo[*a,d*] cycloheptene (230 mg, 1.06 mmol) in methanol (30 ml) were treated with Hünig's base (225 mg, 1.75 mmol) at room temperature. The mixture was stirred for 20 min after which the precipitated product was filtered off and washed with methanol to give the *title compound* (239 mg, 0.65 mmol), m.p. 185–186 °C (decomp.) (from light petroleum–dichloromethane) (Found: C, 55.7; H, 2.5; N, 15.3. $C_{17}H_{10}N_4S_3$ requires C, 55.7; H, 2.7; N, 15.3%); λ_{max}(EtOH)/nm 305 (log ε 4.23) and 345 (4.30); ν_{max}(CCl_4)/cm^{-1} 1489s, 1165vs and 1021vs; δ_H(250 MHz; $CDCl_3$) 7.23–7.38 (6 H, m, ArH), 7.46 (2 H, dd, *J*/Hz 7.5 and 2) and 7.66 (2 H, dd, *J*/Hz 7.5 and 2); δ_C(62.9 MHz; $CDCl_3$) 104.1, 125.8, 128.6, 129.8, 131.1, 133.0, 133.1, 137.4, 153.3 and 157.1; *m/z* (170 °C) 338 ($M^+ - N_2$, 21%) and 292 ($M^+ - N_2 - NS$, 41).

3,3-*Dimethyl*-3H-*pyrazolo*[6,7-c]-1,3λ⁴δ²,5,2,4-*trithiadiazepine*.—6-Bromotrithiadiazepine (100 mg, 0.44 mmol) and 2-diazopropane (367 mg, 8.7 mmol) in methanol (15 ml) were treated with an excess of Hünig's base (563 mg, 4.37 mmol) at room temperature. The mixture was stirred for 10 min after which the solvent was removed under reduced pressure and the residue chromatographed on silica. Light petroleum–dichloromethane (25:75) eluted the *title compound* (46 mg, 0.21 mmol) as a colourless solid, m.p. 110–111 °C (from light petroleum–dichloromethane) (Found: C, 27.6; H, 2.7; N, 25.5. $C_5H_6N_4S_3$ requires C, 27.5; H, 2.75; N, 25.7%); λ_{max}(EtOH)/nm 295 (log ε 3.98) and 335 (3.38); ν_{max}/cm^{-1} 1456vs and 1159vs; δ_H(250 MHz; $CDCl_3$) 1.70 (s, 2 × Me); δ_C(62.9 MHz; $CDCl_3$) 26.0, 96.6, 154.1 and 155.2; *m/z* (120 °C) 218 (M^+, 91%) and 144 ($M^+ - N_2 - NS$, 31).

Solid State Thermolyses of Diarylpyrazolotrithiadiazepines.—(a) 8-*Phenylindeno*[1,2-d]-1,2,3-*dithiazole* **4a**.—3,3-Diphenyl-3*H*-pyrazolotrithiadiazepine **3a** (100 mg, 0.29 mmol) in a 50 ml round-bottomed flask fitted with an air condenser containing a loose glass wool plug was lowered into a Woods metal bath at 210 °C. After *ca.* 5 s the material decomposed suddenly and violently and the flask was raised from the heat and allowed to cool. The product was isolated by dry flash chromatography on silica. Light petroleum–dichloromethane (75:25) eluted the *title compound* (23.0 mg, 30%) as a deep red solid, m.p. 129–130 °C (from light petroleum–dichloromethane) (Found: C, 67.3; H, 3.3; N, 5.2. $C_{15}H_9NS_2$ requires C, 67.4; H, 3.4; N, 5.2%); λ_{max}(EtOH)/nm 280 (log ε 3.84), 315 (3.62) and 352 (3.34); ν_{max}(CCl_4)/cm^{-1} 1439vs and 1121s; δ_H(250 MHz; $CDCl_3$) 7.0–8.1 (m, ArH); δ_C(62.9 MHz; $CDCl_3$) 119.5, 123.4, 123.8, 125.7, 126.9, 127.1, 128.9, 129.1, 130.3, 135.0, 139.7, 149.4 and 168.5; *m/z* (110 °C) 267 (M^+, 7%), 235 ($M^+ - 32$, 6) and 203 ($M^+ - 64$, 12).

(b) 8-(4-*Chlorophenyl*)-5-*chloroindeno*[1,2-d]-1,2,3-*dithiazole*

4b. 3,3-Bis(4-chlorophenyl)-3*H*-pyrazolotrithiadiazepine **3b** (100 mg, 0.24 mmol) was pyrolysed at 210 °C for *ca.* 8 s as described in (a). The product was isolated by dry flash chromatography on silica. Light petroleum–dichloromethane (90:10) eluted the *title compound* (22 mg, 27%) as a red solid, m.p. 218–219 °C (from light petroleum–dichloromethane) (Found: C, 53.35; H, 2.2; N, 4.1. $C_{15}H_7Cl_2NS_2$ requires 53.6; H, 2.1; N, 4.2%); λ_{max}(EtOH)/nm 288 (log ε 3.76) and 325 (3.68); ν_{max}(CCl_4)/cm^{-1} 1486s, 1447vs and 1094s; δ_H(250 MHz; $CDCl_3$) 7.42–7.71 (6 H, m, ArH) and 8.02 (1 H, s, ArH); δ_C(62.9 MHz; $CDCl_3$) 120.0, 123.6, 128.0, 129.4, 129.6, 129.9, 130.0, 130.5, 133.0, 133.4, 135.6, 140.0 and 147.0; *m/z* (150 °C) 335 (M^+, 100%) and 271 ($M^+ - S_2$, 10).

(c) 8-(4-*Methoxyphenyl*)-5-*methoxyindeno*[1,2-d]-1,2,3-*dithiazole* **4c**. 3,3-Bis(4-methoxyphenyl)-3*H*-pyrazolotrithiadiazepine **3c** (100 mg, 0.25 mmol) was pyrolysed briefly at 210 °C as described in (a). The product was isolated by dry flash chromatography on silica. Light petroleum–dichloromethane (85:15) eluted the *title compound* (36 mg, 36%) as a deep purple solid, m.p. 106–107 °C (from light petroleum–dichloromethane) (Found: C, 62.3; H, 4.1; N, 4.1. $C_{17}H_{13}NO_2S_2$ requires C, 62.4; H, 4.0; N, 4.3%); λ_{max}(EtOH)/nm 285 (log ε 3.91), 315 (3.72) and 355 (3.46); ν_{max}(CCl_4)/cm^{-1} 1477s and 1287vs; δ_H(250 MHz; $CDCl_3$) 3.89 (3 H, s, OMe), 3.90 (3 H, s, OMe), 6.95–7.03 (3 H, m, ArH), 7.58 (2 H, d, *J*/Hz 9) and 7.72 (2 H, d, *J*/Hz 9); δ_C(62.9 MHz; $CDCl_3$) 55.3 (Me), 56.0 (Me), 109.1, 114.4, 116.2, 120.2, 125.8, 127.5, 128.6, 129.0, 136.3, 142.5, 157.1, 159.2 and 168.5; *m/z* (140 °C): 327 (M^+, 100%) and 312 (M^+ – Me, 54).

(d) 7,8-*Dihydrodibenz*[3,3a,4;7,8]*azuleno*-[1,2-d]-1,2,3-*dithiazole* **4e**. Spiro[dibenzocycloheptene-5,3′-pyrazolotrithiadiazepine] **3e** (100 mg, 0.27 mmol) was pyrolysed briefly at 210 °C as described in (a). The product was isolated by dry flash chromatography on silica. Light petroleum–dichloromethane (75:25) eluted the *title compound* (31 mg, 39%) as a deep purple solid, m.p. 138–139 °C (from light petroleum–dichloromethane) (Found: C, 69.6; H, 3.7; N, 4.8. $C_{17}H_{11}NS_2$ requires C, 69.6; H, 3.75; N, 4.8%); λ_{max}(EtOH)/nm 281 (log ε 3.88), 320 (3.65) and 358 (3.41); ν_{max}(CCl_4)/cm^{-1} 1482s, 1412vs and 1108s; δ_H(250 MHz; $CDCl_3$) 3.15 (4 H, s, CH_2), 7.10–7.40 (5 H, m) and 7.91 (2 H, d, *J*/Hz 7); δ_C(62.9 MHz; $CDCl_3$) 34.0, 37.2, 121.0, 123.4, 126.7, 126.9, 127.1, 127.5, 130.3, 131.2, 134.0, 136.3, 138.1, 141.7, 147.0 and 168.7; *m/z* (130 °C) 293 (M^+, 100%) and 229 ($M^+ - S_2$, 11). This was followed by compound **4f** (2 mg, 3%) identical with that described below.

(e) *Dibenz*[3,3a,4;7,8]*azuleno*[1,2-*d*]-1,2,3-*dithiazole* **4f**. Spiro-[dibenzocycloheptene-5,3′-pyrazolotrithiadiazepine] **3f** (80 mg, 0.2 mmol) was pyrolysed briefly at 210 °C as described in (a). The product was isolated by dry flash chromatography on silica. Light petroleum–dichloromethane (80:20) eluted the *title compound* (13 mg, 20%) as a deep blue solid, m.p. 183–185 °C (from light petroleum–dichloromethane) (Found: C, 70.2; H, 3.05; N, 4.8. $C_{17}H_9NS_2$ requires C, 70.1; H, 3.1; N, 4.8%); λ_{max}(EtOH)/nm 269 (log ε 4.0) and 345 (3.82); ν_{max}/cm^{-1} 1481vs, 1403vs and 1135s; δ_H(250 MHz; $CDCl_3$) 6.08 (2 H, d, *J*/Hz 2), 6.95–7.01 (3 H, m, ArH), 7.13 (1 H, t, *J*/Hz 7 and 7), 7.27 (1 H, t, *J*/Hz 8 and 6), 7.60 (1 H, d, *J*/Hz 8) and 7.72 (1 H, d, *J*/Hz 6); *m/z* (140 °C) 291 (M^+, 100%), 245 (M^+ – NS, 3) and 227 ($M^+ - S_2$, 7).

8-*Phenylindeno*[1,2-d]-1,2,3-*dithiazole* 2-*Oxide* **6**.—8-Phenylindeno[1,2-*d*]-1,2,3-dithiazole **4a** (30 mg, 0.11 mmol) in dichloromethane (10 ml) was treated dropwise with a dilute solution of N_2O_4 in dichloromethane. The reaction was monitored carefully by TLC. After the starting material had been consumed the solvent was removed under reduced pressure and the residue was purified by dry flash chromatography. Light petroleum–dichloromethane (50:50) eluted the *title compound* (23 mg, 74%) as a black solid, m.p. 179–180 °C (from light petroleum–dichloromethane) (Found: C, 63.5; H, 2.95; N, 5.2. $C_{15}H_9NOS_2$ (requires C, 63.6; H, 3.2; N, 4.95%); λ_{max}(EtOH)/nm 242 (log ε 3.86) and 300 (3.80); ν_{max}(CCl_4)/cm^{-1} 1618s and 1158s; δ_H(250 MHz; $CDCl_3$) 7.15–7.80 (m, ArH); *m/z* (170 °C) 283 (M^+, 21%), 267 (M^+ – O, 74) and 235 (M^+ – S – O, 100).

Solution Thermolyses of Diarylpyrazolotrithiadiazepines.—8-*Phenylindeno*[1,2-d]-1,2,3-*dithiazole* **4a**. (a) 3,3-Diphenyl-3*H*-pyrazolotrithiadiazepine **3a** (100 mg, 0.29 mmol) in xylene (10 ml) was deoxygenated with nitrogen. The solution was then refluxed for 30 min and allowed to cool. The solvent was removed by Kugelrohr distillation and the residue chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted the title compound (15 mg, 20%) identical with that previously described.

(b) 3,3-Diphenyl-3*H*-pyrazolotrithiadiazepine **3a** (100 mg, 0.29 mmol) in bromobenzene (10 ml) was deoxygenated with nitrogen and then refluxed for 6 min. After the mixture had been allowed to cool the solvent was removed by Kugelrohr distillation and the residue chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted compound **4a** (12 mg, 16%) identical with that previously described.

(c) 3,3-Diphenyl-3*H*-pyrazolotrithiadiazepine **3a** (100 mg, 0.29 mmol) in 1,2-dichlorobenzene (10 ml) was deoxygenated as before and then refluxed for 3 min. After the mixture had cooled the solvent was removed by Kugelrohr distillation and the residue chromatographed on silica. Light petroleum–dichloromethane (75:25) eluted compound **4a** (12 mg, 15%) identical with that previously described.

6-*Phenyl*-10bH-*indeno*-[1,2-f]-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* **12**. 3,3-Diphenyl-3*H*-pyrazolotrithiadiazepine **3a** (100 mg, 0.29 mmol) in xylene (150 ml) was deoxygenated with nitrogen and then refluxed for 25 min and allowed to cool. The solvent was removed under reduced pressure at 50–60 °C which required *ca.* 5 min. The products were isolated by dry flash chromatography on Florisil. Light petroleum–dichloromethane (75:25) eluted the *title compound* (42 mg, 46%) as an orange oil (Found: C, 57.7; H, 4.2; N, 7.95. $C_{15}H_{10}N_2S_3$ requires C, 57.3; H, 3.2; N, 8.9%); λ_{max}(EtOH)/nm 350 (log ε 3.91); ν_{max}(CCl_4)/cm^{-1} 1445w and 1137vs; δ_H(250 MHz; $CDCl_3$) 7.25–7.58 (m); δ_C(62.9 MHz; $CDCl_3$) 29.7, 75.2, 121.5, 124.0, 126.9, 128.8, 128.9, 129.0, 129.3, 132.1, 138.6, 144.2 151.1; *m/z* (150 °C): 314 (M^+, 91%), and 267 (M^+ HNS, 100). Light petroleum–dichloromethane (50:50) eluted 6-(6-*phenyl*-10bH-*indeno*-[1,2-f]-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepan-2-yl*]-6-*phenylindeno*-6H-[1,2-f]-1,3$\lambda^4\delta$,5,2,4-*trithiadiazepine* **13** (18 mg, 20%), m.p. 155–156 °C (from light petroleum–dichloromethane) (Found: C, 55.7; H, 3.1; N, 8.4. $C_{30}H_{20}N_4S_6$ requires C, 57.3; H, 3.2; N, 8.9%); λ_{max}(EtOH)/nm 352sh and 402sh; ν_{max}($CHCl_3$)/cm^{-1} 1460vs and 1164vs; δ_H(250 MHz; $CDCl_3$) 6.8–7.8 (m); *m/z* (160 °C) 314 (M^+ – 314, 7%) and 267 (55).

9,10-*Dihydro*-5aH-*dibenz*[3,3a,4;7,8]*azuleno*-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* **14**.—Spiro[(dibenzocycloheptene)pyrazolotrithiadiazepine] **3e** (100 mg, 0.27 mmol) in xylene (100 ml) was deoxygenated and then refluxed for 5 min and allowed to cool. The solvent was removed rapidly under reduced pressure at 50–60 °C and the product isolated by dry flash chromatography on Florisil. Light petroleum–dichloromethane (75:25) eluted the *title compound* (31 mg, 34%) as an orange solid, m.p. 127–130 °C (from light petroleum–dichloromethane) (Found: C, 59.9; H, 3.7; N, 8.0. $C_{17}H_{12}N_2S_3$ requires C, 60.0; H, 3.5; N, 8.2%); λ_{max}(EtOH)/nm 260 (log ε 3.95) and 369 (3.83); ν_{max}(CCl_4)/cm^{-1} 1453m, 1422m and 1140vs; δ_H(250 MHz; $CDCl_3$) 3.02 (4 H, s, 2 × CH2) and 7.2–7.4 (8 H, m); *m/z* (170 °C) 340 (M^+, 2%), 308 (M^+ – S, 6) and 293 (M^+ – HNS, 92). This was followed by the 1,2,3-dithiazole **4f** (10 mg, 13%) identical with that previously described.

8-*Phenylindeno*[1,2-d]-1,2,3-*dithiazole* **4a**.—(a) 6-Phenylindeno-10b*H*-[1,2-*f*]trithiadiazepine **12** (45 mg, 0.14 mmol) was pyrolysed neat at 200 °C for 30 s. The product was isolated by dry flash chromatography on silica. Light petroleum–dichloromethane (75:25) eluted the title compound (9 mg, 24%) identical with that previously described.

(b) 6-Phenylindeno-10b*H*-[1,2-*f*]trithiadiazepine **12** (68 mg, 0.22 mmol) in xylene (5 ml) was deoxygenated and then refluxed under nitrogen for 30 min. The solvent was removed under reduced pressure and the product isolated by dry flash chromatography on silica. Light petroleum–dichloromethane (75:25) eluted the title compound **4a** identical with that previously described.

6-(6-*Phenylindeno*[1,2-f]-1,3,5,2,4-*trithiadiazepin*-2-*yl*)-*indeno*[1,3-*f*]-1,3$\lambda^4\delta^2$,5,2,4-*trithiadiazepine* **13**.—6-Phenyl-10b*H*-indeno[1,2-*f*]trithiadiazepine **12** (55 mg, 0.18 mmol) was adsorbed onto silica (200 mg) scraped from an aluminium plate. The mixture was heated at 60 °C for 20 min and then the product was isolated by dry flash chromatography. Light petroleum–dichloromethane (50:50) eluted the title compound **13** (12 mg, 55%) identical with that previously described.

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