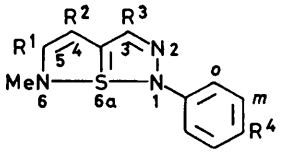
Studies of Heterocyclic Compounds. Part 24.[1] Syntheses of 6aλ⁴-Thia-1,2,6-triazapentalenes

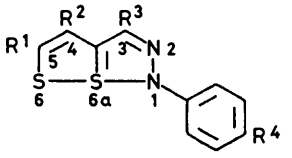
By **Robert M. Christie, David H. Reid,* and Robin Wolfe-Murray,** Department of Chemistry, The Purdie Building, The University, St. Andrews KY16 9ST, Scotland

6aλ⁴-Thia-1,2,6-triazapentalenes, a new class of four-electron three-centre bonded compound, have been synthesised by the reaction of 1-aryl-6,6aλ⁴-dithia-1,2-diazapentalenes in dimethylformamide with ethanolic methylamine; by *S*(6)-methylation of 1-aryl-6,6aλ⁴-dithia-1,2-diazapentalenes with methyl fluorosulphonate and treatment of the resulting 2-aryl-5-(2-methylthiovinyl)-1,2,3-thiadiazolium fluorosulphonates with methylamine; and by the coupling of 1,3,4,6-tetra-alkyl-6aλ⁴-thia-1,6-diazapentalenes with arenediazonium tetrafluoroborates and concomitant elimination of a methyliminomethyl group. 3,4-Dialkyl-6aλ⁴-thia-1,2,6-triazapentalenes react with benzenediazonium tetrafluoroborate to give 3,4-dialkyl-1,6-diphenyl-6aλ⁴-thia-1,2,5,6-tetra-azapentalenes.

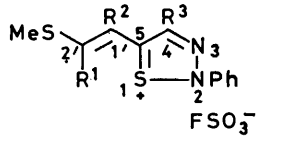
In continuation of our studies of nitrogen-containing 1,6,6aλ⁴-triheterapentalenes,[1,2] we have synthesised 6aλ⁴-thia-1,2,6-triazapentalenes, a previously unknown class of four-electron, three-centre bonded compound, by three routes which start from other types of 1,6,6aλ⁴-triheterapentalenes.



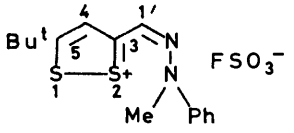
	R¹	R²	R³	R⁴
(1)	H	H	H	H
(2)	H	Me	Me	H
(3)	H	[CH₂]₃		H
(4)	Bu^t	H	H	H
(5)	H	Me	Me	NO₂
(6)	H	[CH₂]₃		NO₂



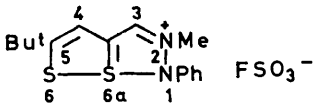
	R¹	R²	R³	R⁴
(7)	H	H	H	H
(8)	H	Me	Me	H
(9)	H	[CH₂]₃		H
(10)	Bu^t	H	H	H
(11)	H	Me	Me	NO₂
(12)	H	[CH₂]₃		NO₂



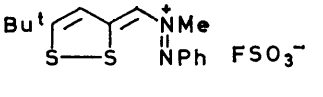
	R¹	R²	R³
(13)	H	H	H
(14)	H	Me	Me
(15)	H	[CH₂]₃	
(16)	Bu^t	H	H



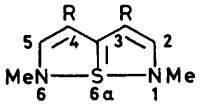
(17)



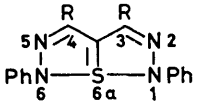
(18a)



(18b)



(19) R = Me
(20) R,R = [CH₂]₃



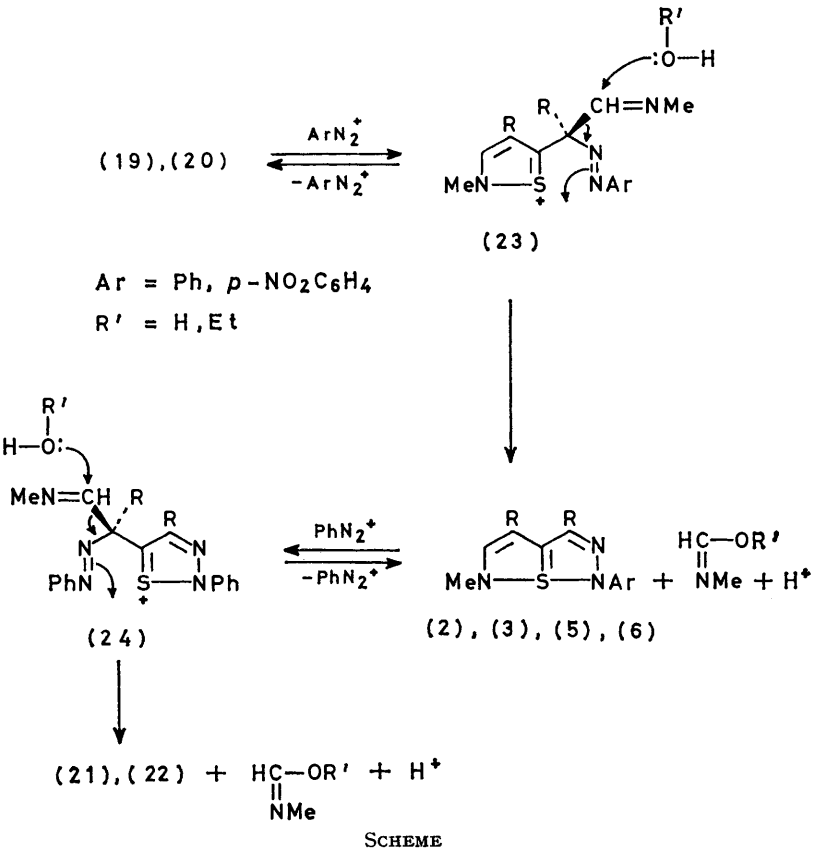
(21) R = Me
(22) R,R = [CH₂]₃

In the first synthesis, the 6aλ⁴-thia-1,2,6-triazapentalenes (1)—(6) were obtained directly, in modest yield, by treatment of the corresponding 6,6aλ⁴-dithia-1,2-diazapentalenes (7)—(12) [2c] in dimethylformamide with ethanolic methylamine. In these reactions the 6,6aλ⁴-dithia-1,2-diazapentalenes behave as masked thiocarbonyl compounds.

In the second synthesis, methylation of the dithia-diazapentalenes (7)—(9) with methyl fluorosulphonate took place at sulphur and gave in high yield the orange 1,2,3-thiadiazolium fluorosulphonates (13)—(15) [δ(CF_3CO_2H) 2.62—2.93 (SMe)]. The MeS group and the thiadiazolium ring in the salt (13) are *trans* about the extracyclic double bond ($J_{1',2'}$ 15.4 Hz). We assume that a *trans* arrangement of the MeS group and the thiadiazolium ring also exists in the salts (14) and (15).

The fluorosulphonates (13)—(15) reacted in acetonitrile with aqueous methylamine to give the thiatriazapentalenes (1)—(3). Compounds (2) and (3) were accompanied by the dithiadiazapentalenes (8) (20%) and (9) (3.5%), respectively, which result from *S*-demethylation of the corresponding fluorosulphonates (14) and (15) by methylamine. Methylation of 1-phenyl-5-t-butyl-6,6aλ^4-dithia-1,2-diazapentalene (10) gave a red oil, which was shown by ^{1}H n.m.r. spectroscopy to be a 5 : 2 mixture of the *S*-methylation product (16) [δ 2.66 (SMe)] and an *N*-methylation product [δ 4.27 (NMe)]. Methylation at N-1 would give the salt (17). Methylation at N-2 would give a salt for which two structures (18a and b) are possible. We are at present unable to determine which of these three structures is correct. Treatment of this oil with methylamine gave the *S*-demethylation product (10) in low yield as the only detectable product. These results indicate that the t-butyl group sterically hinders access of methyl fluorosulphonate to sulphur in the dithiadiazapentalene (10) and inhibits attack by methylamine at C-2′ in the salt (16).

6aλ^4-Thia-1,2,6-triazapentalenes were also obtained by the coupling of 3,4-dialkyl-6aλ^4-thia-1,6-diazapentalenes with arenediazonium tetrafluoroborates in ethanol. Compounds (19) and (20) reacted with *p*-nitrobenzenediazonium tetrafluoroborate to give the thiatriazapentalenes (5) and (6), respectively, as the only product. In contrast, the thiadiazapentalene (19) reacted with benzenediazonium tetrafluoroborate to give both the expected thiatriazapentalene (2) (29%) and the 6aλ^4-thia-1,2,5,6-tetra-azapentalene (21) [1] (8.9%); the thiadiazapentalene (20) gave the thiatetra-azapentalene (22) [1] alone, in low yield. We propose that 6aλ^4-thia-1,6-diazapentalenes which are blocked by alkyl substituents at the reactive positions 3 and 4, react with arenediazonium tetrafluoroborates to give 6aλ^4-thia-1,2,6-triazapentalenes *via* isothiazolium intermediates (23) * (see Scheme). The resulting thiatriazapentalenes (2) and (3) then react partly or completely with an excess of



SCHEME

benzenediazonium tetrafluoroborate to give the thiatetra-azapentalenes (21) and (22), respectively, *via* 1,2,3-thiadiazolium intermediates (24).* Owing to deactivation by the *p*-nitrophenyl group, the thiatriazapentalenes (5) and (6) do not react further with *p*-nitrobenzenediazonium tetrafluoroborate. In keeping with this scheme, the thiatriazapentalene (3), obtained by the first two syntheses, reacted with benzenediazonium tetrafluoroborate to give the thiatetra-azapentalene (22), albeit in low yield (12%).

EXPERIMENTAL

Electronic spectral absorption data refer to solutions in cyclohexane, unless otherwise stated. ^{1}H N.m.r. spectra

* It is likely that the imino-nitrogen atom in the intermediates (23) and (24) is protonated as a result of solvolytic decomposition of the arenediazonium tetrafluoroborate. This protonation would be expected to assist the elimination of the methyliminomethyl group from (23) and (24).

were determined at 100 MHz for 0.4M solutions in deuteriochloroform, unless otherwise indicated, with tetramethylsilane as internal reference. J Values were measured on the 100 Hz scale and, unless otherwise stated, δ values refer to singlet absorptions. Signals assigned to the pairs of *o*- and *m*-protons of the *p*-nitrophenyl group in compounds (5) and (6) are the four most intense signals in the AA'BB' pattern. Solutions were dried over sodium sulphate and evaporated at reduced pressure. Column chromatography was carried out with alumina (activity II; pH *ca.* 9.5; 100—250 mesh) or silica (85—200 mesh). Solvent mixtures are described in ratios by volume. Reaction products were shown to be identical with authentic samples by showing that they had the same m.p. and n.m.r. spectra, and that they displayed the same t.l.c. behaviour on silica (benzene or ether for development) as the authentic samples. Petroleum was of boiling range 40—60 °C. Aqueous methylamine was a 25—30% (w/v) solution; ethanolic methylamine was a 33% (w/w) solution.

Reaction of 1-*Aryl*-6,6aλ⁴-*dithia*-1,2-*diazapentalenes with Methylamine: Synthesis of* 1-*Aryl*-6-*methyl*-6aλ⁴-*thia*-1,2,6-*triazapentalenes*.—The reaction conditions varied and are given in each case. Subsequent work-up was by one of the following procedures.

Procedure A. The reaction solution was diluted with water and extracted with benzene (×2), and the extracts were washed with water (×6), dried, and evaporated. Chromatography [alumina (30 × 2.2 cm)] of the residue with benzene–petroleum (1 : 1) gave orange eluates from which starting material was recovered. Subsequent elution with benzene brought through yellow eluates which yielded the 1-aryl-6-methyl-6aλ⁴-thia-1,2,6-triazapentalene.

Procedure B. The reaction mixture was diluted with water and extracted with benzene (×2), and the residue from the washed (×6), dried, and evaporated extracts was chromatographed [alumina (20 × 2.2 cm)]. Elution with benzene removed a trace of starting material, and subsequent elution with benzene–ether (4 : 1) brought through deep red eluates which yielded the 1-aryl-6-methyl-6aλ⁴-thia-1,2,6-triazapentalene.

6-*Methyl*-1-*phenyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (1) *from* 1-*phenyl*-6,6aλ⁴-*dithia*-1,2-*diazapentalene* (7). Ethanolic methylamine (10 ml) was added to a solution of 1-phenyl-6,6aλ⁴-dithia-1,2-diazapentalene [2c] (2 mmol) in dimethylformamide (60 ml), and the mixture was kept at room temperature for 5 min. Work-up (procedure A) gave starting material (17 mg, 3.9%) and 6-*methyl*-1-*phenyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (86 mg, 20%), orange-yellow needles from petroleum, m.p. 90—92 °C (Found: C, 60.9; H, 5.1; N, 19.3; S, 14.9. $C_{11}H_{11}N_3S$ requires C, 60.8; H, 5.1; N, 19.3; S, 14.8%); *m/e* 217 (M^+); $\lambda_{max.}$ 430 (log ε 4.33), 277 (3.79), 250sh (3.78), and 239 nm (4.10); δ 3.58 (3 H, d, $J_{NMe,5}$ 0.8 Hz, NMe), 6.78 (1 H, d, $J_{4,5}$ 3.6 Hz, 4-H), 7.05 (1 H, t,* *p*-proton of 1-Ph), 7.36 (2 H, t,* 2 *m*-protons of 1-Ph), 7.71 (2 H, d,* 2 *o*-protons of 1-Ph), 7.89 (1 H, dq, $J_{5,4}$ 3.6, $J_{5,NMe}$ 0.8 Hz, 5-H), and 8.16 (1 H, 3-H).

3,4,6-*Trimethyl*-1-*phenyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (2) *from* 3,4-*dimethyl*-1-*phenyl*-6,6aλ⁴-*dithia*-1,2-*diazapentalene* (8). Ethanolic methylamine (10 ml) was added to a solution of 3,4-dimethyl-1-phenyl-6,6aλ⁴-dithia-1,2-diazapentalene [2c] (2 mmol) in dimethylformamide (60 ml), and the mixture was kept at room temperature for 20 min. Work-up (procedure A) gave starting material (25 mg, 5%) and 3,4,6-*trimethyl*-1-*phenyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (61 mg, 12%), orange-yellow spars from petroleum, m.p. 70.5—71.5 °C (Found: C, 63.7; H, 6.3; N, 17.0. $C_{13}H_{15}N_3S$ requires C, 63.6; H, 6.2; N, 17.1%); *m/e* 245 (M^+); $\lambda_{max.}$ 447 (log ε 4.36), 285 (3.90), and 242 nm (4.12); δ 2.51 (3 H, d, $J_{4\text{-}Me,5}$ 0.5 Hz, 4-Me), 2.78 (3 H, 3-Me), 3.52 (3 H, d, $J_{NMe,5}$ 0.7 Hz, NMe), 6.98 (1 H, t,* *p*-proton of 1-Ph), 7.32 (2 H, t,* 2 *m*-protons of 1 Ph), 7.65br (1 H, m, 5-H), and 7.67 (2 H, d,* 2 *o*-protons of 1-Ph).

6,7-*Dihydro*-3-*methyl*-2-*phenyl*-2aλ⁴-*thia*-1,2,3-*triaza*-5H-*cyclopent*[cd]*indene* (3) *from* 6,7-*dihydro*-2-*phenyl*-2aλ⁴,3-*dithia*-1,2-*diaza*-5H-*cyclopent*[cd]*indene* (9). Ethanolic methylamine (20 ml) was added to a solution of 6,7-dihydro-2-phenyl-2aλ⁴,3-dithia-1,2-diaza-5*H*-cyclopent[*cd*]indene [2c] (2 mmol) in dimethylformamide (60 ml), and the mixture was heated at 60 °C for 3 h. Work-up (procedure A) gave starting material (27 mg, 5.2%) and 6,7-*dihydro*-3-*methyl*-2-*phenyl*-2aλ⁴-*thia*-1,2,3-*triaza*-5*H*-*cyclopent*[cd]*indene* (336 mg, 65%), orange-red spars from hexane, m.p. 102—103.5 °C (Found: C, 65.3; H, 5.7; N, 16.2. $C_{14}H_{15}N_3S$ requires C, 65.4; H, 5.9; N, 16.3%); *m/e* 257 (M^+); $\lambda_{max.}$ 458 (log ε 4.33), 286 (3.92), and 243 nm (4.05); δ 2.07 (2 H, quint, 6-H_2), 2.78 (2 H, t, 5-H_2), 3.04 (2 H, t, 7-H_2), 3.58 (3 H, d, $J_{NMe,4}$ 0.8 Hz, NMe), 6.96 (1 H, t,* *p*-proton of 2-Ph), 7.31 (2 H, t,* 2 *m*-protons of 2-Ph), 7.62 (2 H, d,* 2 *o*-protons of 2-Ph), and 7.73br (1 H, 4-H).

6-*Methyl*-1-*phenyl*-5-*t*-*butyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (4) *from* 1-*phenyl*-5-*t*-*butyl*-6,6aλ⁴-*dithia*-1,2-*diazapentalene* (10). Ethanolic methylamine (20 ml) was added to a solution of 1-phenyl-5-t-butyl-6,6aλ⁴-dithia-1,2-diazapentalene [2c] (2 mmol) in dimethylformamide (60 ml), and the mixture was heated at 60 °C for 5 h. More ethanolic methylamine (20 ml) was added, and the solution was heated at 60 °C for a further 5 h. A further quantity of methylamine (20 ml) was then added, and the solution was heated at 60 °C for a final 10 h. Work-up (procedure A) gave starting material (230 mg, 42%) and 6-*methyl*-1-*phenyl*-5-*t*-*butyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (143 mg, 26%), orange-yellow plates from methanol, m.p. 98—99 °C (Found: C, 65.8; H, 7.0; N, 15.3. $C_{15}H_{19}N_3S$ requires C, 65.9; H, 7.0; N, 15.4%); *m/e* 273 (M^+); $\lambda_{max.}$ 429 (log ε 4.39), 278 (3.78), 248sh (4.11), and 242 nm (4.15); δ 1.38 (9 H, Bu^t), 3.65 (3 H, NMe), 6.84 (1 H, 4-H), 7.02 (1 H, t,* *p*-proton of 1-Ph), 7.34 (2 H, t,* 2 *m*-protons of 1-Ph), 7.71 (2 H, d,* 2 *o*-protons of 1-Ph), and 8.12 (1 H, 3-H).

3,4,6-*Trimethyl*-1-p-*nitrophenyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (5) *from* 3,4-*dimethyl*-1-p-*nitrophenyl*-6,6aλ⁴-*dithia*-1,2-*diazapentalene* (11). Ethanolic methylamine (10 ml) was added to a solution of 3,4-dimethyl-1-*p*-nitrophenyl-6,6aλ⁴-dithia-1,2-diazapentalene [2c] (2 mmol) in dimethylformamide (150 ml), and the mixture was kept at room temperature for 15 min. Work-up (procedure B) gave 3,4,6-*trimethyl*-1-p-*nitrophenyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (125 mg, 25%), deep red spars from benzene–cyclohexane, m.p. 227—229 °C (Found: C, 53.5; H, 4.9; N, 19.2. $C_{13}H_{14}N_4O_2S$ requires C, 53.8; H, 4.9; N, 19.3%); *m/e* 290 (M^+); $\lambda_{max.}$ 475 (log ε 4.63), 355br (3.79), 285 (3.64), and 239 nm (4.05); δ 2.59 (3 H, 4-Me), 2.79 (3 H, 3-Me), 3.67 (3 H, NMe), 7.63 and 7.72 (2 H, 2 *o*-protons of 1-Ar), 7.87br (1 H, 5-H), and 8.09 and 8.18 (2 H, 2 *m*-protons of 1-Ar).

6,7-*Dihydro*-3-*methyl*-2-*p*-*nitrophenyl*-2aλ⁴-*thia*-1,2,3-*triaza*-5H-*cyclopent*[cd]*indene* (6) *from* 6,7-*dihydro*-2-p-*nitrophenyl*-2aλ⁴,3-*dithia*-1,2-*diaza*-5H-*cyclopent*[cd]*indene* (12). Ethanolic methylamine (10 ml) was added to a solution of 6,7-dihydro-2-*p*-nitrophenyl-2aλ⁴,3-dithia-1,2-diaza-5*H*-

* Components further weakly split.

cyclopent[*cd*]indene [2c] (2 mmol) in dimethylformamide (150 ml), and the mixture was heated at 60 °C for 2 h. Work-up (procedure B) gave 6,7-*dihydro*-3-*methyl*-2-*p*-*nitrophenyl*-2aλ^4-*thia*-1,2,3-*triaza*-5H-*cyclopent*[cd]*indene* (255 mg, 42%), deep red needles from benzene–cyclohexane, m.p. 244—246.5 °C (Found: C, 55.7; H, 4.7; N, 18.6. $C_{14}H_{14}N_4O_2S$ requires C, 55.6; H, 4.7; N, 18.5%); *m/e* 302 (M^+); $\lambda_{max.}$* 484, 358br, 288, and 238 nm; δ † 2.15 (2 H, m, 6-H_2), 2.85 (2 H, m, 5-H_2), 3.05 (2 H, m, 7-H_2), 3.75 (3 H, NMe), 7.58 and 7.67 (2 H, 2 *o*-protons of 2-Ar), 7.97 (1 H, 4-H), and 8.15 and 8.24 (2 H, 2 *m*-protons of 2-Ar).

Methylation of 1-*Phenyl*-6,6aλ^4-*dithia*-1,2-*diazapentalenes*: *Preparation of* 5-(2-*Methylthiovinyl*)-2-*phenyl*-1,2,3-*thiadiazolium Fluorosulphonates*.—The following general procedure was used. Methyl fluorosulphonate (0.8 ml, 10 mmol) was added to a solution of the 1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (5 mmol) in dichloromethane (25 ml), and the mixture was kept at room temperature for 7 h. Ether (500 ml) was then added, whereupon a red oil separated from solution. The ether layer was decanted off, the oil was dissolved in acetonitrile (25 ml), and the solution was filtered. Gradual addition of ether (500 ml) caused the fluorosulphonate to crystallise. The salt was filtered off, washed with ether, and dried *in vacuo*. The following salts were obtained: 5-(2-*methylthiovinyl*)-2-*phenyl*-1,2,3-*thiadiazolium fluorosulphonate* (13) (1.12 g, 71%) [from 1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (7)], reddish brown needles from acetonitrile (ether), m.p. 149—151 °C (decomp.), $\lambda_{max.}$‡ (MeOH) 448 nm (log ε 4.46), δ (CF_3CO_2H) 2.62 (3 H, SMe), 6.88 (1 H, d, $J_{1',2'}$ 15.4 Hz, 1′-H), 7.63—7.74 (3 H, m, 2 *m*- + *p*-protons of 2-Ph), 7.80—7.95 (2 H, m, 2 *o*-protons of 2-Ph), 8.39 (1 H, d, $J_{2',1'}$, 15.4 Hz, 2′-H), and 8.90 (1 H, 4-H) (Found: C, 39.9; H, 3.6; N, 8.5. $C_{11}H_{11}FN_2O_3S_3$ requires C, 39.5; H, 3.3; N, 8.4%); 4-*methyl*-5-(1-*methyl*-2-*methylthiovinyl*)-2-*phenyl*-1,2,3-*thiadiazolium fluorosulphonate* (14) (1.76 g, 97%) [from 3,4-dimethyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (8)], red prisms from acetonitrile (ether), m.p. 136—138.5 °C, $\lambda_{max.}$ (MeOH) 460 (log ε 4.45), 323vbr (3.51), and 226br,infl nm (3.91), δ(CF_3CO_2H) 2.72 (3 H, d, $J_{1'\text{-Me},2'}$ 1.2 Hz, 1′-Me), 2.92 (3 H, SMe), 3.14 (3 H, 4-Me), 7.65—7.76 (3 H, m, 2 *m*- + *p*-protons of 2-Ph), 7.72 (1 H, 2′-H), and 7.90—8.02 (2 H, m, 2 *o*-protons of 2-Ph) (Found: C, 42.7; H, 4.3; N, 7.5. $C_{13}H_{15}FN_2O_2S_3$ requires C, 43.1; H, 4.2; N, 7.7%); 4,5,6,7-*tetrahydro*-7-*methylthiomethylene*-2-*phenyl*-1,2,3-*benzothiadiazolium fluorosulphonate* (15) (1.64 g, 88%) [from 6,7-dihydro-2-phenyl-2aλ^4,3-dithia-1,2-diaza-5*H*-cyclopent[*cd*]indene (9)], red plates from acetonitrile (ether), m.p. 127—129.5 °C, $\lambda_{max.}$‡ (MeOH) 475 (log ε 4.30) and 339vbr nm (3.63), δ(CF_3CO_2H) 2.24 (2 H, quint, 5-H_2), 2.93 (3 H, SMe), 3.03 (2 H, t, 6-H_2), 3.43 (2 H, t, 4-H_2), 7.65—7.72 (3 H, m, 2 *m*- + *p*- protons of 2-Ph), 7.71 (1 H, 1′-H), and 7.90—8.04 (2 H, m, 2 *o*-protons of 2-Ph) (Found: C, 44.6; H, 4.1; N, 7.4. $C_{14}H_{15}FN_2O_3S_3$ requires C, 44.9; H, 4.0; N, 7.5%).

Methylation of 1-phenyl-5-t-butyl-6,6aλ^4-dithia-1,2-diazapentalene (10) (reaction time 13 h) gave a red oil (990 mg) whose ^{1}H n.m.r. spectrum (CF_3CO_2H) showed it to be a 5 : 2 mixture of the salt (16) [δ 1.49 (9 H, Bu^t), 2.66 (3 H, SMe), and 9.09 (1 H, 4-H)] and a second salt [(17) or (18)][δ 1.67 (9 H, Bu^t), 4.27 (3 H, NMe), and 8.59 (1 H, 1′-H)]. [The remaining signals from the salts (16) and (17) or (18) consisted of a multiplet (δ 7.25—8.07).]

Reaction of 5-(2-*Methylthiovinyl*)-2-*phenyl*-1,2,3-*thiadiazolium Fluorosulphonates with Methylamine: Synthesis of* 6-*Methyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalenes*.— The following general procedure was used. Aqueous methylamine (10 ml) was added to a solution of the 5-(2-methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium fluorosulphonate (2 mmol) in acetonitrile (25 ml) at room temperature. The resulting mixture was diluted with water and extracted with benzene (× 2). The residue from the washed (× 2), dried, and evaporated extracts was chromatographed [silica (40 × 2.2 cm)]. Elution with benzene gave orange eluates, and subsequent elution with benzene–ether (19 : 1) brought through yellow eluates; details are given in each case.

5-(2-*Methylthiovinyl*)-2-*phenyl*-1,2,3-*thiadiazolium fluorosulphonate* (13). The orange eluates contained a trace of an orange solid which was discarded. The yellow eluates afforded 6-methyl-1-phenyl-6aλ^4-thia-1,2,6-triazapentalene (1) (65 mg, 15%).

4-*Methyl*-5-(1-*methyl*-2-*methylthiovinyl*)-2-*phenyl*-1,2,3-*thiadiazolium fluorosulphonate* (14). The orange eluates yielded 3,4-dimethyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (8) (97 mg, 20%), and the yellow eluates gave 3,4,6-trimethyl-1-phenyl-6aλ^4-thia-1,2,6-triazapentalene (2) (197 mg, 40%).

4,5,6,7-*Tetrahydro*-7-*methylthiomethylene*-2-*phenyl*-1,2,3-*benzothiadiazolium fluorosulphonate* (15). The orange eluates yielded 6,7-dihydro-2-phenyl-2aλ^4,3-dithia-1,2-diaza-5*H*-cyclopent[*cd*]indene (9) (18 mg, 3.5%), and the yellow eluates gave 6,7-dihydro-3-methyl-2-phenyl-2aλ^4-thia-1,2,3-triaza-5*H*-cyclopent[*cd*]indene (3) (390 mg, 76%).

The red oil obtained by methylation of 6-methyl-2-t-butyl-6,6aλ^4-dithia-1,2-diazapentalene (10) (5 mmol) was dissolved in acetonitrile (40 ml), and the solution was treated with aqueous methylamine (15 ml). Work-up and chromatography according to the general procedure yielded 6-methyl-2-t-butyl-6,6aλ^4-dithia-1,2-diazapentalene (153 mg, 11%).

Coupling of 1,3,4,6-*Tetra-alkyl*-6aλ^4-*thia*-1,6-*diazapentalenes with Arenediazonium Tetrafluoroborates*.—The following general procedure was used. The arenediazonium tetrafluoroborate (10 mmol unless otherwise stated) in ethanol (50 ml) was added to a solution of the 6aλ^4-thia-1,6-diazapentalene (5 mmol) in ethanol (100 ml), and the resulting mixture was stirred at room temperature for 30 min. The mixture was diluted with water and extracted with benzene, and the extracts were washed with water (× 2), dried, and evaporated. Subsequent work-up varied and is described for each reaction.

1,3,4,6-*Tetramethyl*-6aλ^4-*thia*-1,6-*diazapentalene* (19) [2b] *with* p-*nitrobenzenediazonium tetrafluoroborate*. Chromatography [alumina (30 × 2.8 cm)] with benzene–ether (9 : 1) brought through a purple band as red eluates which yielded 3,4,6-trimethyl-1-*p*-nitrophenyl-6aλ^4-thia-1,2,6-triazapentalene (5) (998 mg, 69%).

4,5-*Dihydro*-1,7-*dimethyl*-7aλ^4-*thia*-1,7-*diaza*-3H-*cyclopent*[cd]*indene* (20) [2b] *with* p-*nitrobenzenediazonium tetrafluoroborate*. Chromatography [alumina (70 × 3.2 cm)] with ether brought through successively yellow eluates, which were discarded, and red eluates which afforded 6,7-dihydro-3-methyl-2-*p*-nitrophenyl-2aλ^4-thia-1,2,3-triaza-5*H*-cyclopent[*cd*]indene (6) (336 mg, 22%).

1,3,4,6-*Tetramethyl*-6aλ^4-*thia*-1,6-*diazapentalene* (19) *with benzenediazonium tetrafluoroborate*. 9 mmol of the fluoroborate were used. Chromatography [alumina (70 × 3.2

* Intensities not determined owing to low solubility.

† Compound sparingly soluble; spectrum recorded by accumulation.

‡ Continuous structureless absorption below 350 nm.

cm)] with benzene–petroleum (1 : 1) gave red eluates which yielded 3,4-dimethyl-1,6-diphenyl-6aλ⁴-thia-1,2,5,6-tetra-azapentalene (21) [1] (137 mg, 8.9%). Subsequent elution with benzene–ether (9 : 1) brought through yellow eluates which afforded 3,4,6-trimethyl-1-phenyl-6aλ⁴-thia-1,2,6-tri-azapentalene (2) (358 mg, 29%).

4,5-Dihydro-1,7-dimethyl-7aλ⁴-thia-1,7-diaza-3H-cyclo-pent[cd]indene (20) *with benzenediazonium tetrafluoroborate.* 9 mmol of the fluoroborate were used. Chromatography [alumina (40 × 3.2 cm)] with benzene gave pale yellow eluates which were discarded, and subsequently purple eluates which yielded 6,7-dihydro-2,3-diphenyl-2aλ⁴-thia-1,2,3,4-tetra-aza-5*H*-cyclopent[*cd*]indene (22) [1] (62 mg, 6.2%).

Coupling of 6,7-Dihydro-3-methyl-2-phenyl-2aλ⁴-thia-1,2,3-triaza-5H-cyclopent[cd]indene (3) *with Benzenediazonium Tetrafluoroborate.*— Benzenediazonium tetrafluoroborate (692 mg, 3.6 mmol) in ethanol (20 ml) was added to a solution of the thiatriazacyclopent[*cd*]indene (3) (515 mg, 2 mmol) in ethanol (60 ml), and the resulting mixture was stirred at room temperature for 30 min. The mixture was worked up according to the general procedure of the preceding four experiments. Chromatography [alumina (80 × 1.8 cm)] of the residue with benzene–petroleum (1 : 1) gave inhomogeneous purple-red eluates which were evaporated, and the residual solid was rechromatographed in the same way. The red eluates yielded 6,7-dihydro-2,3-diphenyl-2aλ⁴-thia-1,2,3,4-tetra-aza-5*H*-cyclopent[*cd*]indene (22) (37 mg, 11.6%).

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