Studies of Heterocyclic Compounds. Part 29.[1] The Formation and Reactions of 5-(2-Chlorovinyl)-2-phenyl-1,2,3-thiadiazolylium Salts: Routes to 6aλ⁴-Thia-1,2,6-triazapentalenes and 6aλ⁴-Thia-6-selena-1,2-diazapentalenes

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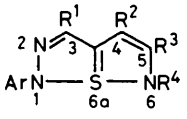
The reaction of 3,4-dimethyl-1-phenyl-6-oxa-6aλ⁴-thia-1,2-diazapentalene and 6,7-dihydro-2-phenyl-5*H*-3-oxa-2aλ⁴-thia-1,2-diazacyclopent[*cd*]indene with phosphoryl chloride in dimethylformamide or 1,2-dichloroethane gave respectively 4-methyl-5-(1-methyl-2-chlorovinyl)-2-phenyl-1,2,3-thiadiazolylium phosphorodichloridate and 7-chloromethylene-4,5,6,7-tetrahydro-2-phenylbenz[*d*][1,2,3]thiadiazolylium phosphorodichloridate as oils which, with perchloric acid, afford the corresponding stable crystalline perchlorates. The mechanism of formation of the phosphorodichloridates is discussed. The phosphorodichloridates reacted with aromatic amines to give in high yield the corresponding 6-aryl-1-phenyl-6aλ⁴-thia-1,2,6-triazapentalenes. With *o*-phenylenediamine reaction took place at one of the amino-groups to give the 6-*o*-aminophenyl-1-phenyl-6aλ⁴-thia-1,2,6-triazapentalenes or at both amino-groups to give 1,2-bis-(1-phenyl-6aλ⁴-thia-1,2,6-triazapentalen-6-yl)benzenes. The perchlorates reacted with 2-amino-4-methylpyridine to give in modest yield 6-(4-methyl-2-pyridyl)-1-phenyl-6aλ⁴-thia-1,2,6-triazapentalenes. The phosphorodichloridates also reacted with methylamine to give the previously reported 6-methyl-1-phenyl-6aλ⁴-thia-1,2,6-triazapentalenes. The phosphorodichloridates reacted with hydroxylamine and *O*-methylhydroxylamine to give, respectively, 6 hydroxy- and 6-methoxy-1-phenyl-6aλ⁴-thia-1,2,6-triazapentalenes. The results of spectral studies of these compounds are discussed in relation to structure. The phosphorodichloridates reacted with *p*-nitrophenylhydrazine and acetylhydrazine to give stable 6-*p*-nitrophenylamino- and 6-acetamido-1-phenyl-6aλ⁴-thia-1,2,6-triazapentalenes. 4-Methyl-5-(1-methyl-2-chlorovinyl)-2-phenyl-1,2,3-thiadiazolylium phosphorodichloridate reacted with sodium hydrogen sulphide to give 3,4-dimethyl-1-phenyl-6,6aλ⁴-dithia-1,2-diazapentalene, together with 3,5-dimethyl-1-phenylpyridazine-4-thione, but 7-chloromethylene-4,5,6,7-tetrahydro-2-phenylbenz-[*d*][1,2,3]thiadiazolylium phosphorodichloridate gave 6,7-dihydro-2-phenyl-5*H*-2aλ⁴,3-dithia-1,2-diazacyclopent[*cd*]indene quantitatively. The phosphorodichloridates reacted with potassium selenosulphate to give 6aλ⁴-thia-6-selena-1,2-diazapentalenes, a new class of four-electron three-centre bonded compound.

We have previously described [2] four routes to 6-methyl-6aλ⁴-thia-1,2,6-triazapentalenes (1; R⁴ = Me). Two[2a] of these routes start from 1-aryl-6,6aλ⁴-dithia-1,2-diazapentalenes (2) and entail the replacement of S-6 by NMe, either directly by the reaction of the dithiadiazapentalenes (2) in dimethylformamide with ethanolic methylamine, or by successive methylation of the dithiadiazapentalenes (2) with methyl fluorosulphonate and treatment of the resulting 2-aryl-5-(2-methylthiovinyl)-1,2,3-thiadiazolylium fluorosulphonates (3) with aqueous methylamine. Preliminary attempts to widen the scope of these syntheses by allowing the 6,6aλ⁴-dithia-1,2-diazapentalenes (2) or the corresponding 1,2,3-thiadiazolylium salts (3) to react with nucleophiles other than methylamine met with limited success. We now report a versatile synthesis of 6aλ⁴-thia-1,2,6-triazapentalenes (1) from two representative oxathiadiazapentalenes (4) and (7). Compounds (4) and (7) are readily obtained [3] in high yield by partial desulphuration of the corresponding dithiadiazapentalenes (5) and (8) with mercury(II) acetate in chloroform.

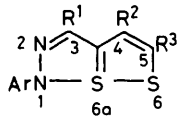
Formation of 5-(2-*Chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium Salts*.—Treatment of the oxathiadiazapentalenes (4) and (7) in 1,2-dichloroethane with phosphoryl chloride gave the 5-(2-chlorovinyl)-2-phenyl-1,2,3-thiadiazolylium phosphorodichloridates (10) and (12) as oils which, when treated with perchloric acid in acetic acid, afforded the stable crystalline perchlorates (11) and (13) in nearly quantitative yield. ^{1}H N.m.r. spectral studies showed that the perchlorate (11) was a 5 : 1 mixture of geometrical isomers [two pairs of methyl signals (see Experimental section)] and that the perchlorate (13) consisted of a single isomer. The chemical shift (δ 7.25) of 2′-H in the major isomer of the salt (11) was identical with that of 1′-H in the salt (13), which suggests that the chlorovinyl group has the same orientation relative to the thiadiazolylium ring in the two salts.

The phosphorodichloridates (10) and (12) are doubtless formed by a mechanism (Scheme 1) similar to that by which Vilsmeier salts are formed from tertiary amides and phosphoryl chloride.[4] The salts (11) and (13) were also obtained in high yield by the addition of phosphoryl chloride to solutions of the oxathiadiazapentalenes (4) and (7) in dimethylformamide followed by treatment of the resulting phosphorodichloridates (10) and (12) in acetic acid with perchloric acid. In dimethylformamide the phosphorodichloridates (10) and (12) could be formed directly from the oxathiadiazapentalenes (4) and (7) (Scheme 1), or indirectly *via* the intermediates (15) (Scheme 2), with the equilibria favouring the formation of the heteroaromatic 1,2,3-thiadiazolylium salts (10) and (12) (*cf.* ref. 4).

Reactions of 5-(2-*Chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium Salts with Nitrogen Nucleophiles*.—The 5-(2-chlorovinyl)-2-phenyl-1,2,3-thiadiazolylium salts (10)—(13) reacted with nitrogen nucleophiles to give a series of 6aλ⁴-thia-1,2,6-triazapentalenes with various types of substituent at N-6. It is unnecessary to prepare the perchlorates (11) and (13); the majority of the reactions were carried out by adding the nucleophile to a solution of the phosphorodichloridate (10)



(1)



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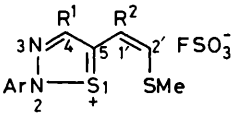
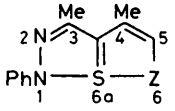
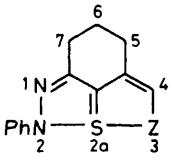


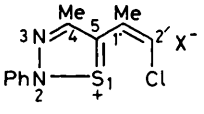
(3)



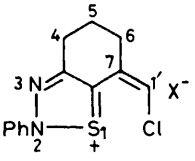
(4) Z = O
(5) Z = S
(6) Z = Se



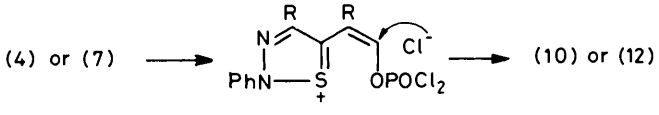
(7) Z = O
(8) Z = S
(9) Z = Se



(10) X = PO_2Cl_2
(11) X = ClO_4



(12) X = PO_2Cl_2
(13) X = ClO_4

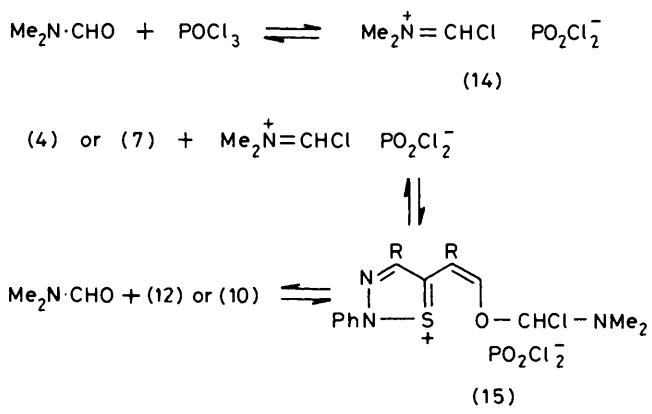


Scheme 1

or (12) prepared immediately beforehand by the addition of phosphoryl chloride to a solution of the oxathiadiazapentalene (4) or (7) in dimethylformamide.

The phosphorodichloridates (10) and (12) reacted with aniline, *p*-methoxyaniline, and *p*-nitroaniline to give the aryl(phenyl)thiatriazapentalenes (16)—(18) and (26)—(28), respectively, in high yield (72—97%). High yields of compounds (16) and (26) were also obtained when the salts (10) and (12) were prepared in 1,2-dichloroethane and allowed to react with aniline. Small amounts of starting material (4) and (7) were recovered from these reactions. Stable charge-transfer complexes were obtained from compound (16) (2 : 3 complex) and compounds (17), (26), and (27) (1 : 1 complexes) with 1,3,5-trinitrobenzene (*cf.* ref. 2*a*).

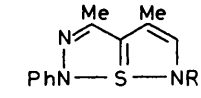
The phosphorodichloridates (10) and (12) reacted with *o*-phenylenediamine (1 : 2 molar ratio) in dimethylformamide to give compounds (19) (48%) and (36) (28%) and compounds (29) (54%) and (37) (36%), respectively. A third, minor product from the salt (10) was identified as the amidine (38) (5.8%). It clearly arises by condensation of the Vilsmeier salt (14) (see Scheme 2) with the primary reaction product (19). A third, minor product from the salt (12) was not fully



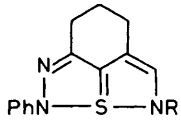
(14)

(15)

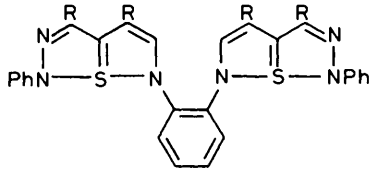
Scheme 2



(16) R = Ph
(17) R = *p*-MeO·C_6H_4
(18) R = *p*-NO_2·C_6H_4
(19) R = *o*-NH_2·C_6H_4
(20) R = 4-Methyl-2-pyridyl
(21) R = Me
(22) R = HO
(23) R = MeO
(24) R = *p*-NO_2·C_6H_4·NH
(25) R = MeCONH



(26) R = Ph
(27) R = *p*-MeO·C_6H_4
(28) R = *p*-NO_2·C_6H_4
(29) R = *o*-NH_2·C_6H_4
(30) R = 4-Methyl-2-pyridyl
(31) R = Me
(32) R = HO
(33) R = MeO
(34) R = *p*-NO_2·C_6H_4·NH
(35) R = MeCONH

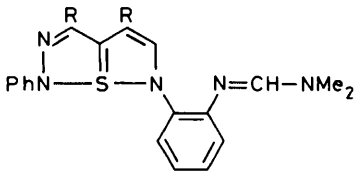


(36) R = Me
(37) R,R = $[CH_2]_3$

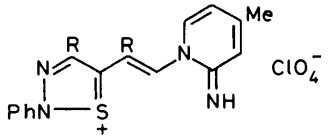
characterised, but its mass spectrum (M^+, 389) indicated that it possesses the amidine structure (39).

The reaction of the perchlorates (11) and (13) in dimethylformamide with 2-amino-4-methylpyridine gave modest yields of the expected products (20) and (30), together with considerable quantities of the corresponding oxathiadiazapentalenes (4) and (7) and the dithiadiazapentalenes (5) and (8), respectively. It is possible that the salts (11) and (13) also react at the ring nitrogen atom of 2-amino-4-methylpyridine to give the salts (40) and (41), which subsequently decompose. We think that the dithiadiazapentalenes (5) and (8) are formed by reaction of the salts (11) and (13) with sulphide ion or an organic equivalent thereof produced by decomposition of the salts (11) and (13), possibly *via* the salts (40) and (41).

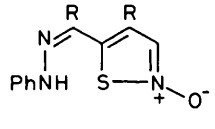
Treatment of the phosphorodichloridates (10) and (12) with aqueous methylamine gave the previously described [2a] thiatriazapentalenes (21) (23%) and (31) (44%). With t-



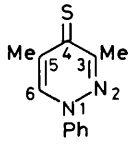
(38) R = Me
(39) R,R = $[CH_2]_3$



(40) R = Me
(41) R,R = $[CH_2]_3$



(42) R = Me
(43) R,R = $[CH_2]_3$

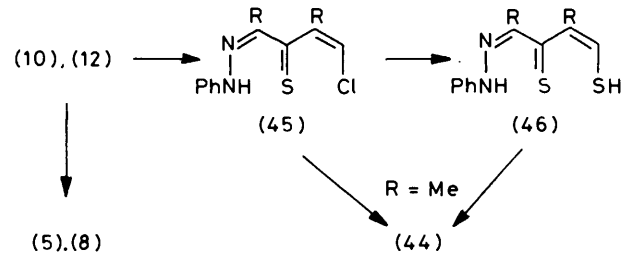


(44)

butylamine, the salts (10) and (12) did not produce any tractable material.

We then set out to prepare 6aλ^4-thia-1,2,6-triazapentalenes with *O*- or *N*-substituents at N-6. The phosphorodichloridates (10) and (12) reacted with hydroxylamine to give the stable *N*-hydroxy-compounds (22) (28%) and (32) (51%), respectively, together with the corresponding oxathiadiazapentalenes (4) (29%) and (7) (35%). The salts (10) and (12) also reacted with *O*-methylhydroxylamine to give the *N*-methoxy-derivatives (23) and (33) nearly quantitatively. The results of spectral studies establish that the products from the reaction of the salts (10) and (12) with hydroxylamine and *O*-methylhydroxylamine have similar structures and thereby exclude the alternative *N*-oxide structures (42) and (43) for the products from the reaction of the salts (10) and (12) with hydroxylamine. Firstly, the i.r. spectra (data in Table 1) of compounds (22) and (32) show strong broad absorption at 3 335 and 3 290 cm^{-1}, respectively, which is characteristic of the OH group, rather than the NH group of aromatic aldehyde phenylhydrazones. [Isothiazole-5-carbaldehyde phenylhydrazone [2b] has ν_{NH} (KBr) at 3 205 cm^{-1}; the absorption band is less intense and much narrower than that assigned to ν_{OH} in compounds (22) and (32).] Secondly, the u.v. spectra (data in Table 1) of the *N*-hydroxy-compounds (22) and (32) are virtually superimposable on those of the corresponding *N*-methoxy-compounds (23) and (33). Finally, the 5-H signals in the ^1H n.m.r. spectra (data in Table 2) of compounds (22), (23), (32), and (33) in [$^2H_6$]dimethyl sulphoxide occur in the narrow range δ 8.01—8.08, and the methyl signals of the *N*-hydroxy-compound (22) (3-Me, δ 2.60; 4-Me, δ 2.41) occur at nearly the same positions as the corresponding methyl signals of the *N*-methoxy-compound (23) (3-Me, δ 2.62; 4-Me, δ 2.40).

The reaction of the phosphorodichloridates (10) and (12) with hydrazine, 1,1-dimethylhydrazine, and phenylhydrazine produced highly coloured products which changed rapidly into



Scheme 3

intractable material. However, the salts (10) and (12) reacted with *p*-nitrophenylhydrazine to give the stable orange-red compounds (24) and (34) in high yield, whose i.r. spectra show ν_{NH} at 3 265 and 3 270 cm^{-1}, respectively [*cf.* isothiazole-5-carbaldehyde *p*-nitrophenylhydrazone: [2b] ν_{NH} (KBr) 3 270 cm^{-1}]. The salts (10) and (12) also reacted with acetylhydrazine to give in high yield the sparingly soluble, stable, orange acetamido-derivatives (25) and (35). In the three-centre bonding scheme the non-bonding orbital concentrates negative charge on the end atoms. The 6-amino-6aλ^4-thia-1,2,6-triazapentalenes are consequently electron-rich hydrazines which will be more than normally susceptible to oxidation. Alternatively, or additionally, the increased electron repulsion between N-6 and its amino-substituent may destabilise the three-centre bond. One or both of these factors may contribute to the instability of the products from the reaction of the salts (10) and (12) with hydrazine, 1,1-dimethylhydrazine, and phenylhydrazine. In contrast, the *p*-nitrophenyl group in compounds (24) and (34) and the acetyl group in compounds (25) and (35) will draw off electron density from N-6. This will reduce the susceptibility of these compounds to oxidation and restore stability to the three-centre bond. Compounds (22)—(25) and (32)—(35) are the first reported nitrogen-containing 1,6,-6aλ^4-triheterapentalenes having substituents other than alkyl, aryl, or heterocyclic groups at N-6(1).

Reactions of 5-(2-*Chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium Salts with Sodium Hydroxide, Sodium Hydrogen Sulphide, and Potassium Selenosulphate.*—Since the majority of the reactions of the salts (10) and (12) with nitrogen nucleophiles produce a small amount of the starting oxathiadiazapentalenes (4) and (7), we investigated the reaction of the salts (10) and (12) in dimethylformamide with aqueous sodium hydroxide. The products (4) and (7) were obtained in unexpectedly low yield [(4), 12%; (7), 25%] and were accompanied by the corresponding dithiadiazapentalenes (5) (4.4%) and (8) (3.5%). The low yield of the oxathiazapentalenes (4) and (7) indicates that the salts (10) and (12) undergo nucleophilic attack at C-2′(C-1′) by hydroxide ion to a minor extent, and that the major reaction, as yet unclarified, takes place with concomitant decomposition of the substrate. Sulphide ion produced by this process generates the dithiadiazapentalenes (5) and (8), as previously discussed. These results suggest that the greater part of the oxathiadiazapentalenes recovered from the reactions of the salts (10) and (12) with nitrogen nucleophiles is material present in the equilibrium (Scheme 2).

The salt (12) in dimethylformamide reacted with aqueous sodium hydrogen sulphide to give the dithiadiazapentalene (8) nearly quantitatively, but the salt (10) gave the dithiadiazapentalene (12) (63%) and the pyridazine-4-thione (44) (31%). Similar results were obtained using sodium sulphide in place of sodium hydrogen sulphide. We propose (Scheme 3) that nucleophilic attack of the salt (10) at C-2′ and the salt (12) at C-1′ by hydrosulphide or sulphide ion gives the dithiadiazapentalenes (5) and (8). Reduction of the salt (10) by hydrosul-

Table 1. U.v. and i.r. spectral data for the 6aλ⁴-thia-6-selena-1,2-diazapentalenes (6) and (9), the 6aλ⁴-thia-1,2,6-triazapentalenes (16)—(19), (22)—(29), and (32)—(38), and the pyridazine-4-thione (44)

Compound	$\lambda_{max.}$/nm (log ε); [$\nu_{max.}$/cm^{-1}]
(6)	514 (4.08), 281infl (4.12), 254 (4.43), 204 (4.27)
(9)	525 (4.07), 300sh (4.10), 279infl (4.12), 250 (4.49), 204 (4.32)
(16)	476 (4.34), 292 (4.18), 251br (4.14), 203 (4.36)
(17)	475 (4.32), 292 (4.22), 228br (4.14), 203 (4.36)
(18)	513 (4.41), 361 (4.05), 284 (4.20), 203 (4.34)
(19)	476 (4.20), 288 (4.10), 235infl (4.17), 210 (4.41); [3 395, 3 325 (NH)]
(22)	436 (4.22), 278 (3.98), 237 (3.93), 200 (4.28); [3 335br s (OH)]
(23)	432 (4.32), 273 (4.02), 241 (4.06), 202 (4.31)
(24) *	517, 501, 373, 327, 220sh, 200; [3 265 (NH)]
(25) *	477sh, 463, 287, 248; [3 178 (NH), 1 650 (C=O)]
(26)	488 (4.35), 295 (4.20), 250br (4.18), 205 (4.41)
(27)	488 (4.34), 295 (4.23), 244br (4.16), 203 (4.43)
(28)	530 (4.43), 361 (4.07), 283br (4.16), 204 (4.37)
(29)	499 (4.30), 289 (4.14), 253sh (4.17), 210 (4.46); [3 430, 3 335 (NH)]
(32)	452 (4.31), 431 (4.33), 278 (3.98), 221sh (4.17), 205 (4.39); [3 290br s (OH)]
(33)	453 (4.34), 434 (4.34), 280 (4.02), 227sh (4.03), 202 (4.41)
(34)	527 (4.31), 499 (4.34), 376 (4.24), 329 (4.21), 225 (4.20), 200 (4.49); [3 270 (NH)]
(35) *	479, 459, 289, 250; [3 198 (NH), 1 646 (C=O)]
(36)	470 (4.57), 291 (4.36), 245 (4.43), 205 (4.58)
(37)	482 (4.55), 294 (4.40), 247 (4.41), 207 (4.59)
(38)	476 (4.30), 290infl (4.23), 247br (4.30), 223infl (4.34), 203 (4.38)
(44)	391 (4.54), 251 (3.69), 203 (4.18)

* Log ε not determined owing to low solubility.

phide or sulphide ion proceeds at a similar rate to nucleophilic attack and gives the intermediate (45; R = Me) which cyclises (loss of hydrogen chloride) to give the pyridazine-4-thione (44) directly, or is converted into the intermediate (46; R = Me) which cyclises (loss of hydrogen sulphide) to give compound (44). Reduction of the salt (12) would give successively the intermediates (45; R,R = $[CH_2]_3$) and (46; R,R = $[CH_2]_3$), neither of which is able to cyclise to a pyridazine-4-thione. Since the dithiadiazapentalene (8) is produced nearly quantitatively, nucleophilic attack of the salt (12) must be very much faster than reduction.

Treatment of the salts (10) and (12) in dimethylformamide with aqueous potassium selenosulphate (*cf.* ref. 5) gave the purple compounds (6) and (9), the first members of the 6aλ⁴-thia-6-selena-1,2-diazapentalene system to be reported.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. U.v./visible absorption spectral data are for solutions in cyclohexane, unless otherwise stated. I.r. spectra refer to solids dispersed in KBr discs. ^{1}H N.m.r. spectra were determined at 100 MHz for 0.4M-solutions in deuteriochloroform, unless otherwise indicated, with tetramethylsilane as internal reference. δ Values refer to singlet absorptions, unless otherwise stated, and *J* values were measured on the 100 Hz scale. Solutions were dried over sodium sulphate and concentrated at reduced pressure. Column chromatography was carried out with alumina (activity II; pH *ca.* 9.5; 100—200 mesh), unless otherwise stated. Solvent mixtures are described in ratios by volume. Light petroleum was of boiling range 40—60 °C.

Table 2. ^{1}H N.m.r. spectral data for the 6aλ⁴-thia-6-selena-1,2-diazapentalenes (6) and (9), the 6aλ⁴-thia-1,2,6-triazapentalenes (16), (17), (19), (20), (22)—(27), (29), (30), and (32)—(38), and the pyridazine-4-thione (44)

Compd.[a]	δ Values (*J* in Hz)
(6)	2.88 (3 H, 3-Me), 2.94 (3 H, d, 4-Me), 7.24—7.50 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.73—7.85 (2 H, m, 2 *o*-protons of 1-Ph), 10.17 (1 H, q, 5-H); $J_{4\text{-Me},5}$ 0.9
(9)	2.05 (2 H, quint, 6-H_2), 3.08 (4 H, t, 5- and 7-H_2), 7.20—7.46 (3 H, m, 2 *m*- + *p*-protons of 2-Ph), 7.70—7.84 (2 H, m, 2 *o*-protons of 2-Ph), 10.02 (1 H, t, 4-H); $J_{4,5\text{-}H_2}$ 0.7
(16)	2.55 (3 H, d, 4-Me), 2.78 (3 H, 3-Me), 6.92—7.38 (8 H, m, 6-Ph + 2 *m* + *p*-protons of 1-Ph), 7.59—7.69 (2 H, m, 2 *o*-protons of 1-Ph), 7.98 (1 H, q, 5-H); $J_{4\text{-Me},5}$ 0.5
(17) [b]	2.52 (3 H, d, 4-Me), 2.77 (3 H, 3-Me), 3.76 (3 H, OMe), 6.84 and 6.93 (2 H, 2 *m*-protons of 6-Ar), 6.99—7.68 (5 H, m, 1-Ph), 7.14 and 7.23 (2 H, 2 *o*-protons of 6-Ar), 7.90 (1 H, q, 5-H); $J_{4\text{-Me},5}$ 0.5
(19)	2.62 (3 H, d, 4-Me), 2.82 (3 H, 3-H), 4.16 (2 H, br, NH_2), 6.75—7.70 (9 H, m, 1-Ph + 6-Ar), 8.06 (1 H, q, 5-H); $J_{4\text{-Me},5}$ 0.5
(19) [c]	2.63 (3 H, d, 4-Me), 2.79 (3 H, 3-Me), 5.12 (2 H, NH_2), 6.58—7.52 (9 H, m, 1-Ph + 6-Ar), 8.33 (1 H, q, 5-H); $J_{4\text{-Me},5}$ 0.5
(20)	2.43 (3 H, 4-Me of pyridine ring), 2.65 (3 H, d, 4-Me), 2.89 (3 H, 3-Me), 6.88 (1 H, d,[d] 5-H of pyridine ring), 7.02—7.83 (6 H, m, 1-Ph + 3-H of pyridine ring), 8.29 (1 H, d,[d] 6-H of pyridine ring), 8.76 (1 H, 5-H); $J_{4\text{-Me},5}$ 0.5, $J_{6,5}$ (pyridine ring) 5.0
(22) [c]	2.41 (3 H, 4-Me), 2.60 (3 H, 3-Me), 7.00—7.40 (5 H, m, 1-Ph), 8.03 (1 H, 5-H), 11.71 (1 H, br, OH)
(23)	2.36 [e] (3 H, 4-Me), 2.62 (3 H, 3-Me), 4.10 (3 H, OMe), 6.87—7.47 (5 H, m, 1-Ph), 7.85 (1 H, br,[e] 5-H)
(23) [c]	2.40 [e] (3 H, 4-Me), 2.62 (3 H, 3-Me), 4.07 (3 H, OMe), 6.94—7.40 (5 H, m, 1-Ph), 8.08 (1 H, br,[e] 5-H)
(24) [b,c,f]	2.36 [e] (3 H, 4-Me), 2.56 (3 H, 3-Me), 6.87—7.36 (5 H, m, 1-Ph), 7.07 and 7.16 (2 H, 2 *o*-protons of 6-Ar), 7.90 [e] (1 H, 5-H), 8.07 and 8.16 (2 H, 2 *m*-protons of 6-Ar), 11.10 (1 H, NH)
(25) [c]	2.06 (3 H, COMe), 2.50 (3 H, 4-Me), 2.70 (3 H, 3-Me), 6.92—7.66 (5 H, m, 1-Ph), 8.10 (1 H, 5-H), 11.80 (1 H, v br, NH)
(26)	2.05 (2 H, quint, 6-H_2), 2.77 (2 H, t, 5-H_2), 3.01 (2 H, t, 7-H_2), 6.92—7.40 (8 H, m, 6-Ph + 2 *m*- + *p*-protons of 1-Ph), 7.55—7.66 (2 H, m, 2 *o*-protons of 1-Ph), 8.12 (1 H, 4-H)
(27) [b]	2.09 (2 H, quint, 6-H_2), 2.80 (2 H, t, 5-H_2), 3.04 (2 H, t, 7-H_2), 3.80 (3 H, OMe), 6.88 and 6.97 (2 H, 2 *m*-protons of 6-Ar), 6.88—7.64 (5 H, m, 1-Ph), 7.20 and 7.29 (2 H, 2 *o*-protons of 6-Ar), 8.12 (1 H, 4-H)
(29)	2.07 (2 H, quint, 6-H_2), 2.78 (2 H, t, 5-H_2), 3.00 (2 H, t, 7-H_2), 4.30 (2 H, br, NH_2), 6.65—7.56 (9 H, m, 1- + 6-Ar), 8.19 (1 H, 4-H)
(29) [c]	2.02 (2 H, quint, 6-H_2), 2.81 (2 H, t, 5-H_2), 2.97 (2 H, t, 7-H_2), 5.25 (2 H, NH_2), 6.52—7.55 (9 H, m, 1- + 6-Ar), 8.42 (1 H, 4-H)
(30)	2.11 (2 H, quint, 6-H_2), 2.41 (3 H, 4-Me of pyridine ring), 2.85 (2 H, t, 5-H_2), 3.08 (2 H, t, 7-H_2), 6.85 (1 H, d,[d] 5-H of pyridine ring), 6.98—7.74 (6 H, m, 2-Ph + 3-H of pyridine ring), 8.26 (1 H, d,[d] 6-H of pyridine ring), 8.90 (1 H, 4-H); $J_{6,5(\text{pyridine ring})}$ 5.2

Table 2 (*continued*)

Compd.[a]	δ Values (*J* in Hz)
(32)[c]	1.93 (2 H, quint, 6-H_2), 2.58 (2 H, t, 5-H_2), 2.85 (2 H, t, 7-H_2), 6.88—7.50 (5 H, m, 2-Ph), 8.01 (1 H, 4-H), 11.60 (1 H, OH)
(33)	1.97 (2 H, quint, 6-H_2), 2.54 (2 H, t, 5-H_2), 2.89 (2 H, t, 7-H_2), 4.06 (3 H, OMe), 6.87—7.43 (5 H, m, 2-Ph), 7.88 (1 H, 4-H)
(33)[c]	1.92 (2 H, quint, 6-H_2), 2.56 (2 H, t, 5-H_2), 2.85 (2 H, t, 7-H_2), 4.00 (3 H, OMe), 6.94—7.37 (5 H, m, 2-Ph), 8.05 (1 H, 4-H)
(34)[b,c,f]	1.93 (2 H, quint, 6-H_2), 2.58 (2 H, t, 5-H_2), 2.84 (2 H, t, 7-H_2), 6.87—7.36 (5 H, m, 2-Ph), 7.08 and 7.17 (2 H, 2 *o*-protons of 6-Ar), 7.92 (1 H. 4-H), 8.11 and 8.20 (2 H, 2 *m*-protons of 6-Ar), 11.18 (1 H, NH)
(35)[c,g]	2.00 (2 H, quint, 6-H_2), 2.03 (3 H, COMe), 2.92 (2 H, t, 7-H_2), 6.95—7.43 (5 H, m, 2-Ph), 8.12 (1 H, 4-H), 11.50 (1 H, v br, NH)
(36)	2.42 (6 H, d, 4- + 4′-Me), 2.67 (6 H, 3- + 3′-Me), 6.97—7.50 [14 H, m, 1-Ph + 1′-Ph + 6(6′)-Ar], 7.91 (2 H, q, 5- + 5′-H); $J_{4(4')\text{-Me},5(5')}$ 0.5
(37)	1.89 (4 H, quint, 6 + 6′-H_2), 2.66 (4 H, t, 5- + 5′-H_2), 2.87 (4 H, t, 7- + 7′-H_2), 6.95—7.41 [14 H, m, 2-Ph + 2′-Ph + 3(3′)-Ar], 8.11 (2 H, 4- + 4′-H)
(38)	2.61 (3 H, d, 4-Me), 2.84 (3 H, 3-Me), 2.84 (6 H, br, NMe_2), 6.85—7.70 (10 H, 1-Ph + 6-Ar + N=CH), 8.34 (1 H, q, 5-H); $J_{4\text{-Me},5}$ 0.5
(44)	2.42 (3 H, d, 5-Me), 2.74 (3 H, 3-Me), 7.54—7.84 (5 H, m, 1-Ph), 8.19 (1 H, q, 6-H); $J_{5\text{-Me},6}$ 0.7

[a] δ and *J* Values for compounds (18) and (28) not obtained owing to low solubility. [b] Signals assigned to the pairs of *o*- and *m*-protons of the *p*-substituted phenyl group are the four most intense signals in the AA′BB′ pattern. [c] In [$^2H_6$]dimethyl sulphoxide. [d] Components further split. [e] Weakly split. [f] At +100 °C. [g] 5-H_2 signal obscured by solvent.

Ether denotes diethyl ether. Dimethylformamide was dried over powdered calcium hydride for *ca.* 1 week and then distilled at *ca.* 15 mmHg. 1,2-Dichloroethane was boiled over phosphoric anhydride for 1 h, distilled, and redistilled. Perchloric acid refers to 70—72% (w/w) perchloric acid. Aqueous methylamine was a 25—30% (w/v) solution. Reference to ' recovery of starting material (4) or (7) ' indicates that compound from which the salts in the preparation were prepared.

Preparation of the 5-(2-*Chlorovinyl*)-1,2,3-*thiadiazolylium Perchlorates* (11) *and* (13) (*with R. Walker*).—The following general procedures were used.

Procedure A. Phosphoryl chloride (1.0 ml, 11 mmol) was added to a solution of the 6-oxa-6aλ⁴-thia-1,2-diazapentalene (10 mmol) in 1,2-dichloroethane (20 ml) at 50 °C, and the resulting solution was kept at 50 °C for 10 min. Addition of ether to the cooled solution precipitated a brown oil. The supernatant liquid was poured off, and the residual oil was washed with ether (×2) before being dissolved in acetic acid (50 ml). Perchloric acid (2.54 ml, 30 mmol) was added to the resulting solution. Gradual addition of ether precipitated the crystalline perchlorate which was filtered off, washed with ether (500 ml), and dried *in vacuo* over potassium hydroxide.

Procedure B. This was identical with procedure A, except that the scale was halved, and dimethylformamide (10 ml) was used in place of 1,2-dichloroethane.

3,4-Dimethyl-6-oxa-6aλ⁴-thia-1,2-diazapentalene (4)[3] gave 4-*methyl*-5-(1-*methyl*-2-*chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium perchlorate* (11) [(A), 3.365 g (96%); (B), 1.21 g (69%)] as a 5 : 1 mixture (n.m.r.) of isomers; major isomer: δ(CF_3CO_2H) 2.46 (3 H, d, $J_{1'\text{-Me},2'\text{-H}}$ 1.6 Hz, 1′-Me), 2.94 (3 H, 4-Me), and 7.25 (1 H, q, $J_{2'\text{-H},1'\text{-Me}}$ 1.6 Hz, 2′-H); minor isomer: δ(CF_3CO_2H) 2.53 (3 H, d, $J_{1'\text{-Me},2'\text{-H}}$ 1.6 Hz, 1′-H) and 3.03 (3 H, 4-Me). The signals from 2-Ph of both isomers and from 2′-H of the minor isomer consisted of a multiplet at δ 7.63—8.04. Recrystallisation from acetic acid gave the major isomer as yellow prisms, m.p. 115—117 °C (Found: C, 41.3; H, 3.7; N, 7.8. $C_{12}H_{12}Cl_2N_2O_4S$ requires C, 41.0; H, 3.5; N, 8.0%); $\lambda_{max.}$ (MeOH) 372 (log ε 4.08), 245sh (3.63), and 208 nm (4.15).

6,7-Dihydro-2-phenyl-5*H*-3-oxa-2aλ⁴-thia-1,2-diazacyclopent[*cd*]indene (7)[3] gave 7-*chloromethylene*-4,5,6,7-*tetrahydro*-2-*phenylbenz*[d][1,2,3]*thiadiazolylium perchlorate* (13) [(A), 3.54 g (97.5%); (B), 1.74 g (96%)], as pale yellow needles from acetic acid, m.p. 201—203 °C (decomp.) (Found: C, 43.0; H, 3.3; N, 7.8. $C_{13}H_{12}Cl_2N_2O_4S$ requires C, 43.0; H, 3.3; N, 7.8%); $\lambda_{max.}$ (MeOH) 397 (log ε 4.21), 240sh (3.75), and 207 nm (4.12); δ(CF_3CO_2H) 2.24 (2 H, quint, 5-H_2), 2.99 (2 H, t,* 6-H_2), 3.47 (2 H, t, 4-H_2), 7.25 (1 H, t, $J_{1'\text{-H},6\text{-}H_2}$ 1.5 Hz, 1′-H), 7.64—7.80 (3 H, m, 2*m*- + *p*-protons of 2-Ph), and 7.99—8.10 (2 H, m, 2*o*-protons of 2-Ph).

Reactions of the 5-(2-*Chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium Phosphorodichloridates* (10) *and* (12) *in Dimethylformamide with Nitrogen Nucleophiles: Synthesis of* 6aλ⁴-*Thia*-1,2,6-*triazapentalenes*.—Solutions of the phosphorodichloridates (10) and (12) in dimethylformamide were prepared by the following general procedure. Phosphoryl chloride (0.5 ml, 5.5 mmol) was added to a stirred solution of the oxathiadiazapentalene (4) (1.16 g, 5 mmol) or (7) (1.22 g, 5 mmol) in dimethylformamide (25 ml) at 50 °C, and the resulting solution was stirred at 50 °C for 10 min. Subsequent procedure varied and is described for each reaction.

Charge-transfer complexes of 6aλ⁴-thia-1,2,6-triazapentalenes with 1,3,5-trinitrobenzene were prepared from the base (1 mmol) and 1,3,5-trinitrobenzene (1 mmol, unless otherwise stated) in boiling ethanol (35 ml, unless otherwise stated). The solid which crystallised and was filtered from the cooled solution was the pure complex [from compounds (17) and (27)] or a mixture of the complex and the base [from compounds (16) and (26)]. The mixtures were discarded; concentration of the mother liquors gave the pure complexes of compounds (16) and (26). The composition (in parentheses) was obtained from the elemental analysis and checked by integration of the ^1H n.m.r. spectrum (solvent $CDCl_3$).

3,4-*Dimethyl*-1,6-*diphenyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (16). Aniline (0.91 ml, 10 mmol) was added to a solution of the phosphorodichloridate (10) in dimethylformamide at 50 °C, and the resulting solution was stirred at 50 °C for 10 min. The cooled solution was poured into water, and the mixture was extracted with benzene. The extracts were washed with water (×6), dried, and evaporated, and the residue was chromatographed [alumina (40 × 3.2 cm)]. Elution with benzene gave red eluates which afforded 3,4-*dimethyl*-1,6-*diphenyl*-6aλ⁴-*thia*-1,2,6-*triazapentalene* (1.36 g, 88%), as red needles from cyclohexane, m.p. 128—129 °C (Found: C, 70.5; H, 5.7; N, 13.7; S, 10.2. $C_{18}H_{17}N_3S$ requires C, 70.3; H, 5.6; N, 13.7; S, 10.4%), *m*/*z* 307 (M^+). The 1,3,5-*trinitrobenzene complex* (2 : 3) (15%) was obtained from (16) (1 mmol), 1,3,5-trinitrobenzene (1.5 mmol), and ethanol (25 ml) as purple needles, m.p. 116—118 °C (Found: C, 51.5; H, 3.4; N, 16.7. $C_{54}H_{43}N_{15}O_{18}S_2$ requires C, 51.7; H, 3.5; N, 16.8%). Subsequent elution with benzene–ether (4 : 1) brought through yellow eluates from which starting material (4) (11%) was recovered.

When the reaction was carried out with 1,2-dichloroethane (25 ml) as solvent, the thiatriazapentalene (16) (1.288 g, 84%) and starting material (4) (9.5%) were obtained.

* Components broadened from coupling with 1′-H.

6,7-*Dihydro*-2,3-*diphenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (26). The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10), and gave 6,7-*dihydro*-2,3-*diphenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (1.54 g, 97%), as red cubes from cyclohexane, m.p. 146—147 °C (Found: C, 71.0; H, 5.3; N, 13.2; S, 10.0. $C_{19}H_{17}N_3S$ requires C, 71.4; H, 5.4; N, 13.2; S, 10.0%), *m/z* 319 (M^+). The 1,3,5-*trinitrobenzene complex* (1 : 1) (13%) of (26) formed black prisms, m.p. 126.5—127.5 °C (Found: C, 56.3; H, 3.6; N, 16.0. $C_{25}H_{20}N_6O_6S$ requires C, 56.4; H, 3.8; N, 15.8%).

When the reaction was carried out with 1,2-dichloroethane (25 ml) as solvent, the thiatriazapentalene (26) (1.507 g, 95%) was obtained.

6-p-*Methoxyphenyl*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (17). A solution of *p*-methoxyaniline (1.23 g, 10 mmol) in dimethylformamide (10 ml) was added to a stirred solution of the phosphorodichloridate (10) in dimethylformamide at 50 °C, and the resulting solution was stirred at 50 °C for 10 min. Work-up according to the procedure of the two preceding experiments gave 6-p-*methoxyphenyl*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (1.42 g, 84%), as red needles from cyclohexane, m.p. 115—116 °C (Found: C, 67.7; H, 5.7; N, 12.4. $C_{19}H_{19}N_3OS$ requires C, 67.6; H, 5.7; N, 12.5%), *m/z* 337 (M^+). Starting material (4) (5%) was recovered. The 1,3,5-*trinitrobenzene complex* (1 : 1) (85%) of (17) formed black prisms, m.p. 135—136 °C (Found: C, 54.8; H, 3.9; N, 15.1. $C_{25}H_{22}N_6O_7S$ requires C, 54.5; H, 4.0; N, 15.3%).

6,7-*Dihydro*-3p-*methoxyphenyl*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (27). The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10), and afforded 6,7-*dihydro*-3-p-*methoxyphenyl*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*-[cd]*indene* (1.60 g, 92%), as red needles from cyclohexane, m.p. 131—132.5 °C (Found: C, 68.6; H, 5.3; N, 12.0. $C_{20}H_{19}N_3OS$ requires C, 68.7; H, 5.5; N, 12.0%), *m/z* 349 (M^+). Starting material (7) (4%) was recovered. The 1,3,5-*trinitrobenzene complex* (1 : 1) (88%) of (27) formed black prisms from ethanol (45 ml), m.p. 155.5—157.5 °C (Found: C, 55.6; H, 3.9; N, 14.9. $C_{26}H_{22}N_6O_7S$ requires C, 55.5; H, 3.9; N, 14.9%).

3,4-*Dimethyl*-6-p-*nitrophenyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (18). A solution of *p*-nitroaniline (1.38 g, 10 mmol) in dimethylformamide (25 ml) was added to a solution of the phosphorodichloridate (10) in dimethylformamide at 50 °C, and the mixture was stirred at 50 °C for 1 h. The cooled solution was diluted with water and extracted with benzene, and the extracts were washed with water (×6), dried, and evaporated. Crystallisation of the residue from benzene gave 3,4-*dimethyl*-6-p-*nitrophenyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (1.075 g) as brown needles, m.p. 215—216 °C (Found: C, 61.4; H, 4.6; N, 15.8. $C_{18}H_{16}N_4O_2S$ requires C, 61.4; H, 4.6; N, 15.9%), *m/z* 352 (M^+). The mother liquors were concentrated and chromatographed [alumina (60 × 2.7 cm)]. Elution with benzene gave successively homogeneous purple eluates and two-component (t.l.c.) red eluates, and subsequent elution with benzene–ether (4 : 1) brought through homogeneous yellow eluates. Rechromatography [alumina (40 × 3.2 cm)] of the residue from the two-component eluates gave homogeneous purple benzene eluates and yellow benzene–ether (4 : 1) eluates. The combined purple eluates yielded more (201 mg) of the thiatriazapentalene [total yield, 1.276 g (72%)]. Starting material (4) (17%) was recovered from the yellow benzene–ether eluates.

6,7-*Dihydro*-3-p-*nitrophenyl*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (28). The reaction was carried out according to the procedure of the preceding experiment, with the phosphorodichloridate (12) in place of (10). Chromatography [alumina (25 × 3.7 cm)] with benzene gave purple eluates which afforded 6,7-*dihydro*-3-p-*nitrophenyl*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (1.56 g, 86%), as brown prisms from benzene, m.p. 217—218 °C (Found: C, 62.4; H, 4.4; N, 15.1. $C_{19}H_{16}N_4O_2S$ requires C, 62.6; H, 4.4; N, 15.4%), *m/z* 364 (M^+). Continued elution with benzene–ether (4 : 1) brought through yellow eluates from which starting material (7) (11%) was recovered.

6-o-*Aminophenyl*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (19) *and* o-*bis*-(3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalen*-6-*yl*)*benzene* (36). A solution of *o*-phenylenediamine (1.08 g, 10 mmol) in dimethylformamide (10 ml) was added to a solution of the phosphorodichloridate (10) in dimethylformamide at 50 °C and the resulting solution was stirred at 50 °C for 10 min, cooled, and poured into water. The mixture was extracted with benzene, and the residue from the washed (×6), dried, and evaporated extracts was chromatographed [alumina (40 × 3.2 cm)]. Elution with benzene gave deep red eluates which afforded o-*bis*-(3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalen*-6-*yl*)*benzene* (373 mg, 28%), deep red prisms from hexane, m.p. 200—202 °C (Found: C, 67.0; H, 5.3; N, 15.6. $C_{30}H_{28}N_6S_2$ requires C, 67.1; H, 5.3; N, 15.7%), *m/z* 536 (M^+). Continued elution with benzene–ether (1 : 1) gave red eluates which were evaporated, and the two-component residue was rechromatographed [silica (30 × 3.7 cm)]. Elution with benzene gave red eluates which afforded 6-o-*aminophenyl*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (773 mg, 48%), red prisms from cyclohexane, m.p. 182—184 °C (Found: C, 66.8; H, 5.7; N, 17.5. $C_{18}H_{18}N_4S$ requires C, 67.1; H, 5.6; N, 17.4%), *m/z* 322 (M^+). Subsequent elution with methanol brought through orange eluates which yielded 3,4-*dimethyl*-6-o-*dimethylaminomethyleneaminophenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (38) (110 mg, 5.8%), red prisms from cyclohexane, m.p. 160—161 °C (Found: C, 66.6; H, 6.3; N, 18.6. $C_{21}H_{23}N_5S$ requires C, 66.8; H, 6.2; N, 18.6%), *m/z* 377 (M^+).

3-o-*Aminophenyl*-6,7-*dihydro*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (29) *and* o-*bis*-(6,7-*dihydro*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*inden*-3-*yl*)*benzene* (37). The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10). Chromatography gave successively o-*bis*-(6,7-*dihydro*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*inden*-3-*yl*)*benzene* (505 mg, 36%), red prisms from hexane, m.p. 207—209 °C (Found: C, 68.3; H, 5.0; N, 14.9. $C_{32}H_{28}N_6S_2$ requires C, 68.5; H, 5.0; N, 15.0%), *m/z* 560 (M^+); 3-o-*aminophenyl*-6,7-*dihydro*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (637 mg, 54%), brown needles from cyclohexane, m.p. 152—153.5 °C (Found: C, 68.5; H, 5.6; N, 16.4. $C_{19}H_{18}N_4S$ requires C, 68.2; H, 5.4; N, 16.8%), *m/z* 334 (M^+); and a small quantity of a red compound (*m/z* 389) (from orange methanol eluates) to which we tentatively assign structure (39).

3,4,6-*Trimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (21). Aqueous methylamine (25 ml) was added to a solution of the phosphorodichloridate (10) in dimethylformamide at room temperature. The mixture was stirred at room temperature for 10 min, diluted with water, and extracted with benzene. The benzene extracts were washed with water (×6), dried, and evaporated, and the residue was chromatographed [alumina (40 × 2.7 cm)]. Elution with benzene gave successively red eluates which yielded 3,4-dimethyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (5)[6] (89 mg, 7.2%), and orange eluates which afforded 3,4,6-trimethyl-1-phenyl-6aλ^4-thia-1,2,6-triazapentalene (286 mg, 23%), orange needles from hexane, m.p. 77—78 °C, undepressed on admixture with an authentic sample[2a] (Found: C, 63.3; H, 6.4; N, 17.4. Calc. for $C_{13}H_{15}N_3S$: C, 63.6; H, 6.2; N, 17.1%), *m/z* 245 (M^+). The ^{1}H n.m.r.

spectrum of the thiatriazapentalene (21) was identical with that previously reported.[2a] Continued elution with benzene–ether (4 : 1) brought through yellow eluates from which starting material (4) (3.5%) was recovered.

6,7-*Dihydro*-3-*methyl*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (31). The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10). Chromatography gave successively 6,7-dihydro-2-phenyl-5*H*-2aλ^4,3-dithia-1,2-diazacyclopent[*cd*]-indene (8)[6] (5 mg, identified by t.l.c.), and 6,7-dihydro-3-methyl-2-phenyl-5*H*-2aλ^4-thia-1,2,3-triazacyclopent[*cd*]indene (583 mg, 44%), orange-red needles from hexane, m.p. and mixed m.p. with an authentic sample[2a] 117—118 °C (Found: C, 65.3; H, 5.7; N, 16.7. Calc. for $C_{14}H_{15}N_3S$: C, 65.4; H, 5.9; N, 16.3%), *m/z* 257 (M^+). The ^{1}H n.m.r. spectrum of the thiatriazapentalene (31) was identical with that previously reported.[2a]

6-*Hydroxy*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (22). A solution of hydroxyammonium chloride (3.48 g, 50 mmol) and sodium carbonate (3.18 g, 30 mmol) in water (25 ml) was added to a solution of the phosphorodichloridate (10) in dimethylformamide at room temperature. The mixture was stirred at room temperature for 30 min, diluted with water, and extracted with benzene. The residue from the washed (×6), dried, and evaporated extracts was chromatographed [alumina; activity II–III, pH *ca.* 9.5, 70—230 mesh (30 × 3.2 cm)]. Elution with benzene gave red eluates which yielded 3,4-dimethyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (5) (121 mg, 10%). Continued elution with benzene–ether (4 : 1) gave yellow eluates from which starting material (4) (29%) was recovered. Subsequent elution with ether–methanol (50 : 1) brought through yellow eluates which afforded 6-*hydroxy*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (349 mg, 28%), orange prisms from cyclohexane, m.p. 113—115 °C (Found: C, 58.2; H, 5.3; N, 16.9. $C_{12}H_{13}N_3OS$ requires C, 58.3; H, 5.3; N, 17.0%), *m/z* 247 (M^+).

6,7-*Dihydro*-3-*hydroxy*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (32). The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10). Chromatography gave successively 6,7-dihydro-2-phenyl-5*H*-2aλ^4,3-dithia-1,2-diazacyclopent[*cd*]-indene (8) (48 mg, 3.7%); starting material (7) (35%); and 6,7-*dihydro*-3-*hydroxy*-2-*phenyl*-5H-2aλ^4-*thia*-,2,3-*triazacyclopent*-[cd]*indene* (663 mg, 51%), orange prisms from hexane, m.p. 126—128 °C (Found: C, 60.0; H, 5.0; N, 16.2. $C_{13}H_{13}N_3OS$ requires C, 60.2; H, 5.1; N, 16.2%), *m/z* 259 (M^+).

6-*Methoxy*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (23). A solution of methoxyammonium chloride (4.18 g, 50 mmol) and sodium carbonate (3.18 g, 30 mmol) in water (25 ml) was added to a solution of the phosphorodichloridate (10) in dimethylformamide at room temperature. The mixture was stirred at room temperature for 30 min, then worked up according to the procedure of the preceding two experiments. Chromatography [alumina (10 × 3.7 cm)] with benzene gave yellow eluates which afforded 6-*methoxy*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (1.246 g, 95%), as red prisms from petroleum, m.p. 89—91 °C (Found: C, 59.9; H, 5.9; N, 16.0. $C_{13}H_{15}N_3OS$ requires C, 59.8; H, 5.8; N, 16.1%), *m/z* 261 (M^+).

6,7-*Dihydro*-3-*methoxy*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (33). The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10). Chromatography gave 6,7-*dihydro*-3-*methoxy*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]-*indene* (1.349 g, 99%), as red cubes from petroleum, m.p. 78—80 °C (Found: C, 61.6; H, 5.6; N, 15.4. $C_{14}H_{15}N_3OS$ requires C, 61.5; H, 5.5; N, 15.4%), *m/z* 273 (M^+).

3,4-*Dimethyl*-6-p-*nitrophenylamino*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (24). A solution of *p*-nitrophenylhydrazine (1.53 g, 10 mmol) in dimethylformamide (25 ml) was added to a stirred solution of the phosphorodichloridate (10) in dimethylformamide at 50 °C, and the resulting mixture was stirred at 50 °C for 10 min. Water (250 ml) was added, and the precipitated black solid was filtered off, washed with water, and dried *in vacuo*. Recrystallisation from ethanol gave 3,4-*dimethyl*-6-p-*nitrophenylamino*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (1.364 g) as black prisms, m.p. 185—186 °C (Found: C, 58.8; H, 4.6; N, 19.1. $C_{18}H_{17}N_5O_2S$ requires C, 58.8; H, 4.7; N, 19.1%), *m/z* 367 (M^+). The ethanol mother liquors were evaporated to dryness and the residue was chromatographed [alumina (15 × 3.2 cm)]. Elution with benzene gave purple eluates which were discarded. Continued elution with benzene–ether (4 : 1) gave yellow eluates from which starting material (4) (19%) was recovered. Subsequent elution with ether–methanol (100 : 1) brought through red eluates which yielded a further quantity (48 mg) of compound (24) [total yield, 1.412 g (77%)].

6,7-*Dihydro*-3-p-*nitrophenylamino*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (34). The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10). 6,7-*Dihydro*-3-p-*nitrophenylamino*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*-[cd]*indene* (1.49 g, 79%) was obtained as black prisms from ethanol, m.p. 193—195 °C (Found: C, 59.8; H, 4.4; N, 18.3. $C_{19}H_{17}N_5O_2S$ requires C, 60.1; H, 4.5; N, 18.5%), *m/z* 379 (M^+). Starting material (7) (16.5%) was recovered.

6-*Acetamido*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (25). A solution of acetylhydrazine (1.85 g, 25 mmol) in dimethylformamide (25 ml) was added to a stirred solution of the phosphorodichloridate (10) in dimethylformamide at 50 °C, and the mixture was stirred at 50 °C for 10 min. Water (250 ml) was added, and the precipitated black solid was filtered off, washed with water, and dried *in vacuo*. Recrystallisation from methanol gave 6-*acetamido*-3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-1,2,6-*triazapentalene* (1.018 g) as red spars, m.p. 221—223 °C (decomp.) (Found: C, 58.2; H, 5.6; N, 19.5; S, 10.9. $C_{14}H_{16}N_4OS$ requires C, 58.3; H, 5.6; N, 19.4; S, 11.1%), *m/z* 288 (M^+). Chromatography [alumina (5 × 3.2 cm)] of the residue from the methanol mother liquors gave successively yellow benzene–ether (4 : 1) eluates from which starting material (4) (0.5%) was recovered, and red ether–methanol (25 : 1) eluates which yielded more (201 mg) of compound (25) [total yield, 1.219 g (85%)].

3-*Acetamido*-6,7-*dihydro*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (35). The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10). 3-*Acetamido*-6,7-*dihydro*-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (1.153 g, 77%) was obtained as orange cubes from methanol, m.p. 212 °C (decomp.) (Found: C, 59.7; H, 5.5; N, 18.7; S, 10.3. $C_{15}H_{16}N_4OS$ requires C, 60.0; H, 5.4; N, 18.7; S, 10.7%), *m/z* 300 (M^+). Starting material (7) (1.2%) was recovered.

Reaction of 4-*Methyl*-5-(1-*methyl*-2-*chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium Perchlorate* (11) *with* 2-*Amino*-4-*methylpyridine* (*with R. Walker*).—A solution of 2-amino-4-methylpyridine (1.08 g, 10 mmol) in dimethylformamide (10 ml) was added to a solution of the perchlorate (11) (1.756 g, 5 mmol) in dimethylformamide (50 ml), and the mixture was stirred at 50 °C for 10 min, cooled, and diluted with water (150 ml). The mixture was extracted with benzene (3 × 150 ml), and the extracts were washed with water (8 × 100 ml), dried, and evaporated. The residual red oil was chromatographed [alumina (50 × 2.6 cm)]. Elution with petroleum–benzene (2 : 1) gave red eluates which yielded 3,4-dimethyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (5) (180 mg, 14.5%). Continued

elution with benzene–ether (4 : 1) gave orange eluates which afforded 3,4-*dimethyl*-1-*phenyl*-6-(4-*methyl*-2-*pyridyl*)-6aλ^4-*thia*-1,2,6-*triazapentalene* (20) (352 mg, 22%), red needles from cyclohexane, m.p. 143—144 °C (Found: C, 67.1, H, 5.4; N, 17.3. $C_{18}H_{18}N_4S$ requires C, 67.1; H, 5.6; N, 17.4%), *m/z* 322 (M^+). Subsequent elution with ether brought through yellow eluates which yielded the oxathiadiazapentalene (4) (103 mg, 8.9%).

Reaction of 7-*Chloromethylene*-4,5,6,7-*tetrahydro*-2-*phenylbenz*[d][1,2,3]*thiadiazolylium Perchlorate* (13) *with* 2-*Amino*-4-*methylpyridine* (*with R. Walker*).—The reaction procedure was identical with that of the preceding experiment, with the perchlorate (13) (1.816 g, 5 mmol) in place of (11). Chromatography [alumina (50 × 2.6 cm)] with petroleum–benzene (2 : 1) gave crimson eluates which yielded 6,7-dihydro-2-phenyl-5*H*-2aλ^4,3-dithia-1,2-diazacyclopent[*cd*]indene (8) (182 mg, 14%). Subsequent elution with benzene–ether (2 : 1) and then with ether gave two-component eluates which were evaporated; the residue was rechromatographed [alumina (50 × 2.6 cm)]. Elution with benzene–ether (4 : 1) gave orange-red eluates which afforded 6,7-*dihydro*-3-(4-*methyl*-2-*pyridyl*)-2-*phenyl*-5H-2aλ^4-*thia*-1,2,3-*triazacyclopent*[cd]*indene* (30) (298 mg, 18%), as red needles from cyclohexane, m.p. 162—163 °C (Found: C, 68.1; H, 5.4; N, 16.7. $C_{19}H_{18}N_4S$ requires C, 68.2; H, 5.4; N, 16.8%), *m/z* 334 (M^+). Continued elution with ether brought through yellow eluates which yielded the oxathiadiazapentalene (7) (113 mg, 9.2%).

Reaction of the 5-(2-*Chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium Phosphorodichloridates* (10) *and* (12) *with Sodium Hydroxide*.—Aqueous 2M-sodium hydroxide (12.5 ml) was added to a solution of the phosphorodichloridate (10) or (12) in dimethylformamide which had been prepared according to the general procedure and then cooled to room temperature. The mixture was extracted with benzene, the extracts were washed with water (× 6), dried, and evaporated, and the residue was chromatographed [alumina (40 × 2.7 cm)]. Elution with benzene gave red eluates which afforded the dithiadiazapentalene, and subsequent elution with benzene–ether brought through yellow eluates from which starting material was recovered. The phosphorodichloridate (10) gave 3,4-dimethyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (5) (54 mg, 4.4%) and starting material (4) (144 mg, 12%), and the phosphorodichloridate (12) gave 6,7-dihydro-2-phenyl-5*H*-2aλ^4,3-dithia-1,2-diazacyclopent[*cd*]indene (8) (45 mg, 3.5%) and starting material (7) (305 mg, 25%).

Reaction of 4-*Methyl*-5-(1-*methyl*-2-*chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium Phosphorodichloridate* (10) *with Sodium Hydrogen Sulphide*.—Aqueous 2M-sodium hydrogen sulphide (12.5 ml) was added to a solution of the phosphorodichloridate (10) in dimethylformamide, prepared from the oxathiadiazapentalene (4) (5 mmol) according to the general procedure and then cooled to 0 °C. The mixture was extracted with benzene, and the extracts were washed with water (× 6), dried, and evaporated. Chromatography [alumina (40 × 3.2 cm)] of the residue with benzene gave red eluates which afforded 3,4-dimethyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (5) (781 mg, 63%), as red spars from cyclohexane, m.p. and mixed m.p. with an authentic sample 136—136.5 °C (lit.,[6] 136—137 °C). Compound (5) had the same ^{1}H n.m.r. spectrum and showed the same t.l.c. behaviour on silica [petroleum–benzene (1 : 1)] as an authentic sample. Subsequent elution with benzene–ether (4 : 1) brought through yellow eluates which yielded 3,5-*dimethyl*-1-*phenylpyridazine*-4-*thione* (44) (338 mg, 31%), as golden yellow needles from cyclohexane, m.p. 118.5—120 °C (Found: C, 66.3; H, 5.6; N, 13.0. $C_{12}H_{12}N_2S$ requires C, 66.6; H, 5.6; N, 13.0%), *m/z* 216 (M^+).

When the reaction was carried out with aqueous 2M-sodium sulphide (12.5 ml) in place of aqueous sodium hydrogen sulphide, the dithiadiazapentalene (5) (693 mg, 56%) and the thione (44) (363 mg, 34%) were obtained.

Reaction of 7-*Chloromethylene*-4,5,6,7-*tetrahydro*-2-*phenylbenz*[d][1,2,3]*thiadiazolylium Phosphorodichloridate* (12) *with Sodium Hydrogen Sulphide*.—The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10). Chromatography [alumina (40 × 3.2 cm)] with benzene gave 6,7-dihydro-2-phenyl-5*H*-2aλ^4,3-dithia-1,2-diazacyclopent[*cd*]indene (8) (1.258 g, 97%), as deep red rods from hexane, m.p. and mixed m.p. with an authentic sample 100.5—101.5 °C (lit.,[6] 100—100.5 °C). Compound (8) had the same ^{1}H n.m.r. spectrum and showed the same t.l.c. behaviour on silica [petroleum–benzene (1 : 1)] as an authentic sample.

When the reaction was carried out with aqueous 2M-sodium sulphide (12.5 ml) in place of aqueous sodium hydrogen sulphide, the dithiadiazapentalene (8) (1.212 g, 93%) (from crimson benzene eluates) and starting material (7) (3.3%) [from yellow benzene–ether (4 : 1)] eluates were obtained.

Reaction of 4-*Methyl*-5-(1-*methyl*-2-*chlorovinyl*)-2-*phenyl*-1,2,3-*thiadiazolylium Phosphorodichloridate* (10) *with Potassium Selenosulphate*.—A solution of potassium selenosulphate (2.375 g, 10 mmol) in water (5 ml) at 65 °C was added to a stirred solution of the phosphorodichloridate (10) in dimethylformamide which had been prepared from the oxathiadiazapentalene (4) (5 mmol) according to the general procedure and then cooled to 0 °C. The resulting mixture was diluted with much benzene and water and filtered to remove selenium. The aqueous layer was neutralised with sodium hydrogen carbonate and extracted with benzene (× 4). The combined benzene extracts were washed with water (× 6), dried, and evaporated. Chromatography [alumina (30 × 3.2 cm)] of the residue with benzene gave purple eluates which afforded 3,4-*dimethyl*-1-*phenyl*-6aλ^4-*thia*-6-*selena*-1,2-*diazapentalene* (6), as deep red needles from cyclohexane, m.p. 144.5—146 °C (Found: C, 49.1; H, 4.1; N, 9.4. $C_{12}H_{12}N_2SSe$ requires C, 48.9; H, 4.1; N, 9.5%), *m/z* 296 (M^+). Subsequent elution with benzene–ether (4 : 1) brought through yellow eluates from which starting material (4) (4%) was recovered.

Reaction of 7-*Chloromethylene*-4,5,6,7-*tetrahydro*-2-*phenylbenz*[d][1,2,3]*thiadiazolylium Phosphorodichloridate* (12) *with Potassium Selenosulphate*.—The procedure was identical with that of the preceding experiment, with the phosphorodichloridate (12) in place of (10). 6,7-*Dihydro*-2-*phenyl*-5H-2aλ^4-*thia*-3-*selena*-1,2-*diazacyclopent*[cd]*indene* (9) (1.008 g, 66%) was obtained as deep green prisms from hexane, m.p. 95—97 °C (Found: C, 50.6; H, 3.9; N, 9.1. $C_{13}H_{12}N_2SSe$ requires C, 50.8; H, 3.9; N, 9.1%), *m/z* 308 (M^+). Starting material (7) (5%) was recovered.

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