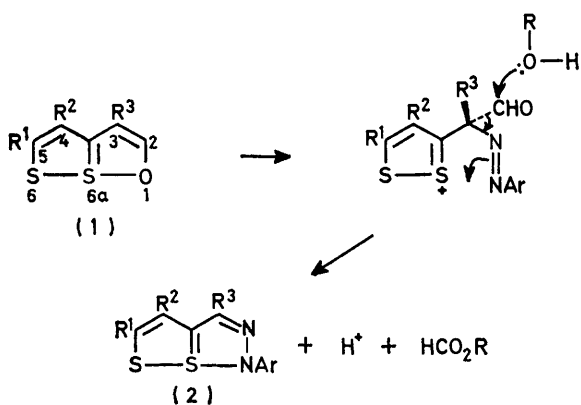


Studies of Heterocyclic Compounds. Part 23.¹ Diazo-coupling-Deformylation of 3,4-Dialkyl-1-aryl-6-oxa-6aλ⁴-thia-1,2-diazapentalenes: Synthesis of 3,4-Dialkyl-1,6-diaryl-6aλ⁴-thia-1,2,5,6-tetra-azapentalenes

By Robert M. Christie, David H. Reid,* Robert Walker, and (in part) Robert G. Webster, Department of Chemistry, The Purdie Building, The University, St. Andrews KY16 9ST, Scotland

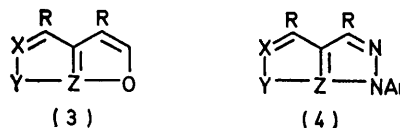
Partial desulphurisation of 3,4-dialkyl-1-aryl-6,6aλ⁴-dithia-1,2-diazapentalenes with mercury(II) acetate affords 3,4-dialkyl-1-aryl-6-oxa-6aλ⁴-thia-1,2-diazapentalenes, which couple with arenediazonium tetrafluoroborates with accompanying deformylation to give 3,4-dialkyl-1,6-diaryl-6aλ⁴-thia-1,2,5,6-tetra-azapentalenes, a new class of four-electron three-centre bonded compound. Reversible exchange of diazo-groups takes place between 3,4-dialkyl-1,6-diaryl-6aλ⁴-thia-1,2,5,6-tetra-azapentalenes and arenediazonium tetrafluoroborates in solution. It is proposed that the formation and the exchange reactions of 3,4-dialkyl-1,6-diaryl-6aλ⁴-thia-1,2,5,6-tetra-azapentalenes proceed by way of 1,2,3-thiadiazolium intermediates.

We have shown recently² that 1-oxa-6,6aλ⁴-dithiapentalenes (1) in which the reactive position 3 is blocked by an



SCHEME 1

alkyl substituent, couple with *p*-nitrobenzenediazonium tetrafluoroborate with accompanying deformylation to give 1-*p*-nitrophenyl-6,6aλ⁴-dithia-1,2-diazapentalenes (2) (Scheme 1). We surmised that analogues of 1-oxa-6,6aλ⁴-dithiapentalenes, for example (3; X = N,

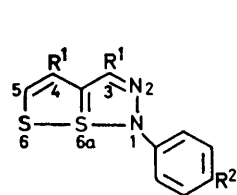


Y = NAr, Z = S), would also couple with arenediazonium salts with deformylation and thereby provide a route to new heterocyclic systems (4). Accordingly we now describe the preparation of 6-oxa-6aλ⁴-thia-1,2-diazapentalenes (3; X = N, Y = NAr, Z = S), the

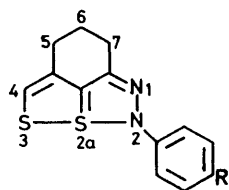
¹ Part 22, D. H. Reid and R. G. Webster, *J.C.S. Perkin I*, 1977, 854.

² R. M. Christie and D. H. Reid, *J.C.S. Perkin I*, 1976, 880.

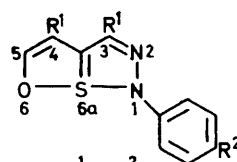
conversion of 6-oxa-6a λ^4 -thia-1,2-diazapentalenes into 6a λ^4 -thia-1,2,5,6-tetra-azapentalenes (4; X = N, Y = NAr, Z = S), and the exchange of diazo-groups between



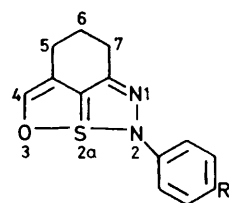
- | | R ¹ | R ² |
|------|-----------------|-----------------|
| (5) | Me | H |
| (6) | Et | H |
| (7) | Pr ⁱ | H |
| (8) | Me | NO ₂ |
| (9) | Me | MeCO |
| (10) | Me | MeO |



- | | |
|------|---------------------|
| (11) | R = H |
| (12) | R = NO ₂ |
| (13) | R = MeCO |
| (14) | R = MeO |



- | | R ¹ | R ² |
|------|-----------------|-----------------|
| (15) | Me | H |
| (16) | Et | H |
| (17) | Pr ⁱ | H |
| (18) | Me | NO ₂ |
| (19) | Me | MeCO |
| (20) | Me | MeO |



- | | |
|------|---------------------|
| (21) | R = H |
| (22) | R = NO ₂ |
| (23) | R = MeCO |
| (24) | R = MeO |

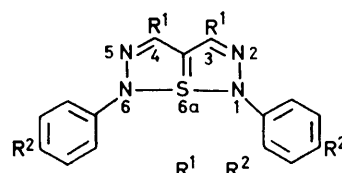
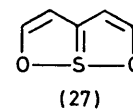
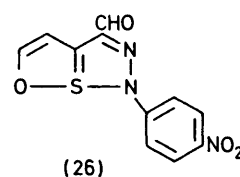
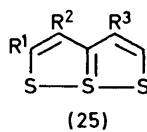
6a λ^4 -thia-1,2,5,6-tetra-azapentalenes and arenediazonium tetrafluoroborates in solution.

Partial desulphurisation of the 6,6a λ^4 -dithia-1,2-diazapentalenes (5)—(14)³ with mercury(II) acetate in chloroform gave the corresponding orange or red 6-oxa-6a λ^4 -thia-1,2-diazapentalenes (15)—(24) in high yield (89—98%). This reaction parallels the conversion of 1,6,6a λ^4 -trithiapentalenes (6a-thiathiophthens) (25) into 1-oxa-6,6a λ^4 -dithiapentalenes (1).⁴ Previously compound (26) was the only known 6-oxa-6a λ^4 -thia-1,2-diazapentalene, and it has been prepared¹ by the coupling of 1,6-dioxa-6a λ^4 -thiapentalene (27) with *p*-nitrobenzenediazonium tetrafluoroborate.

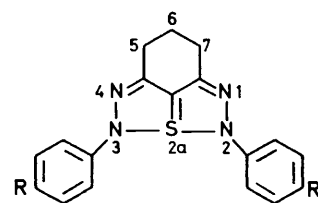
In order to obtain symmetrically substituted 6a λ^4 -thia-1,2,5,6-tetra-azapentalenes, the following coupling reactions were carried out: those of compounds (15)—(17) and (21) with benzenediazonium tetrafluoroborate; those of compounds (18) and (22) with *p*-nitrobenzenediazonium tetrafluoroborate; those of compounds (19) and (23) with *p*-acetylbenzenediazonium tetrafluoroborate; and those of compounds (20) and (24) with *p*-methoxybenzenediazonium tetrafluoroborate. The symmetrically substituted 6a λ^4 -thia-1,2,5,6-tetra-azapentalenes (28)—(37) were obtained from these

reactions, in most cases in high yield (81—99%). Exceptionally, the weakly electrophilic *p*-methoxybenzenediazonium tetrafluoroborate, even when used in large excess, reacted with the oxathiadiazapentalenes (20) and (24) to give only modest yields of the thiatetra-azapentalenes (33) (64%) and (37) (31%).

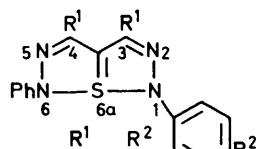
Attempts to obtain unsymmetrically substituted 6a λ^4 -thia-1,2,5,6-tetra-azapentalenes by the use of oxathiadiazapentalenes and arenediazonium tetrafluoroborates in which the respective aryl groups are different were only partly successful, but the results disclosed that ready exchange of diazo-groups occurs between 3,4-dialkyl-1,6-diaryl-6a λ^4 -thia-1,2,5,6-tetra-azapentalenes and arenediazonium tetrafluoroborates in solution. In four reactions [those of compounds (20) and (24) with



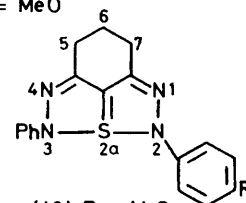
- | | | |
|------|-----------------|-----------------|
| (28) | Me | H |
| (29) | Et | H |
| (30) | Pr ⁱ | H |
| (31) | Me | NO ₂ |
| (32) | Me | MeCO |
| (33) | Me | MeO |



- | | |
|------|---------------------|
| (34) | R = H |
| (35) | R = NO ₂ |
| (36) | R = MeCO |
| (37) | R = MeO |



- | | | |
|------|----|-----------------|
| (38) | Me | MeO |
| (39) | Me | NO ₂ |



- | | |
|------|---------------------|
| (40) | R = MeO |
| (41) | R = NO ₂ |

benzenediazonium tetrafluoroborate and those of compounds (15) and (21) with *p*-methoxybenzenediazonium tetrafluoroborate] the expected unsymmetrical thiatetra-

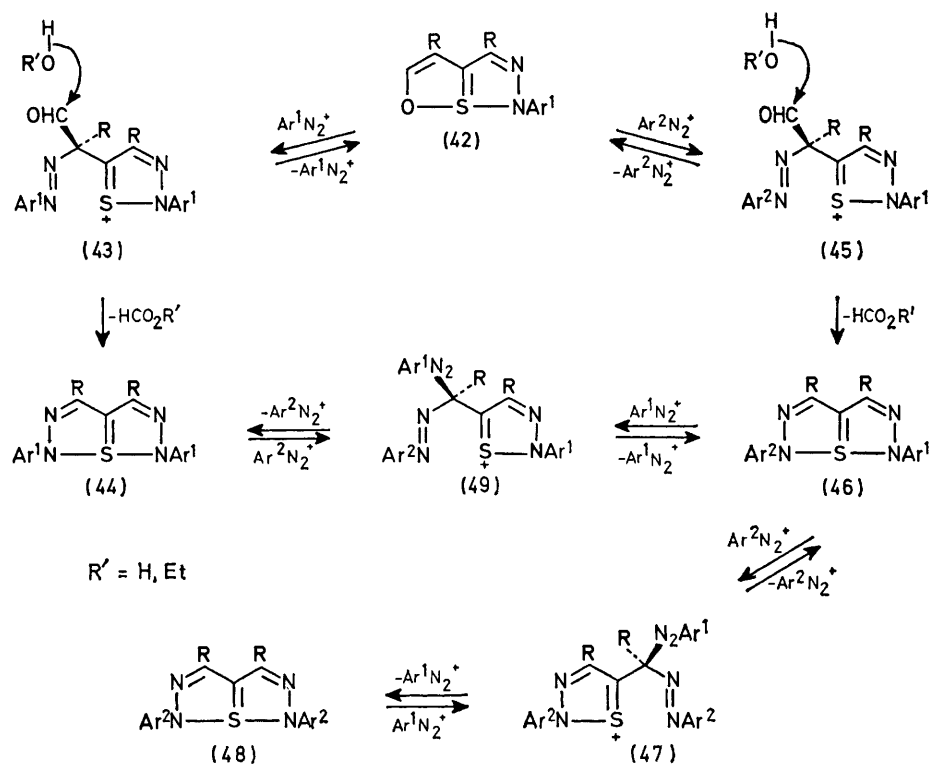
³ R. M. Christie and D. H. Reid, *J.C.S. Perkin I*, 1976, 228.

⁴ E. Klingsberg, *J. Amer. Chem. Soc.*, 1963, **85**, 3244; *J. Org. Chem.*, 1968, **33**, 2915; R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Perkin I*, 1974, 722.

azapentalene was accompanied by two symmetrical thiatetra-azapentalenes; in a further two reactions [those of compounds (15) and (21) with *p*-nitrobenzenediazonium tetrafluoroborate] the expected unsymmetrical thiatetra-azapentalene was accompanied by one of the two possible symmetrical thiatetra-azapentalenes; and in two other reactions [those of compounds (20) and (24) with *p*-nitrobenzenediazonium tetrafluoroborate] a symmetrical thiatetra-azapentalene alone was obtained. Only in the coupling of the unreactive nitro-oxathiadiazapentalenes (18) and (22) with

arene-diazonium tetrafluoroborate are different. In these reactions the primary product (46) must be formed initially by the sequence (42) \rightarrow (45) \rightarrow (46), and it reacts further [(46) \rightarrow (47) \rightarrow (48)] to give one of the symmetrical thiatetra-azapentalenes. The diazonium ion Ar^1N_2^+ subsequently forms the second symmetrical thiatetra-azapentalene (44) by the alternative routes (46) \rightarrow (49) \rightarrow (44) and (42) \rightarrow (43) \rightarrow (44).

Further experiments confirmed that the exchange of diazo-groups between $6a\lambda^4$ -thia-1,2,5,6-tetra-azapentalenes and arene-diazonium tetrafluoroborates takes



SCHEME 2

benzenediazonium tetrafluoroborate did reaction stop with formation of the unsymmetrical thiatetra-azapentalenes (39) and (41), and much starting material was recovered. The weakly electrophilic *p*-methoxybenzenediazonium tetrafluoroborate did not react with compounds (18) and (22).

Formation of symmetrical thiatetra-azapentalenes in addition to the expected unsymmetrical thiatetra-azapentalenes indicated that $6a\lambda^4$ -thia-1,2,5,6-tetra-azapentalenes themselves couple with arene-diazonium tetrafluoroborates. We propose (Scheme 2) that $6a\lambda^4$ -thia-1,2-diazapentalenes react with arene-diazonium tetrafluoroborates to give $6a\lambda^4$ -thia-1,2,5,6-tetra-azapentalenes *via* 1,2,3-thiadiazolium intermediates (43) or (45) which undergo irreversible nucleophilic attack by the solvent. Reactions which lead to the symmetrical thiatetra-azapentalenes (28)–(37) follow the sequence (42) \rightarrow (43) \rightarrow (44), but several pathways are involved in those coupling reactions for which the aryl groups in the oxathiadiazapentalene and the

place reversibly. The reaction of the thiatetra-azapentalene (33) with benzenediazonium tetrafluoroborate and that of the thiatetra-azapentalene (28) with *p*-methoxybenzenediazonium tetrafluoroborate both gave a mixture of the thiatetra-azapentalenes (28), (33), and (38) (see Experimental section). The yields and the relative amounts of the three products were very similar in the two reactions. The reaction of the thiatetra-azapentalene (37) with benzenediazonium tetrafluoroborate and that of the thiatetra-azapentalene (34) with *p*-methoxybenzenediazonium tetrafluoroborate gave results which paralleled the foregoing. The coupling of $6a\lambda^4$ -thia-1,2,5,6-tetra-azapentalenes with arene-diazonium tetrafluoroborates is formulated by the equilibria (44) \rightleftharpoons (49) \rightleftharpoons (46) \rightleftharpoons (47) \rightleftharpoons (48) in Scheme 2.

We think that the concentrations of the three thiatetra-azapentalenes at equilibrium are determined principally by the electrophilicity of the two arene-diazonium ions and by the effect of the electronegativity of the substituents Ar^1 and Ar^2 on the stability of the four-

electron three-centre (N-S-N) bond. If (Scheme 2) Ar^2N_2^+ is a stronger electrophile than Ar^1N_2^+ and, complementary to this, Ar^1N_2^+ is a better leaving group than Ar^2N_2^+ , the concentrations* of the thiatetra-azapentalenes at equilibrium should follow the order

pair Ar^1 and Ar^2 to be retained in the N-S-N sequence; that is, the more electrophilic arenediazonium group ($p\text{-NO}_2\text{-C}_6\text{H}_4\text{N}_2^+ > \text{PhN}_2^+ > p\text{-MeO-C}_6\text{H}_4\text{N}_2^+$) will be incorporated into the thiatetra-azapentalene system, and the equilibrium concentrations should be

TABLE 1
Preparation of 6-oxa-6aλ⁴-thia-1,2-diazapentalenes (15)—(24)

Compound	Yield (%)	Recryst. solvent †	Form	M.p. (°C)	Formula	Found (%)			Required (%)		
						C	H	N	C	H	N
(15)*	99	CH	Orange needles	129—129.5	$\text{C}_{12}\text{H}_{12}\text{N}_2\text{OS}$	62.0	5.1	12.1	62.0	5.2	12.1
(16)	94	H	Yellow spars	85—86	$\text{C}_{14}\text{H}_{16}\text{N}_2\text{OS}$	64.3	6.2	10.8	64.6	6.2	10.8
(17)	98		Yellow oil		$\text{C}_{16}\text{H}_{20}\text{N}_2\text{OS}$	66.3	6.9	9.4	66.3	7.0	9.7
(18)	94	B-CH	Orange-red needles	226—227.5	$\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$	51.9	4.0	15.4	52.0	4.0	15.2
(19)	97	B-CH	Orange needles	142.5—144	$\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$	61.3	5.0	10.0	61.3	5.0	10.0
(20)	90	CH	Orange needles	134	$\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$	59.8	5.4	10.6	59.5	5.4	10.7
(21)	96	H	Orange-red prisms	81.5—83	$\text{C}_{13}\text{H}_{12}\text{N}_2\text{OS}$	64.0	4.8	11.2	63.9	5.0	11.5
(22)	89	B-CH	Red prisms	198—199	$\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$	54.2	4.0	14.8	54.0	3.8	14.5
(23)	94	B-CH	Orange prisms	173—174	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$	62.9	4.8	9.7	62.9	4.9	9.8
(24)	92	CH	Red plates	119	$\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$	61.6	5.2	10.2	61.3	5.1	10.2

* Found: S, 13.9. Required: S, 13.8%. † B = benzene, CH = cyclohexane, H = hexane, P = petroleum, X = xylene.

TABLE 2
Coupling of 6-oxa-6aλ⁴-thia-1,2-diazapentalenes (15)—(24) with arenediazonium tetrafluoroborates: synthesis of 6aλ⁴-thia-1,2,5,6-tetra-azapentalenes (28)—(41)

Starting material	Procedure	Product(s)	Yield (%)	Recryst. solvent †	Form ‡	M.p. (°C)	Formula	Found (%)			Required (%)		
								C	H	N	C	H	N
(15)	A	(28) ^a	98	CH	Dark red	157—158	$\text{C}_{17}\text{H}_{16}\text{N}_4\text{S}$	66.2	5.2	18.4	66.2	5.2	18.2
(16)	A ^b	(29)	92	P	Red	101—102	$\text{C}_{19}\text{H}_{20}\text{N}_4\text{S}$	67.5	5.8	16.8	67.8	6.0	16.7
(17)	A ^b	(30)	81	P	Red	124.5—125	$\text{C}_{21}\text{H}_{24}\text{N}_4\text{S}$	69.0	6.6	15.4	69.2	6.6	15.4
(18)	B	(31)	96	X	Dark red	<i>c</i>	$\text{C}_{17}\text{H}_{14}\text{N}_6\text{O}_4\text{S}$	51.2	3.5	21.2	51.5	3.5	21.1
(19)	C	(32)	95	B-CH	Dark red	234—236	$\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$	64.4	5.1	14.3	64.2	5.1	14.3
(20)	D	(33)	64	H	Red	135—136	$\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$	62.1	5.5	15.3	61.9	5.5	15.2
(21)	A	(34)	99	CH	Dark red	204—205.5	$\text{C}_{18}\text{H}_{16}\text{N}_4\text{S}$	67.5	5.0	17.5	67.5	5.0	17.5
(22)	B	(35)	86	X	Green	<i>c</i>	$\text{C}_{18}\text{H}_{14}\text{N}_6\text{O}_4\text{S}$	52.7	3.5	20.4	52.7	3.4	20.5
(23)	C	(36)	85	B-CH	Green	242—242.5	$\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$	65.3	4.8	13.9	65.3	5.0	13.9
(24)	D ^d	(37)	31	H	Purple	159	$\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$	63.3	5.3	14.8	63.1	5.3	14.7
(20)	E	→ ^e (28), (38), (33)	50, 32, 3.6	CH	Red	138	$\text{C}_{18}\text{H}_{18}\text{N}_4\text{OS}$	64.0	5.4	16.6	63.9	5.4	16.6
(15)	F	→ ^e (28), (38), (33)	7.2, 26, 13.9										
(15)	G	→ ^e (39), (31)	81, 5.7	B	Purple	247—248	$\text{C}_{17}\text{H}_{16}\text{N}_5\text{O}_2\text{S}$	57.8	4.3	20.0	57.8	4.3	19.8
(24)	E	→ ^e (34), (40), (37)	62, 13.2, 0.8	H	Purple	174	$\text{C}_{19}\text{H}_{18}\text{N}_4\text{OS}$	65.3	5.2	16.0	65.1	5.2	16.0
(21)	F	→ ^e (34), (40), (37)	11.5, 21, 5.3										
(21)	H	→ ^e (47), (35)	30, 50	B	Purple	230—231	$\text{C}_{18}\text{H}_{16}\text{N}_5\text{O}_2\text{S}$	59.3	4.1	19.4	59.2	4.1	19.2
(18) ^f	I	→ ^g (39), s.m.	14, 69										
(22) ^f	I	→ ^g (41), s.m.	40, 36										
(20)	J	(31)	99										
(24)	J	(35)	96										

* Found: S, 10.4. Required: S, 10.4%. ^b Product chromatographed twice [alumina (35 × 2.2 cm), petroleum-benzene (1 : 1); alumina (70 × 2.2 cm), petroleum-benzene (4 : 1)]. ^c Does not melt below 350 °C. ^d Product chromatographed [alumina (30 × 2.2 cm)] with petroleum-benzene (1 : 1). ^e Arrow indicates order of elution; new compound in italics. ^f No reaction with *p*-methoxybenzenediazonium tetrafluoroborate. † See Table 1. ‡ Needles. § s.m. = starting material.

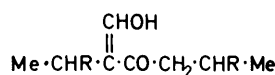
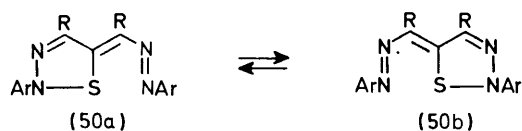
[(48)] > [(46)] > [(44)]. In the three-centre bonding scheme the non-bonding orbital concentrates negative charge on the end atoms, and this type of bond is strongest when the central atom is relatively electro-positive and the end atoms have high electronegativities. This will give rise to a thermodynamic preference for the more strongly electron-withdrawing aryl group of the

[(48)] > [(46)] > [(44)]. The results of the majority of the coupling experiments (see Experimental section) bear out these conclusions. Gradual decomposition of the diazonium ions Ar^1N_2^+ and Ar^2N_2^+ at different rates by reaction with the solvent will alter the equilibrium concentrations of the three thiatetra-azapentalenes. However, the results indicate that the depletion of the diazonium ions is not sufficiently rapid in most cases to upset the expected order of the equilibrium concentrations of the thiatetra-azapentalenes.

* The coupling experiments start with a 2 : 1 molar ratio of the arenediazonium tetrafluoroborate $\text{Ar}^2\text{N}_2^+\text{BF}_4^-$ (or $\text{Ar}^1\text{N}_2^+\text{BF}_4^-$) and the thiatetra-azapentalene (44) [or (48)].

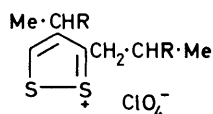
The ^1H n.m.r. spectra of the $6a\lambda^4$ -thia-1,2,5,6-tetraazapentalenes (28)—(30), (32)—(34), (36), and (37) in CDCl_3 (see Table 3) show magnetic equivalence of substituents at C-3 and C-4 and of corresponding ring protons and substituents in 1- and 6-Ar. This demonstrates that $6a\lambda^4$ -thia-1,2,5,6-tetraazapentalenes in solution possess real or time-averaged C_{2v} symmetry. We have not found any evidence for a rapid valence isomerisation (50a) \rightleftharpoons (50b), and these compounds are satisfactorily represented by the bicyclic formulations (28)—(37).

For the synthesis of the hitherto unknown $6,6a\lambda^4$ -dithia-1,2-diazapentalenes (6) and (7) the hydroxymethylene ketones (51) and (52) were prepared from the corresponding ketones by the Claisen condensation and thence converted into the new dithiolium salts (53) and (54) by established procedures.⁵ Coupling of these salts with benzenediazonium tetrafluoroborate gave the dithiadiazapentalenes (6) and (7) (*cf.* ref. 3).



(51) R = H

(52) R = Me



(53) R = H

(54) R = Me

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were measured with a Unicam SP 800 spectrophotometer. Light absorption data (Table 4) refer to solutions in cyclohexane, unless otherwise stated. I.r.

TABLE 3

^1H N.m.r. spectral data for the 6-oxa- $6a\lambda^4$ -thia-1,2-diazapentalenes (15)—(24) and the $6a\lambda^4$ -thia-1,2,5,6-tetraazapentalenes (28)—(30), (32)—(34), (36)—(38), and (40)

Compound	δ values; J in Hz
(15)	2.46 (3 H, d, $J_{4-\text{Me},5}$ 0.4, 4-Me), 2.77 (3 H, 3-Me), 7.15—7.46 (3 H, m, 2 <i>m</i> - + <i>p</i> -protons of 1-Ph), 7.63—7.73 (2 H, m, 2 <i>o</i> -protons of 1-Ph), and 8.89 (1 H, q, $J_{5,4-\text{Me}}$ 0.4, 5-H)
(16)	1.26 (3 H, t, $J_{\text{Me},\text{CH}_2}$ 7.8, 4- CH_2Me), 1.43 (3 H, t, $J_{\text{Me},\text{CH}_2}$ 7.5, 3- CH_2Me), 2.90 (2 H, q, $J_{\text{CH}_2,\text{Me}}$ 7.8, 4- CH_2Me), 3.17 (2 H, q, $J_{\text{CH}_2,\text{Me}}$ 7.5, 3- CH_2Me), 7.09—7.47 (3 H, m, 2 <i>m</i> - + <i>p</i> -protons of 1-Ph), 7.68—7.79 (2 H, m, 2 <i>o</i> -protons of 1-Ph), and 8.98 (1 H, 5-H)
(17)	1.38 (6 H, d, $J_{\text{Me},\text{CH}}$ 7.1, 4- CHMe_2), 1.46 (6 H, d, $J_{\text{Me},\text{CH}}$ 6.9, 3- CHMe_2), 3.55 (2 H, sept, 3- and 4- CHMe_2), 7.10—7.49 (3 H, m, 2 <i>m</i> - + <i>p</i> -protons of 1-Ph), 7.73—7.83 (2 H, m, 2 <i>o</i> -protons of 1-Ph), and 9.14 (1 H, 5-H)

TABLE 3 (Continued)	
(18)	2.56 (3 H, 4-Me), 2.83 (3 H, 3-Me), 7.76 and 7.85 (2 H, 2 <i>o</i> -protons of 1-Ar), 8.22 and 8.31 (2 H, 2 <i>m</i> -protons of 1-Ar), and 9.09 (1 H, 5-H)
(19)	2.49 (3 H, d, $J_{4-\text{Me},5}$ 0.4, 4-Me), 2.56 (3 H, COMe), 2.78 (3 H, 3-Me), 7.66 and 7.75 (2 H, 2 <i>o</i> -protons of 1-Ar), 7.92 and 8.01 (2 <i>m</i> -protons of 1-Ar), and 8.99 (1 H, q, $J_{5,4-\text{Me}}$ 0.4, 5-H)
(20)	2.45 (3 H, d, $J_{4-\text{Me},5}$ 0.4, 4-Me), 2.77 (3 H, 3-Me), 3.79 (3 H, OMe), 6.88 and 6.97 (2 H, 2 <i>m</i> -protons of 1-Ar), 7.57 and 7.66 (2 <i>o</i> -protons of 1-Ar), and 8.86 (1 H, q, $J_{5,4-\text{Me}}$ 0.4, 5-H)
(21)	2.04 (2 H, quint, 6- H_2), 2.77 (2 H, t, 5- H_2), 3.03 (2 H, t, 7- H_2), 7.04—7.64 (5 H, m, 2-Ph), and 9.19 (1 H, 4-H)
(22)	2.10 (2 H, quint, 6- H_2), 2.83 (2 H, t, 5- H_2), 3.06 (2 H, t, 7- H_2), 7.57 and 7.66 (2 H, 2 <i>o</i> -protons of 2-Ar), 8.17 and 8.26 (2 H, 2 <i>m</i> -protons of 2-Ar), and 9.36 (1 H, 4-H)
(23)	2.08 (2 H, quint, 6- H_2), 2.55 (3 H, COMe), 2.79 (2 H, t, 5- H_2), 3.03 (2 H, t, 7- H_2), 7.54 and 7.63 (2 H, 2 <i>o</i> -protons of 2-Ar), 7.90 and 7.99 (2 <i>m</i> -protons of 2-Ar), and 9.25 (1 H, 4-H)
(24)	2.04 (2 H, quint, 6- H_2), 2.78 (2 H, t, 5- H_2), 3.03 (2 H, t, 7- H_2), 3.79 (3 H, OMe), 6.88 and 6.97 (2 <i>m</i> -protons of 2-Ar), 7.48 and 7.57 (2 <i>o</i> -protons of 2-Ar), and 9.17 (4-H)
(28)	2.86 (6 H, 3- and 4-Me), 7.08—7.45 (6 H, m, 2 <i>m</i> - + <i>p</i> -protons of 1- and 6-Ph), and 7.67—7.79 (4 H, m, 2 <i>o</i> -protons of 1- and 6-Ph)
(29)	1.46 (6 H, t, $J_{\text{Me},\text{CH}_2}$ 7.6, 3- and 4- CH_2Me), 3.30 (4 H, q, $J_{\text{CH}_2,\text{Me}}$ 7.6, 3- and 4- CH_2Me), 7.10—7.48 (6 H, 2 <i>m</i> - + <i>p</i> -protons of 1- and 6-Ph), and 7.73—7.85 (4 H, m, 2 <i>o</i> -protons of 1- and 6-Ph)
(30)	1.51 (12 H, d, $J_{\text{Me},\text{CH}}$ 7.0, 3- and 4- CHMe_2), 3.80 (2 H, sept, $J_{\text{CH},\text{Me}_2}$ 7.0, 3- and 4- CHMe_2), 7.10—7.50 (6 H, m, 2 <i>m</i> - + <i>p</i> -protons of 1- and 6-Ph), and 7.77—7.87 (4 H, m, 2 <i>o</i> -protons of 1- and 6-Ph)
(32)	2.58 (6 H, 1- and 6- $\text{MeCO} \cdot \text{C}_6\text{H}_4$), 2.86 (6 H, 3- and 4-Me), 7.73 and 7.82 (4 H, 2 <i>o</i> -protons of 1- and 6-Ar), and 7.94 and 8.03 (4 H, 2 <i>m</i> -protons of 1- and 6-Ar)
(33)	2.90 (6 H, 3- and 4-Me), 3.83 (6 H, 1- and 6- $\text{MeO} \cdot \text{C}_6\text{H}_4$), 6.91 and 7.00 (4 H, 2 <i>m</i> -protons of 1- and 6-Ar), and 7.62 and 7.71 (4 H, 2 <i>o</i> -protons of 1- and 6-Ar)
(34)	2.28 (2 H, quint, 6- H_2), 3.17 (4 H, t, 5- and 7- H_2), 7.07—7.47 (6 H, m, 2 <i>m</i> - + <i>p</i> -protons of 2- and 3-Ph), and 7.69—7.79 (4 H, 2 <i>o</i> -protons of 2- and 3-Ph)
(36)	2.32 (2 H, quint, 6- H_2), 2.59 (6 H, 2- and 3- $\text{MeCO} \cdot \text{C}_6\text{H}_4$), 3.20 (4 H, t, 5- and 7- H_2), 7.78 and 7.87 (4 H, 2 <i>o</i> -protons of 2- and 3-Ar), and 7.98 and 8.07 (4 H, 2 <i>m</i> -protons of 2- and 3-Ar)
(37)	2.23 (2 H, quint, 6- H_2), 3.11 (4 H, t, 5- and 7- H_2), 3.79 (6 H, 2- and 3- $\text{MeO} \cdot \text{C}_6\text{H}_4$), 6.88 and 6.97 (4 H, 2 <i>m</i> -protons of 2- and 3-Ar), and 7.59 and 7.68 (2 <i>o</i> -protons of 2- and 3-Ar)
(38)	2.83 (6 H, 3- and 4-Me), 3.79 (3 H, 1- $\text{MeO} \cdot \text{C}_6\text{H}_4$), 6.88 and 6.97 (2H, 2 <i>m</i> -protons of 1-Ar), 7.14—7.45 (3 H, m, 2 <i>m</i> - + <i>p</i> -protons of 6-Ph), 7.60 and 7.69 (2 H, 2 <i>o</i> -protons of 1-Ar), and 7.61—7.77 (2 H, m, 2 <i>o</i> -protons of 6-Ph)
(40)	2.23 (2 H, quint, 6- H_2), 3.12 (4 H, t, 5- and 7- H_2), 3.80 (3 H, 2- $\text{MeO} \cdot \text{C}_6\text{H}_4$), 6.88 and 6.97 (2 H, 2 <i>m</i> -protons of 2-Ar), 7.12—7.45 (3 H, m, 2 <i>m</i> - + <i>p</i> -protons of 3-Ph), 7.61 and 7.70 (2 H, 2 <i>o</i> -protons of 2-Ar), and 7.66—7.76 (2 H, m, 2 <i>o</i> -protons of 3-Ph)

spectra were recorded with a Perkin-Elmer 621 spectrometer, and refer to solids dispersed in KBr discs. ^1H N.m.r. spectra (Table 3) were determined at 100 MHz with a Varian HA 100 spectrometer for 0.4M-solutions in deuteriochloroform, unless otherwise stated. Tetramethylsilane was used as internal reference and J values were measured

⁵ J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc. (C)*, 1968, 2543; J. G. Dingwall, A. S. Ingram, D. H. Reid, and J. D. Symon, *J.C.S. Perkin I*, 1973, 2351, and references therein.

TABLE 4

U.v. and i.r. spectral data for the 6-oxa-6a λ^4 -thia-1,2-diazapentalenes (15)—(24) and the 6a λ^4 -thia-1,2,5,6-tetra-azapentalenes (28)—(41)

Compound	$\lambda_{\max.}/\text{nm}$ (log ϵ); $[\nu_{\max.}/\text{cm}^{-1}]$
(15)	447(4.32), 275(3.83), 236(3.98)
(16)	446(4.34), 275(3.91), 235(4.03)
(17)	441(4.43), 274(3.90), 234(4.03)
(18)	460(4.53), 325br(3.75), 243inf(3.91)
(19)	458(4.47), 299(4.15), 233(4.00); [1664]
(20)	453(4.32), 280(3.90), 236(4.02)
(21)	467(4.33), 456(4.37), 277(3.88), 238br(3.94)
(22)	485(4.60), 459(4.53), 332br plateau(3.77), 247inf(3.85)
(23)	483(4.45), 475(4.44), 458(4.48), 306(4.16), 235(3.95); [1666]
(24)	466(4.34), 284(3.89), 237(4.00)
(28)	491(4.32), 300(4.20), 246(4.25)
(29)	489(4.33), 300(4.25), 265sh(4.08), 245(4.27)
(30)	485(4.32), 300(4.25), 266sh(4.06), 245(4.27)
(31)*	524, 343, 254
(32)*	517, 322, 273inf, 255; [1668]
(33)	505(4.32), 310(4.27), 247(4.27)
(34)	519(4.33), 306(4.15), 247(4.26)
(35)*	550, 349, 264
(36)*	542, 527, 280inf, 258; [1668]
(37)	535(4.34), 315(4.22), 249(4.28)
(38)	500(4.32), 306(4.23), 246(4.27)
(39)	513(3.41), 342(4.14), 297(4.01), 248(4.14)
(40)	529(4.34), 312(4.19), 248(4.28)
(41)	538(4.43), 350(4.17), 303(4.00), 263(4.12), 249(4.13)

* Log ϵ not determined owing to low solubility

on the 100 Hz scale. Unless otherwise stated values refer to singlet absorptions. Signals assigned to the pairs of *o*- and *m*-protons of the *p*-substituted phenyl group(s) in compounds (18)—(20), (22)—(24), (32), (33), (36)—(38), and (40) are the four most intense peaks in the AA'BB' pattern(s). The ^1H n.m.r. spectra of compounds (31), (35), (39), and (41) were not determined owing to low solubility. Mass spectra were obtained with an A.E.I. MS902 spectrometer. Criteria used in the identification of products included m.p.s, t.l.c. behaviour, and n.m.r. and mass spectra. Solutions were dried over sodium sulphate or magnesium sulphate and evaporated at reduced pressure. Column chromatography was carried out with Spence grade H alumina, unless otherwise indicated. Solvent mixtures are described in ratios by volume. Petroleum was of boiling range 40—60 °C. Acetonitrile, dimethylformamide, and ethanol were dried by standard methods, distilled, and redistilled. Perchloric acid refers to 70—72% (w/w) perchloric acid.

Preparation of 3,4-Diethyl-1-phenyl- (6) and 3,4-Diisopropyl-1-phenyl-6,6a λ^4 -dithia-1,2-diazapentalene (7).—3-Hydroxymethyleneheptan-4-one (51) (56%) (from heptan-4-one), b.p. 82—84° at 18 mmHg (Found: C, 67.7; H, 9.8. $\text{C}_8\text{H}_{14}\text{O}_2$ requires C, 67.6; H, 9.9%), and 3-hydroxymethylene-2,6-dimethylheptan-4-one (52) (42%) (from 2,6-dimethylheptan-4-one), b.p. 98° at 16 mmHg (Found: C, 70.8; H, 10.7. $\text{C}_{10}\text{H}_{18}\text{O}_2$ requires C, 70.6; H, 10.7%), were prepared by the method used for 2-hydroxymethylenecyclohexanone.⁶ The hydroxymethylene ketone (150 mmol), hydrogen disulphide (9 ml), and perchloric acid (18.9 ml) were allowed to react in acetic acid (300 ml) according to the procedure of Dingwall, McKenzie, and Reid.⁵ The salt was washed with much ether followed by ether-carbon disulphide (1:1) before being dried. 3-Hydroxymethyleneheptan-4-one (51) gave 4-ethyl-3-propyl-1,2-dithiolium

perchlorate (53) (29.2 g, 71%), plates from acetic acid (addition of ether), m.p. 51—56° (Found: C, 35.1; H, 4.8. $\text{C}_8\text{H}_{13}\text{ClO}_4\text{S}_2$ requires C, 35.2; H, 4.8%); $\lambda_{\max.}$ (MeOH) 305 (log ϵ 3.82), 255 (3.62), and 211 nm (3.29); $\delta(\text{CF}_3\text{CO}_2\text{H})$ 1.22 (3 H, t, $J_{\text{Me,CH}_2}$ 7.5 Hz, 3- $\text{CH}_2\text{CH}_2\text{Me}$), 1.49 (3 H, t, $J_{\text{Me,CH}_2}$ 7.6 Hz, 4- CH_2Me), 2.09 (2 H, sext, $J_{\text{CH}_2,\text{Me};\text{CH}_2,\text{CH}_2}$ 7.5 Hz, 3- $\text{CH}_2\text{CH}_2\text{Me}$), 3.07 (2 H, q, $J_{\text{CH}_2,\text{Me}}$ 7.6 Hz, 4- CH_2Me), 3.38 (2 H, t, $J_{\text{CH}_2,\text{CH}_2}$ 7.5 Hz, 3- $\text{CH}_2\text{CH}_2\text{Me}$), and 9.92 (1 H, 5-H). 3-Hydroxymethylene-2,6-dimethylheptan-4-one (52) yielded 3-isobutyl-4-isopropyl-1,2-dithiolium perchlorate (54) (26.3 g, 58%), needles from acetic acid (addition of ether), m.p. 89—93° (Found: C, 39.8; H, 5.7. $\text{C}_{10}\text{H}_{17}\text{ClO}_4\text{S}_2$ requires C, 39.9; H, 5.7%); $\lambda_{\max.}$ (MeOH) 306 (log ϵ 3.83), 258 (3.62), and 211 nm (3.31); $\delta(\text{CF}_3\text{CO}_2\text{H})$ 1.17 (6 H, d, $J_{\text{Me}_2,\text{CH}}$ 6.4 Hz, 3- CH_2CHMe_2), 1.49 (6 H, d, $J_{\text{Me}_2,\text{CH}}$ 6.7 Hz, 4- CHMe_2), 2.32 (1 H, m, 3- CH_2CHMe_2), 3.37 (2 H, d, $J_{\text{CH}_2,\text{CH}}$ 7.2 Hz, 3- CH_2CHMe_2), 3.48 (1 H, sept, $J_{\text{CH},\text{Me}_2}$ 6.7 Hz, 4- CHMe_2), and 10.00 (1 H, 5-H).

Coupling of the dithiolium salts (53) and (54) with benzenediazonium tetrafluoroborate according to established procedures³ gave respectively 3,4-diethyl-1-phenyl-6,6a λ^4 -dithia-1,2-diazapentalene (6) (99%), deep red prisms from hexane, m.p. 69.5—70° (Found: C, 60.8; H, 5.7; N, 10.1. $\text{C}_{14}\text{H}_{16}\text{N}_2\text{S}_2$ requires C, 60.8; H, 5.8; N, 10.1%); $\lambda_{\max.}$ 489 (log ϵ 4.12), 293 (4.04), 253sh (4.20), and 238 nm (4.52); δ 1.33 (3 H, t, $J_{\text{Me,CH}_2}$ 7.6 Hz, 4- CH_2Me), 1.43 (3 H, t, $J_{\text{Me,CH}_2}$ 7.5 Hz, 3- CH_2Me), 3.22 (2 H, q, $J_{\text{CH}_2,\text{Me}}$ 7.6 Hz, 4- CH_2Me), 3.29 (2 H, q, $J_{\text{CH}_2,\text{Me}}$ 7.5 Hz, 3- CH_2Me), 7.22—7.51 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.74—7.84 (2 H, m, 2 *o*-protons of 1-Ph), and 9.11 (1 H, 5-H), and 3,4-diisopropyl-1-phenyl-6,6a λ^4 -dithia-1,2-diazapentalene (7) (99%), red prisms from petroleum, m.p. 81.5—82° (Found: C, 62.9; H, 6.8; N, 8.9. $\text{C}_{16}\text{H}_{20}\text{N}_2\text{S}_2$ requires C, 63.1; H, 6.6; N, 9.2%); $\lambda_{\max.}$ 474 (log ϵ 4.14), 292 (4.05), 255sh (4.20), and 235 nm (4.40); δ 1.41 (6 H, d, $J_{\text{Me}_2,\text{CH}}$ 6.8 Hz, 4- CHMe_2), 1.48 (6 H, d, $J_{\text{Me}_2,\text{CH}}$ 6.6 Hz, 3- CHMe_2), 3.83 (1 H, sept, $J_{\text{CH},\text{Me}_2}$ 6.8 Hz, 4- CHMe_2), 3.86 (1 H, sept, $J_{\text{CH},\text{Me}_2}$ 6.6 Hz, 3- CHMe_2), 7.22—7.52 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.78—7.90 (2 H, m, 2 *o*-protons of 1-Ph), and 9.28 (1 H, 5-H).

Preparation of 6-Oxa-6a λ^4 -thia-1,2-diazapentalenes: Partial Desulphurisation of 6,6a λ^4 -Dithia-1,2-diazapentalenes.—The following procedure was used. Mercury(II) acetate (3.19 g, 10 mmol) was added to a solution of the dithiadiazapentalene (5 mmol) in chloroform (250 ml), and the stirred mixture was boiled for 30 min., cooled, and filtered. The filtrates were diluted with benzene, and the resulting solution was washed with water (\times 3), dried, and evaporated. Chromatography [alumina (30 \times 2.8 cm)] of the residual solid with benzene removed traces of starting material. Subsequent elution with benzene-ether (4:1) brought through yellow or orange eluates which yielded the product. Details are given in Tables 1, 3, and 4.

Coupling of 6-Oxa-6a λ^4 -thia-1,2-diazapentalenes with Arenediazonium Tetrafluoroborates: Synthesis of 6a λ^4 -Thia-1,2,5,6-tetra-azapentalenes.—Details are given in Tables 2—4. The following general procedures were used.

Procedure A. Benzenediazonium tetrafluoroborate (1.15 g, 6 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (150 ml) and the mixture was stirred at 60 °C for 1 h. The cooled mixture was diluted with water and extracted with ether, and the extracts were washed with water, dried, and evaporated. Chromatography [alumina (35 \times 2.2 cm)] of the residue with petroleum-benzene (1:1) gave red eluates which yielded the thiatetra-azapentalene.

⁶ C. Ainsworth, *Org. Synth.*, 1959, **39**, 27.

Procedure B. *p*-Nitrobenzenediazonium tetrafluoroborate (948 mg, 4 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (250 ml), and the resulting mixture was stirred at 60 °C for 30 min. Filtration of the cooled solution gave the thiatetra-azapentalene.

Procedure C. *p*-Acetylbenzenediazonium tetrafluoroborate (936 mg, 4 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (150 ml), and the mixture was stirred at 60 °C for 30 min. The cooled mixture was diluted with water and extracted with benzene, and the extracts were washed with water, dried, and evaporated. Crystallisation of the residue from benzene-cyclohexane gave the thiatetra-azapentalene. Chromatography [alumina (15 × 2.8 cm)] of the residue from the mother liquors gave successively pale yellow eluates [benzene-ether (2 : 1)] which were discarded and deep red eluates (ether) which afforded a further quantity of product.

Procedure D. *p*-Methoxybenzenediazonium tetrafluoroborate (1.78 g, 8 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (150 ml), and the mixture was stirred at 60 °C for 2 h. The cooled mixture was diluted with water and extracted with ether, and the extracts were washed with water, dried, and evaporated. Crystallisation of the residue gave the thiatetra-azapentalene.

Procedure E. Benzenediazonium tetrafluoroborate (768 mg, 4 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (150 ml), and the mixture was stirred at 60 °C for 2 h. The cooled mixture was worked up as in procedure A. Chromatography [alumina (60 × 2.7 cm)] of the residue with petroleum-benzene (1 : 1) brought through three well-separated red fractions which yielded the three products.

Procedure F. *p*-Methoxybenzenediazonium tetrafluoroborate (1.78 g, 8 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (150 ml), and the mixture was stirred at 60 °C for 2 h. The cooled mixture was worked up and chromatographed as in procedure E.

Procedure G. *p*-Nitrobenzenediazonium tetrafluoroborate (948 mg, 4 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (150 ml), and the mixture was stirred at 60 °C for 2 h. The purple solid was filtered off, washed with ethanol and ether, and dried. The combined filtrates were diluted with water and extracted with ether, and the extracts were washed with water, dried, and evaporated. The residue together with the purple solid was dissolved in boiling benzene (200 ml), and the hot solution was filtered before being allowed to cool to room temperature. The crystals (homogeneous on t.l.c.; slower-moving component) which had separated from solution were filtered off, and the filtrates on being evaporated to ca. 100 ml gave a second crop of homogeneous crystals. Chromatography [alumina (50 × 2.8 cm)] of the final filtrates with benzene gave red eluates which afforded the first product. Subsequent elution with ether brought through purple eluates, the residue from which was combined with the foregoing two crops of crystals to give the second product.

Procedure H. The reaction was carried out and the product was collected according to procedure G. The two-component product was fractionally crystallised from benzene (2 l). After collection of the first crop of crystals (homogeneous on t.l.c.; slower-moving component), concentration of the filtrates to 1 l gave a second homogeneous crop of crystals. Chromatography [alumina (50 × 2.8 cm)] of the residue from the final filtrates with benzene gave

purple eluates which yielded the first product. Subsequent elution with ether gave a further quantity of the second (slower) product.

Procedure I. Benzenediazonium tetrafluoroborate (1.54 g, 8 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (400 ml), and the mixture was stirred at 60 °C for 2 h. The cooled solution was diluted with water and extracted with ether, and the residue from the washed, dried, and evaporated extracts was chromatographed [alumina (50 × 2.8 cm)]. Elution with benzene gave red eluates which afforded the thiatetra-azapentalene. Continued elution with ether brought through orange eluates from which starting material was isolated.

Procedure J. *p*-Nitrobenzenediazonium tetrafluoroborate (948 mg, 4 mmol) was added to a solution of the oxathiadiazapentalene (2 mmol) in ethanol (150 ml), and the mixture was stirred at 60 °C for 2 h. The solid which had crystallised was filtered off, washed with ethanol and ether, and dried. Dilution of the combined filtrates and washings with water and extraction with ether gave a further quantity of the same (t.l.c.) solid. Recrystallisation of the combined solids gave the thiatetra-azapentalene.

Coupling of 6aλ⁴-Thia-1,2,5,6-tetra-azapentalenes with Arenediazonium Tetrafluoroborates.—The following general procedures were used. (Deviations are described fully in individual cases.)

Procedure A. The arenediazonium tetrafluoroborate (2 mmol) was added to a solution of the 6aλ⁴-thia-1,2,5,6-tetra-azapentalene (1 mmol) in ethanol (75 ml), and the resulting solution was stirred at 60 °C for 2 h, cooled, and diluted with water. The mixture was extracted with ether, and the extracts were washed with water, dried, and evaporated. Chromatography [alumina (70 × 1.8 cm)] of the residue with benzene-petroleum (1 : 1) brought through three well-separated red fractions which yielded the three products.

Procedure B. The arenediazonium tetrafluoroborate (2 mmol) was added to a solution of the 6aλ⁴-thia-1,2,5,6-tetra-azapentalene (1 mmol) in ethanol (75 ml), and the resulting mixture was stirred at 60 °C for 2 h, then cooled. The solid which had crystallised was filtered off, washed with ether, and dried. Dilution of the combined filtrates with water and extraction with ether gave a further quantity of solid. The combined solids were recrystallised from xylene.

The following results were obtained (procedure in parentheses).

(i) 1,6-Bis-(*p*-methoxyphenyl)-3,4-dimethyl-6aλ⁴-thia-1,2,5,6-tetra-azapentalene (33) reacted (A) with benzenediazonium tetrafluoroborate to give the thiatetra-azapentalenes (28) (36%), (38) (32%), and (33) (6.2%).

(ii) 3,4-Dimethyl-1,6-diphenyl-6aλ⁴-thia-1,2,5,6-tetra-azapentalene (28) reacted (A) with *p*-methoxybenzenediazonium tetrafluoroborate to give the thiatetra-azapentalenes (28) (35%), (38) (31%), and (33) (7.6%).

(iii) 6,7-Dihydro-2,3-bis-(*p*-methoxyphenyl)-5H-2aλ⁴-thia-1,2,3,4-tetra-azacyclopent[*cd*]indene (37) reacted (A) with benzenediazonium tetrafluoroborate to give the thiatetra-azacyclopent[*cd*]indenes (34) (39%), (40) (13%), and (37) (3.1%).

(iv) 6,7-Dihydro-2,3-diphenyl-5H-2aλ⁴-thia-1,2,3,4-tetra-azacyclopent[*cd*]indene (34) reacted (A) with *p*-methoxybenzenediazonium tetrafluoroborate to give the thiatetra-azacyclopent[*cd*]indenes (34) (43%), (40) (15%), and (37) (2.1%).

(v) 3,4-Dimethyl-1,6-diphenyl-6a λ^4 -thia-1,2,5,6-tetra-azapentalene (28) (1 mmol) and *p*-nitrobenzenediazonium tetrafluoroborate (2 mmol) were treated according to procedure B. The solid which had separated from solution was filtered off, washed with ether, and dried. Dilution of the combined filtrates with water and extraction with ether gave a further quantity of solid. Chromatography [alumina (50 \times 2.8 cm)] of the combined solids gave successively the thiatetra-azapentalenes (39) (87%) (from benzene eluates) and (31) (2%) (from ether eluates).

(vi) 6,7-Dihydro-2,3-diphenyl-5*H*-2a λ^4 -thia-1,2,3,4-tetra-azacyclopent[*cd*]indene (34) (1 mmol) and *p*-nitrobenzenediazonium tetrafluoroborate (2 mmol) were treated according to procedure B. The two-component product was fractionally crystallised from benzene (200 ml). After collection of the first crop of crystals, concentration of the filtrates to *ca.* 100 ml gave a second crop (both crops homogeneous on t.l.c.; slower-moving component). Chromatography [alumina (50 \times 2.8 cm)] of the residue from the

final filtrates gave successively the thiatetra-azacyclopent[*cd*]indene (41) (35%) (from purple benzene eluates) and a further quantity of the slower component (from purple ether eluates). Recrystallisation of the combined crops of the slower-moving component from toluene afforded the thiatetra-azacyclopent[*cd*]indene (35) (36%).

(vii) 1,6-Bis-(*p*-methoxyphenyl)-3,4-dimethyl-6a λ^4 -thia-1,2,5,6-tetra-azapentalene (33) reacted (B) with *p*-nitrobenzenediazonium tetrafluoroborate to give the thiatetra-azapentalene (31) (98%).

(viii) 6,7-Dihydro-2,3-bis-(*p*-methoxyphenyl)-5*H*-2a λ^4 -thia-1,2,3,4-tetra-azacyclopent[*cd*]indene (37) reacted (B) with *p*-nitrobenzenediazonium tetrafluoroborate to give the thiatetra-azacyclopent[*cd*]indene (35) (98%).

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