Studies of Heterocyclic Compounds. Part 27.[1] Routes to 1,6-Dioxa-6aλ⁴-thia-2-azapentalenes, 1,6-Dioxa-6aλ⁴-selena-2-azapentalenes, and 1-Oxa-6aλ⁴-thia-2,5,6-triazapentalenes

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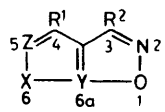
Partial desulphurisation of 3,4-dialkyl-1-oxa-6,6aλ⁴-dithia-2-azapentalenes with mercury(II) acetate gives 3,4-dialkyl-1,6-dioxa-6aλ⁴-thia-2-azapentalenes. 3,4-Dimethyl-1-oxa-6,6aλ⁴-diselena-2-azapentalene likewise gave 3,4-dimethyl-1,6-dioxa-6aλ⁴-selena-2-azapentalene. Peracid oxidation of 1-oxa-6,6aλ⁴-dithia-2-azapentalenes afforded 3-nitromethylene-3*H*-1,2-dithioles in low yield. 3,4-Dialkyl-6-oxa-6aλ⁴-thia-1,2-diazapentalenes in which the reactive position 3 is blocked, react with nitrous acid to give 3,4-dialkyl-1-oxa-6aλ⁴-thia-2,5,6-triazapentalenes by nitroso-deformylation, together with smaller amounts of the corresponding 5-nitromethylene-5*H*-1,2,3-thiadiazoles by nitro-deformylation. Peracid oxidation of 3,4-dialkyl-1-oxa-6aλ⁴-thia-2,5,6-triazapentalenes gave the corresponding 5-nitromethylene-5*H*-1,2,3-thiadiazoles in modest yield. 1,6-Dioxa-6aλ⁴-selena-2-azapentalenes and 1-oxa-6aλ⁴-thia-2,5,6-triazapentalenes are two new classes of four-electron, three-centre bonded compound.

We required for other studies a series of 1,6,6aλ⁴-triheterapentalenes (1) which contain the 1-oxa-2-aza unit. Few classes of 1,6,6aλ⁴-triheterapentalenes of type (1) have hitherto been reported. 1-Oxa-6,6aλ⁴-dithia-2-azapentalenes (2; X = S) and 1-oxa-6,6aλ⁴-diselena-2-azapentalenes (2; X = Se) are conveniently prepared by the nitrosation of 3-methyl(ene)-1,2-dithiolium and 3-methyl(ene)-1,2-diselenolium salts, respectively.[2] 1-Oxa-6,6aλ⁴-dithia-2-azapentalenes (2; X = S, R³ = CHO, Me·CO, Bz, CS_2Me, CS·NMe_2) have



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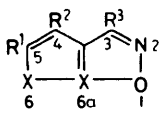

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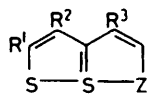

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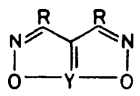

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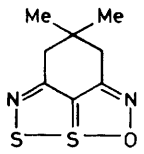

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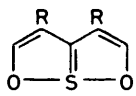
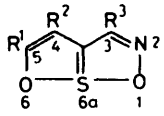


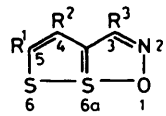
(6)

also been obtained[3] by the nitrosation of 1,6,6aλ⁴-trithiapentalenes (6a-thiathiophthens) (3; Z = S), 1-oxa-6,6aλ⁴-dithiapentalenes (3; Z = O), and 1,6aλ⁴-dithia-6-azapentalenes (3; Z = NMe). 1,6-Dioxa-6aλ⁴-selena-2,5-diazapentalenes (4; Y = Se)[4] and the tellurium analogues (4; Y = Te)[4c] are readily obtained by reaction of the dioximes of 1,3-dicarbonyl compounds with selenium dioxide and tellurium dioxide, respectively. Other reported methods have limited preparative usefulness. Thus treatment of dimedone dioxime with sulphur dichloride at −70 °C gave[5] a mixture of compounds (4; Y = S, R^1R^2 = CH_2·CMe_2·CH_2) and (5), and nitrosation of 1,6-dioxa-6aλ⁴-thiapentalene (6; R = H) afforded[3a] the aldehyde (7). We now describe routes to 1,6-dioxa-6aλ⁴-thia-2-azapentalenes (1; X = O, Y = S, Z = CH), 1,6-dioxa-6aλ⁴-selena-2-azapentalenes (1; X = O, Y = Se, Z = CH), and 1-oxa-6aλ⁴-thia-2,5,6-triazapentalenes (1; X = NAr, Y = S, Z = N).

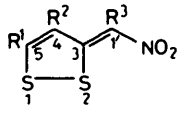
1,6-Dioxa-6aλ⁴-thia-2-azapentalenes and 1,6-Dioxa-6aλ⁴-selena-2-azapentalenes.—The 1-oxa-6,6aλ⁴-dithia-2-azapentalenes (14)—(17),[2] when treated with mercury(II)



	R^1	R^2	R^3
(7)	H	H	CHO
(8)	H	Me	Me
(9)	H	Et	Et
(10)	H	Pr^i	Pr^i
(11)	H	$[CH_2]_3$	
(12)	H	H	H
(13)	Bu^t	H	H



	R^1	R^2	R^3
(14)	H	Me	Me
(15)	H	Et	Et
(16)	H	Pr^i	Pr^i
(17)	H	$[CH_2]_3$	
(18)	H	H	H
(19)	Bu^t	H	H

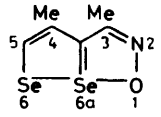


	R^1	R^2	R^3
(20)	H	Me	Me
(21)	H	H	H
(22)	Bu^t	H	H

acetate in boiling acetic acid, underwent sulphur (S-6)–oxygen exchange and gave the 1,6-dioxa-6aλ⁴-thia-2-azapentalenes (8)—(11), respectively, in satisfactory yield. The oxadithia-azapentalene (14) also reacted with mercury(II) acetate under milder conditions, in boiling chloroform–acetic acid [2 : 1 v/v] to give the dioxathia-azapentalene (8) in high yield, but under these conditions the oxadithia-azapentalene (17) gave the product (11) in poor yield (12%).

The reaction of the oxadithia-azapentalenes (18) and (19) with mercury(II) acetate in chloroform–acetic acid did not give any of the desired dioxathia-azapentalenes (12) and (13), and only some starting material was isolated. It is likely that the dioxathia-azapentalenes (12) and (13) were indeed formed and that they immediately underwent acetoxymercuriation at the unsubstituted position 4. Acetoxymercuriation of compound (12) is closely analogous to the reaction of 1,6-dioxa-6aλ⁴-thiapentalene (6; R = H) with mercury(II) acetate in acetic acid at room temperature, which gave an insoluble bisacetoxymercurio-derivative (6; R = Hg-OAc).

In a further attempt to convert 1-oxa-6,6aλ⁴-dithia-2-azapentalenes into the corresponding 1,6-dioxa-6aλ⁴-thia-2-azapentalenes, we treated compounds (14), (18),



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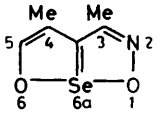

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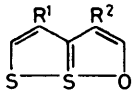
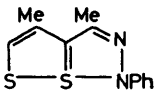


(25) $R^1 = R^2 = Me$

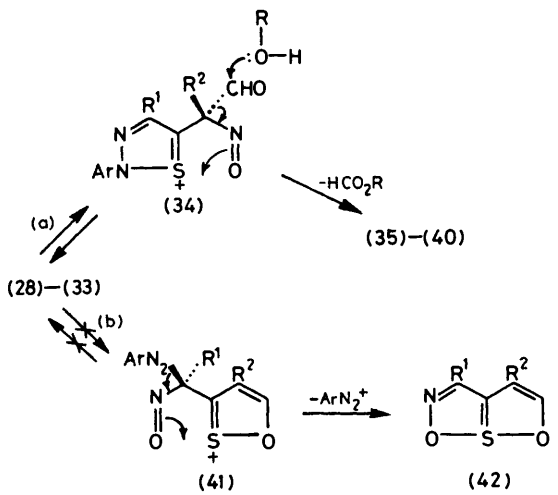
(26) $R^1R^2 = [CH_2]_3$



(27)

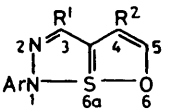
and (19) with *m*-chloroperbenzoic acid. However, *N*-oxidation took place and gave the 3-nitromethylene-3*H*-1,2-dithioles (20)—(22) in low yield. Previously the aldehyde (7) had been the only known 1,6-dioxa-6aλ⁴-thia-2-azapentalene.[3a] The dioxathia-azapentalenes (7)—(11) are stable pale yellow solids.

3,4-Dimethyl-1-oxa-6,6aλ⁴-diselena-2-azapentalene (23) [2] reacted rapidly with mercury(II) acetate in boiling acetic acid to give in high yield compound (24), the first derivative of the 1,6-dioxa-6aλ⁴-selena-2-azapentalene system to be reported.

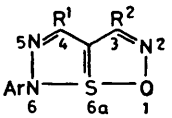


SCHEME 1

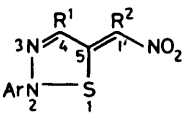
1-*Oxa*-6aλ⁴-*thia*-2,5,6-*triazapentalenes*.—We have shown that nitroso-deformylation of the blocked 1-oxa-6,6aλ⁴-dithiapentalenes (25) and (26) gives [3a] the 1-oxa-6,6aλ⁴-dithia-2-azapentalenes (14) and (17), respectively, and that nitroso-dediazoniation of the blocked 6,6aλ⁴-dithia-1,2-diazapentalene (27) also gives [7] compound (14). This suggested (Scheme 1; see ref. 3*a*) that the 6-oxa-6aλ⁴-thia-1,2-diazapentalenes (28)—(33),[8] in which



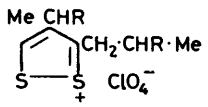
	R^1	R^2	R^3
(28)	Me	Me	Ph
(29)	Et	Et	Ph
(30)	Pr^i	Pr^i	Ph
(31)	$[CH_2]_3$		Ph
(32)	Me	Me	*p*-MeO·C_6H_4
(33)	$[CH_2]_3$		*p*-MeO·C_6H_4



	R^1	R^2	R^3
(35)	Me	Me	Ph
(36)	Et	Et	Ph
(37)	Pr^i	Pr^i	Ph
(38)	$[CH_2]_3$		Ph
(39)	Me	Me	*p*-MeO·C_6H_4
(40)	$[CH_2]_3$		*p*-MeO·C_6H_4



	R^1	R^2	R^3
(43)	Me	Me	Ph
(44)	Et	Et	Ph
(45)	Pr^i	Pr^i	Ph
(46)	$[CH_2]_3$		Ph
(47)	Me	Me	*p*-MeO·C_6H_4
(48)	$[CH_2]_3$		*p*-MeO·C_6H_4



(49) R = H

(50) R = Me

both reactive positions 3 and 4 are blocked, might undergo either nitroso-deformylation [path (a)] to give 1-oxa-6aλ⁴-thia-2,5,6-triazapentalenes (35)—(40) *via* 1,2,3-thiadiazolium intermediates (34), or nitroso-dediazoniation [path (b)] to give 1,6-dioxa-6aλ⁴-thia-2-azapentalenes (42) *via* 1,2-oxathiolium intermediates (41). In the event, treatment of the oxathiadiazapentalenes (28)—(33) with sodium nitrite in acetic acid–acetonitrile gave the oxathiatriazapentalenes (35)—(40), in most cases in excellent yield, but none of the corresponding dioxathia-azapentalenes (42). Compounds (35)—(40) were accompanied by small amounts of

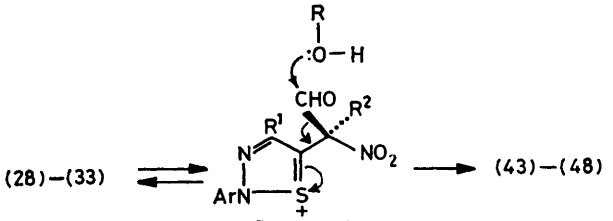
TABLE 1

1-Oxa-6aλ⁴-thia-2,5,6-triazapentalenes (35)—(40) and 5-nitromethylene-5*H*-1,2,3-thiadiazoles (43)—(48) from the reaction of the 1-oxa-6aλ⁴-thia-5,6-diazapentalenes (28)—(33) with nitrous acid

Starting material *	Products	Yield (%)	Recryst. solvent †	Form	M.p. (°C)	Formula	Found (%) C	H	N	Required (%) C	H	N
(28)	(35)	95	H	Orange spars	118—119	$C_{11}H_{11}N_3OS$	56.4	4.8	18.0	56.6	4.8	18.0
	(43)	2.8	CH	Red needles	184—187	$C_{11}H_{11}N_3O_2S$	53.0	4.3	16.6	53.0	4.5	16.9
(29)	(36)	93	H	Yellow spars	83—84	$C_{13}H_{15}N_3OS$	59.6	5.8	16.1	59.8	5.8	16.1
	(44)	1.4	CH	Orange prisms	149—150	$C_{13}H_{15}N_3O_2S$	56.6	5.5	15.1	56.3	5.5	15.2
(30)	(37)	77		Orange-yellow oil		$C_{15}H_{19}N_3OS$	62.5	6.7	14.4	62.3	6.6	14.5
	(45)	4.4	H	Yellow spars	104—105	$C_{15}H_{19}N_3O_2S$	58.9	6.3	13.7	59.0	6.3	13.8
(31)	(38)	88	CH	Orange needles	134—135	$C_{12}H_{11}N_3OS$	58.7	4.5	17.0	58.8	4.5	17.1
	(46)	6.5	CH	Red needles	156—159	$C_{12}H_{11}N_3O_2S$	55.1	4.2	15.9	55.2	4.2	16.1
(32)	(39)	83	CH	Orange needles	159—160	$C_{12}H_{13}N_3O_2S$	55.0	5.0	16.1	54.7	5.0	16.0
	(47)	9.8	B-CH	Red prisms	191—192	$C_{12}H_{13}N_3O_3S$	51.7	4.7	15.1	51.6	4.7	15.0
(33)	(40)	64	CH	Orange needles	159—160	$C_{13}H_{13}N_3O_2S$	56.5	4.8	15.4	56.7	4.8	15.3
	(48)	16	B-CH	Red needles	206—207	$C_{13}H_{13}N_3O_3S$	53.7	4.3	14.5	53.6	4.5	14.4

* Ref. 8. † B = Benzene, CH = cyclohexane, H = hexane.

the 5-nitromethylene-5*H*-1,2,3-thiadiazoles (43)—(48), respectively, which arise by a nitro-deformylation process (Scheme 2). The nitromethylene-1,2,3-thiadiazoles (43) and (46) were also obtained in modest yield by *N*(2)-oxidation of the corresponding oxathiatriazapentalenes (35) and (38) with *m*-chloroperbenzoic acid [*cf.* (14), (18), and (19) ⟶ (20)—(22), respectively].



SCHEME 2

Compounds (35)—(40) are the first members of the 1-oxa-6aλ⁴-thia-2,5,6-triazapentalene system to be reported. The failure of the oxathiadiazapentalenes (28)—(33) to undergo nitrosation or diazo-coupling [8] at position 4 suggests that the 1,2-oxathiolum system is less aromatic than the 1,2,3-thiadiazolium system (*cf.* ref. 9).

An attempt to nitroso-deformylate the blocked dioxathia-azapentalene (14) with nitrosyl hexafluorophosphate in the presence of calcium carbonate [*cf.* (6) ⟶ (7) [3a]] and thereby to obtain the dioxathiadiazapentalene (4; Y = S, $R^1 = R^2$ = Me) was unsuccessful.

The 1-oxa-6,6aλ⁴-dithia-2-azapentalenes (15) and (16), hitherto unknown, were prepared by nitrosation of the dithiolium salts (49) and (50) by established procedures.[2]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Electronic spectral absorption data (Table 3) refer to solutions in cyclohexane. ^{1}H N.m.r. spectra (data in Table 2) were determined at 100 MHz for 0.4M-solutions in deuteriochloroform, with tetramethylsilane as internal reference. Unless otherwise stated δ values refer to singlet absorptions. *J* Values were measured on the 100 Hz scale. Signals assigned to the pairs of *o*- and *m*-protons of the *p*-methoxyphenyl group in compounds (39), (40), (47), and (48) are the four most intense signals in the AA'BB' pattern. Solutions were dried over sodium sulphate or magnesium sulphate and evaporated at reduced pressure. Column chromatography was carried out with alumina (activity II, pH *ca.* 9.5, 100—250 mesh). Solvent mixtures are described in ratios by volume. Reaction products were shown to be identical with authentic samples by showing that they had the same m.p. and n.m.r. spectra, and that they displayed the same t.l.c. behaviour on silica (benzene or ether for development) as the authentic samples. Light petroleum was of boiling range 40—60 °C. *m*-Chloroperbenzoic acid refers to material containing 80 or 78% (w/w) *m*-chloroperbenzoic acid.

3,4-*Diethyl*- (15)- *and* 3,4-*Di-isopropyl*-1-*oxa*-6,6aλ⁴-*dithia*-2-*azapentalene* (16).—Nitrosation of the dithiolium salts (49) [8] and (50) [8] according to established procedures [2] gave respectively 3,4-*diethyl*-1-*oxa*-6,6aλ⁴-*dithia*-2-*azapentalene* (15) (92%), red spars from hexane, m.p. 50—50.5 °C (Found: C, 47.6; H, 5.5; N, 6.9. $C_8H_{11}NOS_2$ requires C, 47.7; H, 5.5; N, 7.0%); $\lambda_{max.}$ 409 (log ε 3.79), 269sh (3.42), and 230 nm (4.35); δ 1.39 (3 H, t, J_{Me,CH_2} 7.6 Hz, 4-CH_2*Me*), 1.44 (3 H, t, J_{Me,CH_2} 7.6 Hz, 3-CH_2*Me*), 3.31 (2 H, q, $J_{CH_2,Me}$ 7.6 Hz, 4-C*H*$_2$Me), 3.32 (2 H, q, $J_{CH_2,Me}$ 7.6 Hz, 3-C*H*$_2$Me), and 9.18 (1 H, 5-H), and 3,4-*di-isopropyl*-1-*oxa*-6,6aλ⁴-*dithia*-2-*azapentalene* (16) (96%), red prisms from light petroleum, m.p. 62—63 °C (Found: C, 52.3; H, 6.6; N, 5.9. $C_{10}H_{15}NOS_2$ requires C, 52.6; H, 6.6; N, 6.1%); $\lambda_{max.}$ 407 (log ε 3.78), 270sh (3.43), and 231 nm (4.38); δ 1.43 (6 H, d, $J_{Me_2,CH}$ 6.9 Hz, 4-CH*Me*$_2$), 1.49 (6 H, d, $J_{Me_2,CH}$ 6.8 Hz, 3-CH*Me*$_2$), 3.78 (1 H, sept, J_{CH,Me_2} 6.9 Hz, 4-C*H*Me$_2$), 3.97 (1 H, sept, J_{CH,Me_2} 6.8 Hz, 3-C*H*Me$_2$), and 9.35 (1 H, 5-H).

1,6-*Dioxa*-6aλ⁴-*thia*-2-*azapentalenes*. *Partial Desulphurisation of* 1-*Oxa*-6,6aλ⁴-*dithia*-2-*azapentalenes*.—The following general procedures were used.

Procedure A. A solution of the 1-oxa-6,6aλ⁴-dithia-2-azapentalene (5 mmol) and mercury(II) acetate (2.39 g, 7.5 mmol) in acetic acid (50 ml) was boiled for 15 min, cooled, and poured into water. The resulting mixture was extracted with benzene, and the extracts were washed successively with water (×2), aqueous sodium carbonate (×2), and water, dried, and evaporated. Chromatography [alumina (25 × 2.2 cm)] of the residue with benzene gave pale yellow eluates which afforded the 1,6-dioxa-6aλ⁴-thia-2-azapentalene. Subsequent elution with benzene–ether (9 : 1) gave yellow eluates from which starting material was recovered.

Procedure B. A mixture of the 1-oxa-6,6aλ⁴-dithia-2-azapentalene (5 mmol), mercury(II) acetate (1.595 g, 5

mmol), chloroform (50 ml), and acetic acid (25 ml) was boiled for 30 min. More mercury(II) acetate (1.595 g, 5 mmol) was added, and the mixture was boiled for a further 1 h before being cooled and poured into water. Subsequent work-up was as described in procedure A.

TABLE 2

^{1}H N.m.r. spectral data for the 1,6-dioxa-6aλ^4-thia-2-azapentalenes (8)—(11), 3,4-dimethyl-1,6-dioxa-6aλ^4-selena-2-azapentalene (24), the 1-oxa-6aλ^4-thia-2,5,6-triazapentalenes (35)—(40), and the 5-nitromethylene-5*H*-1,2,3-thiadiazoles (43)—(48)

Compound	δ Values; *J* values in Hz
(8)	2.53 (3 H, d, $J_{4\text{-Me},5}$ 0.5, 4-Me), 2.79 (3 H, 3-Me), 8.93 (1 H, q, $J_{5,4\text{-Me}}$ 0.5, 5-H)
(9)	1.33 (3 H, t, J_{Me,CH_2} 7.6, 4-CH_2*Me*), 1.46 (3 H, t, J_{Me,CH_2} 7.5, 3-CH_2*Me*), 2.98 (2 H, q, J_{CH_2Me} 7.6, 4-*C*H_2Me), 3.20 (2 H, q, J_{CH_2Me} 7.5, 3-*C*H_2Me), 9.02 (1 H, 5-H)
(10)	1.39 (6 H, d, J_{Me_2CH} 7.1, 4-CH*Me*$_2$), 1.48 (6 H, d, J_{Me_2CH} 7.0, 3-CH*Me*$_2$), 3.56 (1 H, sept, J_{CH,Me_2} 7.1, 4-C*H*Me$_2$), 3.59 (1 H, sept, J_{CH,Me_2} 7.0, 3-C*H*Me$_2$), 9.13 (1 H, 5-H)
(11)	2.11 (2 H, quint, 6-H_2), 2.84 (2 H, t, 5-H_2), 3.10 (2 H, t, 7-H_2), 9.23 (1 H, 4-H)
(24)	2.57 (3 H, d, $J_{4\text{-Me},5}$ 0.5, 4-Me), 2.85 (3 H, 3-Me), 9.29 (1 H, q, $J_{5,4\text{-Me}}$ 0.5, 5-H)
(35)	2.90 (3 H, 4-Me), 2.95 (3 H, 3-Me), 7.36—7.56 (3 H, m, 2 *m*- + *p*-protons of 6-Ph), 7.79—7.89 (2 H, m, 2 *o*-protons of 6-Ph)
(36)	1.48 (6 H, t, J_{Me,CH_2} 7.5, 3- and 4-CH_2*Me*), 3.30 (2 H, q, $J_{CH_2,Me}$ 7.5, 4-*C*H_2Me), 3.31 (2 H, q, $J_{CH_2,Me}$ 7.5, 3-*C*H_2Me), 7.34—7.57 (3 H, m, 2 *m*- + *p*-protons of 6-Ph), 7.81—7.93 (2 H, m, 2 *o*-protons of 6-Ph)
(37)	1.52 (6 H, d, J_{Me_2CH} 7.0, 4-CH*Me*$_2$), 1.54 (6 H, d, J_{Me_2CH} 7.0, 3-CH*Me*$_2$), 3.72 (1 H, sept, J_{CH,Me_2} 7.0, 4-C*H*Me$_2$), 3.82 (1 H, sept, J_{CH,Me_2} 7.0, 3-C*H*Me$_2$), 7.32—7.57 (3 H, m, 2 *m*- + *p*-protons of 6-Ph), 7.85—7.96 (2 H, m, 2 *o*-protons of 6-Ph)
(38)	2.31 (2 H, quint, 6-H_2), 3.20 (2 H, t, 5-H_2), 3.27 (2 H, t, 7-H_2), 7.31—7.58 (3 H, m, 2 *m*- + *p*-protons of 3-Ph), 7.77—7.88 (2 H, m, 2 *o*-protons of 3-Ph)
(39)	2.86 (3 H, 4-Me), 2.91 (3 H, 3-Me), 3.85 (3 H, OMe), 6.91 and 7.00 (2 H, 2 *m*-protons of 6-Ar), 7.69 and 7.78 (2 H, 2 *o*-protons of 6-Ar)
(40)	2.29 (2 H, quint, 6-H_2), 3.18 (2 H, t, 5-H_2), 3.25 (2 H, t, 7-H_2), 3.86 (3 H, OMe), 6.94 and 7.03 (2 H, 2 *m*-protons of 3-Ar), 7.71 and 7.80 (2 H, 2 *o*-protons of 3-Ar)
(43)	2.68 (3 H, 1′-Me), 2.81 (3 H, 4-Me), 7.32—7.57 (3 H, m, 2 *m*- + *p*-protons of 2-Ph), 7.65—7.75 (2 H, m, 2 *o*-protons of 2-Ph)
(44)	1.39 (3 H, t, J_{Me,CH_2} 7.6, 1′-CH_2*Me*), 1.48 (3 H, t, J_{Me,CH_2} 7.5, 4-CH_2*Me*), 3.13 (2 H, q, $J_{CH_2,Me}$ 7.6, 1′-*C*H_2Me), 3.17 (2 H, q, $J_{CH_2,Me}$ 7.5, 4-*C*H_2Me), 7.33—7.56 (3 H, m, 2 *m*- + *p*-protons of 2-Ph), 7.68—7.79 (2 H, m, 2 *o*-protons of 2-Ph)
(45)	1.48 (6 H, d, J_{Me_2CH} 6.9, 1′-CH*Me*$_2$), 1.50 (6 H, d, J_{Me_2CH} 6.9, 4-CH*Me*$_2$), 3.63 (2 H, sept, J_{CH,Me_2} 6.9, 1′- and 4-C*H*Me$_2$), 7.30—7.57 (3 H, m, 2 *m*- + *p*-protons of 2-Ph), 7.69—7.80 (2 H, m, 2*o*-protons of 2-Ph)
(46)	2.13 (2 H, quint, 5-H_2), 2.97 (2 H, t, 6-H_2), 3.04 (2 H, t, 4-H_2), 7.32—7.68 (5 H, m, 2-Ph)
(47)	2.67 (3 H, 1′-Me), 2.81 (3 H, 4-Me), 3.86 (3 H, OMe), 6.93 and 7.02 (2 H, 2 *m*-protons of 2-Ar), 7.57 and 7.66 (2 H, 2 *o*-protons of 2-Ar)
(48)	2.14 (2 H, quint, 5-H_2), 2.98 (2 H, t, 6-H_2), 3.04 (2 H, t, 4-H_2), 3.86 (3 H, OMe), 6.94 and 7.03 (2 H, 2 *m*-protons of 2-Ar), 7.52 and 7.61 (2 H, 2 *o*-protons of 2-Ar)

The following 1,6-dioxa-6aλ^4-thia-2-azapentalenes were obtained [% recovered starting material (s.m.) and procedure in parentheses]: 3,4-*dimethyl*-1,6-*dioxa*-6aλ^4-*thia*-2-*azapentalene* (8) {[648 mg, 82% (s.m. 8.5%)] (A); [740 mg, 92% (s.m. 4.7%)] (B)} [from (14) [2]], pale yellow spars from hexane, m.p. 117—118 °C, *m/e* 157.0200 (M^+) (Found: C, 46.0; H, 4.6; N, 9.0; S, 20.2. $C_6H_7NO_2S$ requires C, 45.7; H, 4.5; N, 8.9; S, 20.4%); 3,4-*diethyl*-1,6-*dioxa*-6aλ^4-*thia*-2-*azapentalene* (9) (527 mg, 57%) (A) [from (15)], pale yellow spars from light petroleum, m.p. 58—59 °C, *m/e* 185.0513 (M^+) (Found: C, 51.8; H, 6.0; N, 7.5. $C_8H_{11}NO_2S$ requires C, 51.9; H, 6.0; N, 7.6%); 3,4-*diisopropyl*-1,6-*dioxa*-6aλ^4-*thia*-2-*azapentalene* (10) [416 mg, 39% (s.m. 1.8%)] (A) [from (16)], pale yellow prisms from light petroleum, m.p. 65—66 °C, *m/e* 213.0816 (M^+) (Found: C, 56.3; H, 7.1; N, 6.4. $C_{10}H_{15}NO_2S$ requires C, 56.3; H, 7.1; N, 6.6%); 6,7-*dihydro*-5H-2,3-*dioxa*-2aλ^4-*thia*-1-*azacyclopent*[cd]*indene* (11) {[499 mg, 59%)] (A); [105 mg, 12% (s.m. 30%)] (B)} [from (17)[2]], pale yellow spars from light petroleum, m.p. 73—75 °C, *m/e* 169.0198 (M^+) (Found: C, 49.9; H, 4.4; N, 8.3; S, 18.7. $C_7H_7NO_2S$ requires C, 49.6; H, 4.2; N, 8.3; S, 18.9%).

TABLE 3

U.v. spectral data for the 1,6-dioxa-6aλ^4-thia-2-azapentalenes (8)—(11), 3,4-dimethyl-1,6-dioxa-6aλ^4-selena-2-azapentalene (24), the 1-oxa-6aλ^4-thia-2,5,6-triazapentalenes (35)—(40), and the 5-nitromethylene-5*H*-1,2,3-thiadiazoles (43)—(48)

Compound	$\lambda_{max.}$/nm (log ε)
(8)	367 (3.87), 238infl (3.34), 216 (3.73)
(9)	365 (3.88), 238br infl (3.35), 215 (3.77)
(10)	363 (3.89), 240vbr (3.37), 216 (3.78)
(11)	385 (3.83), 251infl (3.19), 216sh (3.74)
(24)	394 (3.93), 282br (2.49), 249br (3.14), 223 (3.68)
(35)	398 (4.10), 260sh (3.85), 235 (4.15)
(36)	396 (4.12), 260sh (3.89), 235 (4.19)
(37)	394 (4.12), 260sh (3.90), 236 (4.19)
(38)	420 (4.11), 265sh (3.88), 236 (4.17)
(39)	414 (4.11), 273 (3.84), 236 (4.10)
(40)	439 (4.11), 279 (3.91), 237 (4.10)
(43)	476 (4.45), 294 (3.82), 250sh (3.92), 235 (4.01)
(44)	473 (4.47), 295 (3.84), 250sh (3.93), 235 (4.04)
(45)	470 (4.40), 295 (3.79), 250sh (3.91), 235 (4.01)
(46)	502sh (4.43), 492 (4.47), 476 (4.44), 293 (3.83), 254sh (3.92), 246 (3.96), 234sh (3.91)
(47)	478 (4.39), 301 (3.89), 240 (4.05)
(48)	488 (4.39), 302 (3.90), 241 (3.99)

When the oxadithia-azapentalenes (18) and (19) were treated with mercury(II) acetate according to procedure B, only starting material [(18), 11%; (19), 62%] was isolated.

Oxidation of 1-*Oxa*-6,6aλ^4-*dithia*-2-*azapentalenes with* m-*Chloroperbenzoic Acid: Formation of* 3-*Nitromethylene*-3H-1,2-*Dithioles*.—The following general procedure was used. *m*-Chloroperbenzoic acid [80% (*w/w*), 1.19 g, 5.5 mmol equiv.] was added to a solution of the 1-oxa-6,6aλ^4-dithia-2-azapentalene (5 mmol) in dichloromethane (50 mmol). The mixture was kept for 30 min, poured into water, and extracted with ether. The extracts were washed successively with water, aqueous sodium carbonate, and water, dried, and evaporated, and the residue was chromatographed [alumina (20 × 2.2 cm)]. Elution with benzene gave red eluates from which starting material was recovered. Subsequent elution with ether–ethanol (99 : 1) brought through yellow eluates which afforded the 3-nitromethylene-3*H*-1,2-dithiole. The following were obtained [% recovered starting material (s.m.) in parentheses]: 4-methyl-3-(1-nitroethylidene)-3*H*-1,2-dithiole (20) [2,7] [46 mg, 4.9% (s.m. 28%)] [from (14)[2]], orange needles from benzene, m.p. 191—192 °C; 3-*nitromethylene*-3H-1,2-*dithiole* (21) [56 mg, 7.6% (s.m. 30%)] [from (18)[2]], yellow needles from benzene,

m.p. 168—170 °C (decomp.) (Found: C, 29.9; H, 1.9; N, 8.7. $C_4H_3NO_2S$ requires C, 29.8; H, 1.9; N, 8.7%), $\lambda_{max.}$ 440 (log ε 4.26), 432sh (4.15), 415 (4.22), 400sh (4.02), 281br (3.41), and 226sh nm (3.92), δ 7.23 (1 H, d, $J_{4.5}$ 6.1 Hz, 4-H), 7.91 (1 H, 1'-H), and 8.19 (1 H, d, $J_{5,4}$ 6.1 Hz, 5-H); *3-nitromethylene-5-t-butyl-3H-1,2-dithiole* (22) [54 mg, 5% (s.m. 37%)] [from (19)[2]], yellow needles from benzene, m.p. 161—163 °C (Found: C, 44.5; H, 5.3; N, 6.5. $C_8H_{11}NO_2S_2$ requires C, 44.2; H, 5.1; N, 6.5%), $\lambda_{max.}$ 438 (log ε 4.32), 414 (4.30), 400sh (4.13), 380sh (3.48), 255br infl (3.74), and 232br infl nm (3.88), δ 1.45 (9 H, Bu^t), 7.05 (1 H, 4-H), and 7.81 (1 H, 1'-H).

3,4-Dimethyl-1,6-dioxa-6aλ⁴-selena-2-azapentalene (24).—A solution of 3,4-dimethyl-1-oxa-6,6aλ⁴-diselena-2-azapentalene (23) (1.305 g, 5 mmol) and mercury(II) acetate (2.39 g, 7.5 mmol) in acetic acid (50 ml) was boiled for 5 min. Subsequent work-up was as described for the preparation of 1,6-dioxa-6aλ⁴-thia-2-azapentalenes (procedure A). Chromatography [alumina (25 × 2.2 cm)] with benzene–ether (9 : 1) gave *3,4-dimethyl-1,6-dioxa-6aλ⁴-selena-2-azapentalene* (911 mg, 89%), yellow plates from cyclohexane, m.p. 126.5—127.5 °C (sublimation >113 °C), *m/e* 204.9633 (M^+) (Found: C, 35.4; H, 3.5; N, 6.7; Se, 38.7. $C_6H_7NO_2Se$ requires C, 35.3; H, 3.4; N, 6.9; Se, 38.7%).

1-Oxa-6aλ⁴-thia-2,5,6-triazapentalenes and 5-Nitromethylene-5H-1,2,3-thiadiazoles: Reaction of 6-Oxa-6aλ⁴-thia-1,2-diazapentalenes with Nitrous Acid.—The following general procedure was used. Sodium nitrite (276 mg, 4 mmol) was added to a stirred solution of the oxathiadiazapentalene (2 mmol) in acetonitrile (20 ml) and acetic acid (10 ml) at room temperature. The mixture was stirred for 10 min, a second portion of sodium nitrite (138 mg, 2 mmol) was added, and the mixture was stirred for a further 10 min before being poured into water and extracted with benzene. The extracts were washed successively with water, saturated aqueous sodium carbonate, and water, dried, and evaporated. Chromatography [alumina (35 × 2.2 cm)] of the residue with benzene gave pale yellow eluates which were discarded. Subsequent elution with benzene–ether (9 : 1) gave yellow eluates which afforded the 1-oxa-6aλ⁴-thia-2,5,6-triazapentalene. Elution finally with ether–ethanol (99 : 1) brought through orange eluates which yielded the 5-nitromethylene-5*H*-1,2,3-thiadiazole. Details are given in Tables 1—3.

Oxidation of 1-Oxa-6aλ⁴-thia-2,5,6-triazapentalenes with m-Chloroperbenzoic Acid: Formation of 5-Nitromethylene-5H-1,2,3-thiadiazoles.—The following procedure was used. *m*-Chloroperbenzoic acid [78% (w/w), 884 mg, 4 mmol equiv.] was added to a solution of the oxathiatriazapentalene (2 mmol) in dichloromethane (20 ml). The mixture was kept for 1.5 h, poured into water, and extracted with benzene. The extracts were washed successively with water, aqueous sodium carbonate, and water, dried, and evaporated, and the residue was chromatographed [alumina (35 × 2.2 cm)]. Elution with benzene–ether (4 : 1) gave yellow eluates from which starting material was recovered. Subsequent elution with ether–ethanol (99 : 1) afforded orange eluates which afforded the 5-nitromethylene-5*H*-1,2,3-thiadiazole. The following were obtained [% recovered starting material (s.m.) in parentheses]: 4-methyl-5-(1-nitroethylidene)-2-phenyl-5*H*-1,2,3-thiadiazole (43) [113 mg, 23% (s.m. 25%)] [from (35)]; 5,6-dihydro-7-nitro-2-phenyl-4*H*-benzo[d][1,2,3]thiadiazole (46) [71 mg, 14% (s.m. 17%)] [from (38)].

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