Studies of Heterocyclic Compounds. Part 22.[1] Reactions of 1,6-Dioxa-6aλ⁴-thiapentalenes [2]

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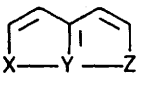
Electrophilic substitution of 1,6-dioxa-6aλ⁴-thiapentalene involves attack at position(s) 3 (and 4) and gives either normal substitution products or products of substitution with rearrangement. Bromination of 1,6-dioxa-6aλ⁴-thiapentalene invariably gave 3,4-dibromo-1,6-dioxa-6aλ⁴-thiapentalene. Iodination with iodine and silver acetate could be controlled to give either 3,4-di-iodo- or 3-iodo-1,6-dioxa-5aλ⁴-thiapentalene. Tritylation with trityl perchlorate in the presence of calcium carbonate gave 3-trityl-1,6-dioxa-6aλ⁴-thiapentalene. Acetoxymercuration in acetic acid afforded an insoluble bisacetoxymercurio-derivative quantitatively. The position of substitution was established by comparative ^{1}H n.m.r. spectral studies. Attempts to formylate, acetylate, and nitrate 1,6-dioxa-6aλ⁴-thiapentalene were unsuccessful. 1,6-Dioxa-6aλ⁴-thiapentalene couples with *p*-nitrobenzenediazonium tetrafluoroborate with rearrangement to give 1-*p*-nitrophenyl-6-oxa-6aλ⁴-thia-1,2-diazapentalene-3-carbaldehyde, the first derivative of the 6-oxa-6aλ⁴-thia-1,2-diazapentalene system to be reported. 1,6-Dioxa-6aλ⁴-thiapentalenes show aldehyde reactivity. 3,4-Dibromo- and 3,4-di-iodo-1,6-dioxa-6aλ⁴-thiapentalene reacted with methylamine in aqueous acetonitrile to give 3,4-dibromo-6-methyl- and 3,4-di-iodo-6-methyl-1-oxa-6aλ⁴-thia-6-azapentalene, respectively, the first derivatives of the 1-oxa-6aλ⁴-thia-6-azapentalene system to be reported. 3-Iodo-1,6-dioxa-6aλ⁴-thiapentalene reacted with methylamine to give a mixture of 3-iodo-6-methyl- and 4-iodo-6-methyl-1-oxa-6aλ⁴-thia-6-azapentalene, which were not separated. 3-Iodo-1,6-dioxa-6aλ⁴-thiapentalene underwent halogen–metal exchange with n-butyl-lithium at −70 °C. The resulting 3-lithio-derivative reacted *in situ* with dimethylformamide or with the Vilsmeier reagent ($Me_2\overset{+}{N}$=CHCl·$PO_2Cl_2^-$) to give 1,6-dioxa-6aλ⁴-thiapentalene-3-carbaldehyde in low yield.

1,6-DIOXA-6aλ⁴-THIAPENTALENES [2,3] constitute the simplest class of compound based on structure (1), in which X, Y, and Z are heteroatoms of Groups 5 and 6, Y is a second or lower row element, and the heteroatom sequence X, Y, Z employs four-electron three-centre bonding. 1,6-Dioxa-6aλ⁴-thiapentalenes are readily obtained by a two-step synthesis from γ-pyrones.[2,3] Preliminary experiments [3] have established the structural relationship between 1,6-dioxa-6aλ⁴-thiapentalene (2) and other four-electron three-centre bonded compounds. Thus 1,6-dioxa-6aλ⁴-thiapentalene reacted with phosphorus pentasulphide to give 6a-thiathiophthen (1; X = Y = Z = S), and underwent oxygen–sulphur exchange in boiling thioacetic acid to give both 6a-thiathiophthen and 1-oxa-6,6aλ⁴-dithiapentalene (1; X = Y = S, Z = O). This paper describes further studies of the reactivity of 1,6-dioxa-6aλ⁴-thiapentalenes.

We have previously shown [4] that 1,6-dioxa-6aλ⁴-thiapentalene (2) and its dimethyl derivative (11) undergo H–D exchange at C-3 and C-4 in trifluoroacetic [^{2}H]acid. The 3,4-dideuterio-derivatives (3) and (12) were subsequently obtained by quenching the acidic solutions with sodium carbonate in deuterium oxide. The formation of compounds (3) and (12) foreshadowed the behaviour of 1,6-dioxa-6aλ⁴-thiapentalene (2) in other electrophilic substitution reactions. 1,6-Dioxa-6aλ⁴-thiapentalene was strikingly selective in its reactions with electrophiles. It underwent substitution smoothly with 'weak' electrophiles, but with 'strong' electrophiles it gave no product, regardless of the method used, and suffered partial or complete destruction depending on the severity of the reaction conditions.

Bromination of 1,6-dioxa-6aλ⁴-thiapentalene (2) with an excess of bromine (2 : 1 molar ratio) in carbon tetrachloride rapidly gave 3,4-dibromo-1,6-dioxa-6aλ⁴-thiapentalene (4) (79%). Lowering the bromine : substrate ratio did not lead to a monobromo-derivative; compound (4) was again obtained, together with starting material. However, iodination with iodine and silver acetate could be controlled to give either 3,4-di-iodo-1,6-dioxa-6aλ⁴-thiapentalene (5) (59%) or 3-iodo-1,6-dioxa-6aλ⁴-thiapentalene (6) (73%), depending on the relative amounts of substrate and reagents. Tritylation with trityl perchlorate in the presence of calcium carbonate proceeded slowly but efficiently to give 3-trityl-1,6-dioxa-6aλ⁴-thiapentalene (7) (94%). Acetoxymercuration in acetic acid immediately gave a colourless powder which gave the correct analytical figures for the 3,4-bisacetoxymercurio-derivative (8) (100%) but was not further characterised owing to its low solubility.



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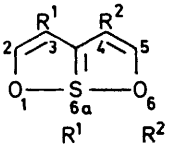
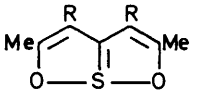


	R^1	R^2
(2)	H	H
(3)	D	D
(4)	Br	Br
(5)	I	I
(6)	I	H
(7)	Ph_3C	H
(8)	HgOAc	HgOAc
(9)	CHO	H
(10)	Li	H



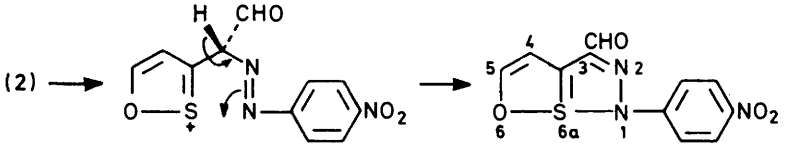
(11) R = H
(12) R = D

The position of substitution was determined from the

[1] Part 21, R. M. Christie and D. H. Reid, preceding paper.
[2] Preliminary communication, D. H. Reid and R. G. Webster, *J.C.S. Chem. Comm.*, 1972, 1283.
[3] D. H. Reid and R. G. Webster, *J.C.S. Perkin I*, 1975, 775.
[4] D. H. Reid and R. G. Webster, *J.C.S. Perkin I*, 1975, 2097.

^{1}H n.m.r. spectra ($CDCl_3$) of the 3,4-dihalogeno-derivatives (4) and (5). Introduction of a bromine or iodine atom into a benzene ring is known to alter the chemical shifts of the *ortho*-protons by no more than *ca.* +0.3 p.p.m. If we assume that a similar rule holds for the halogenodioxathiapentalenes, the proton signals of the dibromo- and di-iodo-compounds (4) and (5) should indicate the position of substitution, since there is a considerable difference between the chemical shifts of 2(5)-H (δ 8.64) and 3(4)-H (δ 6.90) in the parent compound.[3] The spectra in fact consisted of singlets whose positions [(4), δ 8.66; (5), δ 8.78] were only slightly shifted from that of the 2(5)-H signal in the spectrum of 1,6-dioxa-6aλ^4-thiapentalene (2). Thus substitution must have occurred at positions 3 and 4. The proton shifts of the iodo-derivative (6) [δ 8.67, 6.98(d), and 8.68(d)] likewise show that monosubstitution had occurred at position 3(4).

1,6-Dioxa-6aλ^4-thiapentalene coupled with *p*-nitrobenzenediazonium tetrafluoroborate with rearrangement (see Scheme) to give the aldehyde (13), the first



(13)

SCHEME

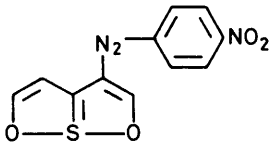
derivative of the 6-oxa-6aλ^4-thia-1,2-diazapentalene system to be reported. The product is shown to possess structure (13) rather than the unrearranged dioxathiapentalene structure (14) by its i.r. spectrum, which shows strong carbonyl absorption [ν (KBr) 1 682 cm^{-1}], and its ^{1}H n.m.r. spectrum ($CDCl_3$), which shows a formyl proton singlet at δ 10.24. This behaviour parallels the previously reported rearrangement of 1,6-dioxa-6aλ^4-thiapentalene into the 1,6-dioxa-6aλ^4-thia-2-azapentalene (15) during nitrosation.[5]

Attempted Vilsmeier formylation (dimethylformamide–phosphoryl chloride) of 1,6-dioxa-6aλ^4-thiapentalene did not give the desired aldehyde (9); the substrate was completely destroyed. Since the aldehyde was subsequently obtained by another route and is stable, the failure of the Vilsmeier reaction cannot be due to instability of the product (9). Attempted acetylation with boiling acetic anhydride containing sodium acetate or with acetyl chloride and tin(IV) chloride gave back starting material, as did attempted trifluoroacetylation with trifluoroacetic anhydride and triethylamine. Attempts to nitrate 1,6-dioxa-6aλ^4-thiapentalene with concentrated nitric acid, with copper nitrate in acetic anhydride, with tetranitromethane in pyridine and ethanol, and with nitronium tetrafluoroborate in the presence of calcium carbonate, also failed.

Several 1,6-dioxa-6aλ^4-thiapentalenes showed aldehyde

[5] R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Perkin I*, 1974, 722.

reactivity in their reactions with amines. 1,6-Dioxa-6aλ^4-thiapentalene reacted to an insignificant extent with methylamine and with aniline in boiling acetic acid, but the halogenated derivatives (4)—(6) reacted readily with methylamine in aqueous acetonitrile at room temperature. 3,4-Dibromo- (4) and 3,4-di-iodo-1,6-dioxa-6aλ^4-thiapentalene (5) gave the oxathia-azapentalenes (16) and (17), respectively, in high yield. Compounds (16) and (17) are the first derivatives of the 1-oxa-6aλ^4-thia-6-azapentalene system to be reported. 3-Iodo-1,6-dioxa-6aλ^4-thiapentalene (6) also gave a product, in 95% yield, which was homogeneous to t.l.c., but the n.m.r. spectrum of which showed two sets of signals corresponding to the iodo-oxathia-azapentalenes (18) and (19) in a 2 : 1 ratio. Attempts to separate compounds (18) and (19) by crystallisation and by chromatography were unsuccessful, and the assignments of structure rest on the following ^{1}H n.m.r. data. The signals from the major component included a double quartet centred at δ 7.74. This can only arise from 5-H in structure (18) ($J_{5,4}$ 3.4, $J_{5,NMe}$ 0.4 Hz). The key signal from the minor component was a closely spaced quartet at δ 7.70, which must arise from 5-H ($J_{5,NMe}$ 0.4 Hz) in



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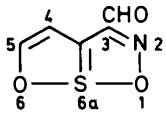

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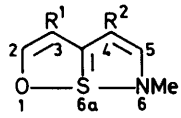
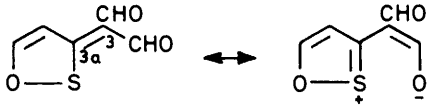


	R^1	R^2
(16)	Br	Br
(17)	I	I
(18)	I	H
(19)	H	I



(20)

structure (19). All other spectral data (see Experimental section) were consistent with these assignments.

Attempts to introduce other substituents into the 1,6-dioxa-6aλ⁴-thiapentalene nucleus *via* halogen–metal exchange-reactions of 3-iodo-1,6-dioxa-6aλ⁴-thiapentalene (6) met with limited success. The iodo-compound (6) reacted with n-butyl-lithium at −70 °C to give a green solution containing the lithiated species (10). Addition to this solution of dimethylformamide or the Vilsmeier reagent ($Me_2\overset{+}{N}$=CHCl·$PO_2Cl_2^-$) in dimethylformamide gave the aldehyde (9) in 5—7% yield. Treatment of solutions of the intermediate (10) with carbon dioxide, acetaldehyde, and benzaldehyde gave intractable tars.

The aldehyde (9) has $\nu_{C=O}$ (CCl_4) 1 686 cm^{-1}, which indicates that the 1,6-dioxa-6aλ⁴-thiapentalene system releases electrons at its 3-position as effectively as thiophen does at its 2-position [2-formylthiophen, $\nu_{C=O}$ (CCl_4) 1 688 cm^{-1} (ref. 6)].

The pattern of the ^1H n.m.r. spectrum of the aldehyde (9) in [$^2H_6$]dimethyl sulphoxide was unchanged by raising the temperature of the solution to 150 °C, above which decomposition occurred. This indicates that there is no noticeable tendency for the O(1)–S bond to break to give an oxathiole derivative (20) in which there is free rotation about the C(3a)–C(3) bond.

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 refer to solutions in cyclohexane. I.r. spectra were recorded with a Perkin-Elmer 621 spectrometer. ^1H N.m.r. spectra were determined at 100 MHz with a Varian HA100 spectrometer for 0.4M-solutions in deuteriochloroform, unless otherwise stated, with tetramethylsilane as internal reference; J values were measured on the 100 Hz scale and, unless otherwise stated, δ values refer to singlet absorptions. Mass spectra were obtained with an A.E.I. MS902 spectrometer. Solutions were dried over sodium sulphate and evaporated at reduced pressure. Column chromatography was carried out with Spence grade H alumina. Solvent mixtures are described in ratios by volume. Petroleum was of boiling range 40—60 °C. Acetonitrile was boiled over sodium hydride for 30 min, distilled, then boiled over phosphoric anhydride for 1 h, distilled, and redistilled. Dichloromethane was boiled over phosphoric anhydride for 1 h, distilled, and redistilled. Aqueous methylamine was a 25—30% (w/v) solution.

Electrophilic Substitution Reactions of 1,6-*Dioxa*-6aλ⁴-*thiapentalene* (2).—*Bromination.* A solution of bromine (10 mmol) in carbon tetrachloride (2 ml) was added to a solution of 1,6-dioxa-6aλ⁴-thiapentalene [3] (641 mg, 5 mmol) in carbon tetrachloride (10 ml). Liberation of hydrogen bromide began immediately. After 5 min the solution was diluted with benzene (75 ml), an excess of powdered sodium carbonate was added, and the resulting mixture was swirled thoroughly before being filtered. The filtrates were evaporated and the residue was chromatographed [alumina (10 × 2.2 cm)] with benzene. The pale yellow eluates afforded 3,4-*dibromo*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (4) (1.13 g, 79%), volatile pale yellow needles (from petroleum), m.p. 133—135° (Found: C, 21.0; H, 0.63. $C_5H_2Br_2O_2S$ requires C, 21.0; H, 0.71%); *m/e* 285.812 2 (M^+); $\lambda_{max.}$ 374 (log ε 4.02), 277br, infl (3.25), 242 (3.56), and 215 nm (3.81); δ 8.66 (2- and 5-H).

Iodination. (*a*) Silver acetate (3.57 g, 22 mmol) was added to a solution of 1,6-dioxa-6aλ⁴-thiapentalene (5 mmol) and iodine (5.08 g, 20 mmol) in dichloromethane (200 ml). The mixture was stirred at room temperature for 1 h, poured into water, and extracted with ether. The extracts were washed successively with water (× 3), aqueous sodium thiosulphate, and water (× 3), dried, and evaporated. Chromatography [alumina (10 × 2.2 cm)] of the residue with benzene gave yellow eluates which yielded 3,4-*di-iodo*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (5) (1.13 g, 59%), pale yellow spars (from hexane), m.p. 153—156° (sublimation) (Found: C, 15.9; H, 0.45. $C_5H_2I_2O_2S$ requires C, 15.8; H, 0.55%); *m/e* 379.786 4 (M^+); $\lambda_{max.}$ 381 (log ε 3.90), 289br, infl (3.36), 248 (3.76), and 229 nm (3.85); δ 8.78 (2- and 5-H).

(*b*) Silver acetate (891 mg, 5.5 mmol) was added to a solution of 1,6-dioxa-6aλ⁴-thiapentalene (5 mmol) and iodine (1.27 g, 5 mmol) in dichloromethane (50 ml). The mixture was stirred for 15 min, poured into water, and extracted with ether. The extracts were washed with water (× 3), dried, and evaporated, and the residue was chromatographed [alumina (10 × 2.2 cm)] with benzene. The residue (1.25 g) from the pale yellow eluates contained small quantities (t.l.c.) of starting material and the di-iodo-compound (5), both of which were removed by one crystallisation from hexane. 3-*Iodo*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (6) (932 mg, 73%) was obtained as pale yellow spars, m.p. 74—75° (sublimation) (Found: C, 23.8; H, 1.1. $C_5H_3IO_2S$ requires C, 23.6; H, 1.2%); *m/e* 253.889 4 (M^+); $\lambda_{max.}$ 355 (log ε 4.00), 263 (3.29), 231 (3.71), and 213 nm (3.81); δ 6.98 (1 H, d, $J_{4,5}$ 2.6 Hz, 4-H), 8.67 (1 H, 2-H), and 8.68 (1 H, d, $J_{5,4}$ 2.6 Hz, 5-H).

Tritylation. Trityl perchlorate (8.58 g, 25 mmol) was added to a stirred solution of 1,6-dioxa-6aλ⁴-thiapentalene (5 mmol) in dichloromethane (250 ml) containing powdered calcium carbonate (20 g) in suspension. The mixture was stirred at room temperature for 21 h, poured into water, and extracted with ether. The extracts were washed with water, dried, and evaporated, and the residue was chromatographed [alumina (50 × 2.2 cm)] with petroleum–benzene (1 : 1). The composition of the eluates was monitored by t.l.c., and the early fractions (450 ml) containing a small quantity of starting material were discarded. The succeeding eluates furnished 3-*trityl*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (7) (1.75 g, 94%), small needles [from benzene–cyclohexane) (1 : 1)], m.p. 201—203° (Found: C, 78.0; H, 4.9. $C_{24}H_{18}O_2S$ requires C, 77.8; H, 4.9%); $\lambda_{max.}$ 346 (log ε 4.09), 267sh (3.35), 262 (3.42), 252infl (3.41), and 214 nm (4.38); δ 5.97 (1 H, d, $J_{4,5}$ 2.7 Hz, 4-H), 7.20 (15 H, CPh_3), 8.23 (1 H, 2-H), and 8.33 (1 H, d, $J_{5,4}$ 2.7 Hz, 5-H).

Acetoxymercuration. A solution of mercury(II) acetate (3.19 g, 10 mmol) in acetic acid (50 ml) was added to a solution of 1,6-dioxa-6aλ⁴-thiapentalene (5 mmol) in acetic acid (10 ml). The resulting solution immediately deposited 3,4-*bisacetoxymercurio*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (8) as a powder which, after 5 min, was filtered off, washed with acetic acid followed by ether, and dried *in vacuo* (yield 3.22 g, 100%). It decomposes gradually above 190 °C (Found: C, 17.0; H, 1.35. $C_9H_8Hg_2O_6S$ requires C, 16.7; H, 1.25%).

[6] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Chem. Comm.*, 1972, 742; C. Andrieu, R. Pinel, and Y. Mollier, *Bull. Soc. chim. France*, 1971, 1314.

Coupling with p-*nitrobenzenediazonium tetrafluoroborate*. *p*-Nitrobenzenediazonium tetrafluoroborate (3.55 g, 15 mmol) was added to a stirred solution of 1,6-dioxa-6aλ⁴-thiapentalene (5 mmol) in acetonitrile (50 ml). The mixture became orange and was stirred for 1 h at room temperature before being diluted with water and extracted with benzene. The extracts were washed with water (× 3), dried, and evaporated, and the residue was chromatographed [alumina (20 × 2.2 cm)]. Elution with benzene gave colourless eluates from which starting material (474 mg, 74%) was recovered. Continued elution with ether brought through orange eluates which yielded 1-p-*nitrophenyl*-6-*oxa*-6aλ⁴-*thia*-1,2-*diazapentalene*-3-*carbaldehyde* (13) (98 mg, 7.1%), small orange needles (from benzene), m.p. 246—252° (decomp.) (Found: C, 47.8; H, 2.4; N, 14.9. $C_{11}H_7N_3O_4S$ requires C, 47.7; H, 2.5; N, 15.2%); *m/e* 277.016 3 (M^+); $\lambda_{max.}$ 431 (log ε 4.26), 334 (3.93), 305br, infl (3.84), and 240 nm (3.94); $\nu_{max.}$ (KBr) 1 682 cm^{-1} (C=O); δ * 7.90 1 H, d, 4-H), 8.00 and 8.09 (2 H, 2 *o*-protons of 1-Ar), 8.36 and 8.45 (2 *m*-protons of 1-Ar), 9.44 (1 H, d, 5-H), and 10.24 (1 H, CHO).

Reactions of 1,6-*Dioxa*-6aλ⁴-*thiapentalenes with Methylamine*.—3,4-*Dibromo*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (4). Aqueous methylamine (25 ml) was added to a solution of 3,4-dibromo-1,6-dioxa-6aλ⁴-thiapentalene (1.43 g, 5 mmol) in acetonitrile (50 ml) at room temperature. The solution darkened and deposited a flocculent precipitate. After 5 min the mixture was diluted with water and extracted with ether, and the extracts were washed with water (× 3), dried, and evaporated. Chromatography [alumina (10 × 2.2 cm)] with benzene gave colourless eluates which were discarded. Subsequent elution with benzene–ether (9 : 1) brought through pale yellow eluates which afforded 3,4-*dibromo*-6-*methyl*-1-*oxa*-6aλ⁴-*thia*-6-*azapentalene* (16) (1.43 g, 96%), yellow needles (from benzene–cyclohexane), m.p. 138—139° (Found: C, 24.1; H, 1.7; N, 4.7. $C_6H_5Br_2NOS$ requires C, 24.1; H, 1.7; N, 4.7%), $\lambda_{max.}$ 404 (log ε 4.05), 275sh (3.43), 257 (3.67), and 216br nm (3.91); δ 3.66 (3 H, d, $J_{NMe,5}$ 0.4 Hz, NMe), 7.78 (1 H, d, $J_{5,NMe}$ 0.4 Hz, 5-H), and 8.80 (1 H, 2-H).

3,4-*Di-iodo*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (5). The procedure was identical with that of the preceding experiment, with 3,4-di-iodo-1,6-dioxa-6aλ⁴-thiapentalene (1.90 g, 5 mmol) in place of compound (4). 3,4-*Di-iodo*-6-*methyl*-1-*oxa*-6aλ⁴-*thia*-6-*azapentalene* (17) (1.42 g, 72%) was obtained as brown spars (from benzene–cyclohexane) which decompose gradually above 110 °C (Found: C, 18.4; H, 1.3; N, 3.7. $C_6H_5I_2NOS$ requires C, 18.3; H, 1.3; N, 3.6%); $\lambda_{max.}$† 407, 266, and 226 nm; δ 3.68 (3 H, NMe), 7.91 (1 H, 5-H), and 8.98 (1 H, 2-H).

3-*Iodo*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (6). The reaction was carried out according to the procedure of the preceding two experiments; compound (6) (1.27 g, 5 mmol) was used. Chromatography gave an inseparable (2 : 1) mixture (95%) of 3-iodo-6-methyl-1-oxa-6aλ⁴-thia-6-azapentalene (18) [δ 3.64 (3 H, NMe), 6.74 (1 H, d, $J_{4,5}$ 3.4 Hz, 4-H), 7.74 (1 H, dq, $J_{5,4}$ 3.4 Hz, $J_{5,NMe}$ 0.4 Hz, 5-H), and 8.81 (1 H, 2-H)] and 4-iodo-6-methyl-1-oxa-6aλ⁴-thia-6-azapentalene (19) [δ 3.64 (3 H, NMe), 6.38 (1 H, d, $J_{3,2}$ 2.6 Hz, 3-H), 7.70 (1 H, q, $J_{5,NMe}$ 0.4 Hz, 5-H), and 8.95 (1 H, d, $J_{2,3}$ 2.6 Hz, 2-H)], which crystallised as yellow needles (from cyclohexane), m.p. 104—111° (Found: C, 26.8; H, 2.4; N, 5.2. Calc. for C_6H_6INOS: C, 27.0; H, 2.3; N, 5.2%).

Halogen-Metal Exchange Reaction of 3-*Iodo*-1,6-*dioxa*-6aλ⁴-*thiapentalene* (6): *Synthesis of* 1,6-*Dioxa*-6aλ⁴-*thiapentalene*-3-*carbaldehyde* (9).—A solution of n-butyl-lithium (7.5 mmol) in pentane (10 ml) was added to a stirred solution of the iodo-compound (6) (1.27 g, 5 mmol) in ether (50 ml) at −70 °C. The solution became green, and after 1 min a solution of dimethylformamide (5 ml) in ether (50 ml) was added. The solution was kept at −70 °C during the addition and for a further 5 min. It was then allowed to warm up to room temperature, poured into water, and extracted with ether. The extracts were washed with water (× 6), dried, and evaporated, and the residue was chromatographed [alumina (15 × 2.2 cm)]. Successive elution with benzene (200 ml), benzene–ether (1 : 1; 200 ml), and ether (200 ml) gave homogeneous (t.l.c.) colourless eluates which yielded 1,6-*dioxa*-6aλ⁴-*thiapentalene*-3-*carbaldehyde* (54 mg, 6.9%), straw-coloured needles (from hexane), m.p. 98—100° (Found: C, 46.1; H, 2.5. $C_6H_4O_3S$ requires C, 46.1; H, 2.6%); *m/e* 155.987 3 (M^+); $\lambda_{max.}$ 340 (log ε 4.04), 249 (4.15), and 204sh nm (3.58); $\nu_{max.}$ (CCl_4) 1 686 cm^{-1} (C=O); δ 8.02 (1 H, d, $J_{4,5}$ 2.4 Hz, 4-H), 8.74 (1 H, d, $J_{5,4}$ 2.4 Hz, 5-H), 9.30 (1 H, 2-H), and 9.90 (1 H, CHO). When the reaction was carried out with a solution of phosphoryl chloride (2 ml) in dimethylformamide (20 ml) in place of dimethylformamide in ether, the yield of the aldehyde (9) was 43 mg (5.5%).

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* Compound sparingly soluble; spectrum recorded by accumulation; *J* values not determined; signals assigned to the pairs of *ortho*- and *meta*-protons of 1-Ar are the four most intense signals in the AA'BB' pattern.

† Intensities not determined owing to low solubility.