Studies of Heterocyclic Compounds. Part 21.[1] Reactions of 1-Aryl-6,6a-dithia-1,2-diazapentalenes with Electrophiles

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

1-Aryl-6,6a-dithia-1,2-diazapentalenes react with electrophiles at position 3. Bromination of 1-phenyl-, 1-*p*-bromophenyl-, 1-phenyl-5-t-butyl-, and 1-*p*-bromophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene gave the 3-bromo-derivatives as the major products. Vilsmeier formylation of 1-phenyl-, 1-phenyl-5-t-butyl,- and 1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene took place with difficulty to give the corresponding 6,6a-dithia-1,2-diazapentalene-3-carbaldehydes. Nitration of 1-phenyl- and 1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene gave the 3-nitro-derivatives as the main products. 3-Nitro-1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene, a minor product from the nitration of 1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene, was also synthesised by the coupling of 3-nitromethylene-5-t-butyl-3*H*-1,2-dithiole with *p*-nitrobenzenediazonium tetrafluoroborate. Nitration of 3,4-dimethyl-1-phenyl-6,6a-dithia-1,2-diazapentalene, in which the reactive position 3 is blocked, gave as the major product 4-methyl-3-(1-nitroethylidine)-3*H*-1,2-dithiole by nitro-dediazoniation at position 3, together with 3,4-dimethyl-1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene. Nitrosation of 1-phenyl- and 1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene took place with rearrangement to give 3-phenylazo- and 3-phenylazo-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene, respectively, as the main products. Nitrosation of the blocked 3,4-dimethyl-1-phenyl-6,6a-dithia-1,2-diazapentalene gave mainly 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene by nitroso-dediazoniation, some 4-methyl-3-(1-nitroethylidene)-3*H*-1,2-dithiole by nitro-dediazoniation, and a small amount of 3,4-dimethyl-1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene. Coupling of 1-aryl-5-t-butyl-6,6a-dithia-1,2-diazapentalenes with arenediazonium tetrafluoroborates took place in acetonitrile with exchange of the arylazo-units. These results are interpreted on the basis of a previously proposed mechanism of electrophilic substitution of 6a-thiathiophthens and related four-electron three-centre bonded structures.

ALTHOUGH the chemistry (in particular the substitution reactions) of 6a-thiathiophthens has been investigated in considerable detail, few studies have been made of the reactivity of other four-electron three-centre bonded compounds of the 6a-thiathiophthen type. Recently, 1-aryl-6,6a-dithia-1,2-diazapentalenes have become readily available by the coupling of 3-methyl(ene)-1,2-dithiolium salts with arenediazonium tetrafluoroborates.[2] This paper describes the behaviour of some 1-aryl-6,6a-dithia-1,2-diazapentalenes with electrophilic reagents. The following reactions were studied: bromination; Vilsmeier formylation; nitration; nitrosation; and diazo-coupling. In all cases the main primary process was attack at position 3 of the dithiadiazapentalene. The outcome depended on the nature of the reagent and on whether position 3 was free or blocked by an alkyl substituent. In several reactions substitution occurred to a minor extent at the *para*-position of a 1-phenyl substituent.

Bromination.— 1-Phenyl-6,6a-dithia-1,2-diazapentalene (1) [2] reacted with 2 equiv. of bromine in carbon tetrachloride at room temperature (standard conditions) to give a mixture of compounds (4) (67%) and (5) (13%). 1-Phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (8) [2] also gave a mixture of a monobromo- (11) (79%) and a dibromo-derivative (12) (13%). Bromination of the 1-*p*-bromophenyldithiadiazapentalenes (2) and (9), previously synthesised,[2] also gave the dibromo-derivatives (5) (74%) and (12) (97%). On the other hand, the 3-bromodithiadiazapentalenes (4) and (11) underwent further bromination less readily. The dibromo-derivatives (5) and (12) were again obtained, in 23 and 52% yield, respectively, and much starting material [(4), 37%; (11), 28%] was recovered. We infer that bromination of 1-phenyl-6,6a-dithia-1,2-diazapentalene (1) and its 5-t-butyl derivative (8) produces small amounts of the corresponding 1-*p*-bromophenyl derivatives (2) and (9), respectively, as intermediates, in addition to the main products (4) and (11). The dibromination products (5) and (12) then arise mainly by further bromination of the intermediates (2) and (9), but possibly also to a minor extent by further bromination of the major products (4) and (11).

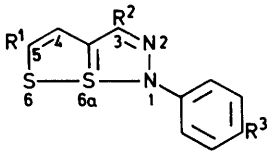
Formylation.—Vilsmeier formylation of 1-aryl-6,6a-dithia-1,2-diazapentalenes with dimethylformamide and phosphoryl chloride took place with difficulty. 1-Phenyl-6,6a-dithia-1,2-diazapentalene (1) gave a 15% yield of the aldehyde (6) and was largely destroyed. However, the t-butyl compound (8) gave the aldehyde (13) in 57% yield, and starting material (34%) was recovered. 1-*p*-Nitrophenyl-6,6a-dithia-1,2-diazapentalene (3) decomposed completely upon attempted formylation. The 5-t-butyl derivative (10) gave the aldehyde (14) in 18% yield, and only 27% of starting material was recovered. The aldehydes (6) and (13) had previously been obtained [1] in high yield in a rearrangement process which involves as the first step the coupling of the 1-oxa-6,6a-dithiapentalenes (18) and (19), respectively, with benzenediazonium tetrafluoroborate, and the nitro-aldehyde (14) had resulted [1] from the coupling of the oxadithiapentalene (19) with *p*-nitrobenzenediazonium tetrafluoroborate.

Nitration.— 1-Phenyl-6,6a-dithia-1,2-diazapentalene (1) reacted with concentrated nitric acid in acetic acid to give a mixture of two mononitro-derivatives (7) (48%) and (3) (12%). Nitration of the 5-t-butyl compound (8) gave a 9.5% yield of the dinitro-derivative (16) in addition to two mononitration products (15) (55%) and (10) (7.5%). The dinitration product (16) must arise

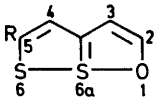
[1] Part 20, R. M. Christie and D. H. Reid, *J.C.S. Perkin I*, 1976, 880.

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

exclusively by further nitration of the first-formed 1-*p*-nitrophenyl derivative (10) because, in subsequent experiments, nitration of compound (10) gave the dinitro-derivative (16) (25%), and much starting material



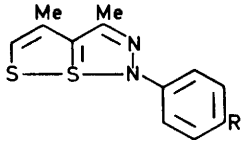
	R^1	R^2	R^3
(1)	H	H	H
(2)	H	H	Br
(3)	H	H	NO_2
(4)	H	Br	H
(5)	H	Br	Br
(6)	H	CHO	H
(7)	H	NO_2	H
(8)	Bu^t	H	H
(9)	Bu^t	H	Br
(10)	Bu^t	H	NO_2
(11)	Bu^t	Br	H
(12)	Bu^t	Br	Br
(13)	Bu^t	CHO	H
(14)	Bu^t	CHO	NO_2
(15)	Bu^t	NO_2	H
(16)	Bu^t	NO_2	NO_2
(17)	Bu^t	H	MeO



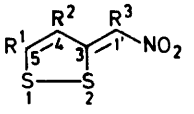
(18) R = H
(19) R = Bu^t

(69%) was recovered, but attempted nitration of the 3-nitrodithiadiazapentalene (15) gave back starting material nearly quantitatively.

Despite being blocked at the reactive position 3, 3,4-dimethyl-1-phenyl-6,6a-dithia-1,2-diazapentalene (20) [2] was also attacked mainly at position 3 and gave the 3-nitromethylene-1,2-dithiole (22) (35%) together with the 1-*p*-nitrophenyl derivative (21) (15%). We envisage the



(20) R = H
(21) R = NO_2

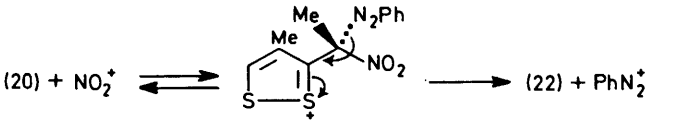


	R^1	R^2	R^3
(22)	H	Me	Me
(23)	Bu^t	H	H

formation of the dithiole (22) as a nitro-dediazoniation process (Scheme 1), which conforms to a mechanism

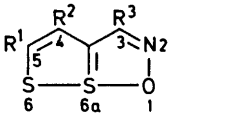
[3] R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Perkin I*, 1974, 722.

previously proposed [3] to account for the electrophilic substitution of 6a-thiathiophthens and related four-electron three-centre bonded compounds.

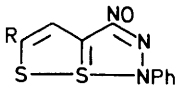


SCHEME 1

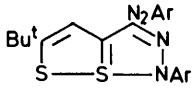
Nitrosation.—In contrast to the bromination, formylation, and nitration of 6,6a-dithia-1,2-diazapentalenes, which proceed normally to give 3-substituted 6,6a-dithia-1,2-diazapentalenes, nitrosation of 1-phenyl-6,6a-dithia-1,2-diazapentalene (1) and its 5-t-butyl derivative (8) with sodium nitrite in acetic acid–acetonitrile occurred with rearrangement and gave the 3-phenylazo-1-oxa-6,6a-dithia-2-azapentalenes (24) (50%) and (25) (87%),



	R^1	R^2	R^3
(24)	H	H	PhN_2
(25)	Bu^t	H	PhN_2
(26)	H	Me	Me

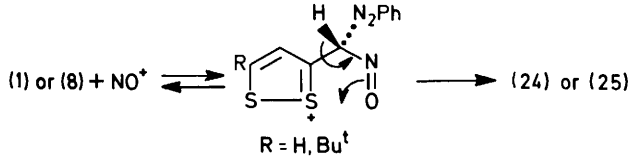


(27) R = H
(28) R = Bu^t



(29) Ar = Ph, *p*-MeCO·C_6H_4, *p*-MeO·C_6H_4, *p*-BrC_6H_4, *p*-MeC_6H_4
(30) Ar = *p*-NO_2·C_6H_4

respectively, as the major products (Scheme 2). We assign the oxadithia-azapentalene structures to the



SCHEME 2

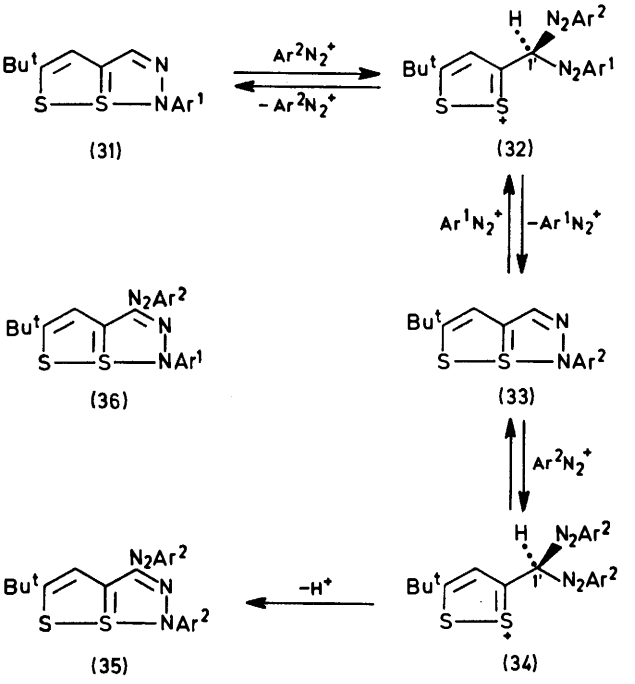
nitrosation products rather than the isomeric 3-nitroso-6,6a-dithia-1,2-diazapentalene structures (27) and (28), since the nitrosation products give golden yellow solutions in cyclohexane which do not show detectable u.v. absorption above 600 nm, even at concentrations at which the N=O group would give rise to measurable $n \longrightarrow \pi^*$ absorption ($\varepsilon \geqslant 20$). The mass spectra of the nitrosation products are free from peaks above *m/e* 249 and 305, respectively. However, this is not compelling evidence for the monomeric nature of the nitrosation products, since the M^+ peak of *C*-nitroso dimers is often weak or unobservable.

The major nitrosation products (24) and (25) were each

accompanied by small quantities of two isomeric nitration products (3) (1.2%) and (7) (6.4%) [from compound (1)] and (10) (1.5%) and (15) (4.4%) [from compound (8)]. The minor products (7) and (15) must arise by direct nitration of compounds (1) and (8), respectively, rather than by subsequent *N*-oxidation of the major products (24) and (25), since compound (25), when subjected to the nitrosation conditions, gave none of the nitro-compound (15) and was recovered almost quantitatively.

Nitrosation of the blocked dithiadiazapentalene (20) gave the oxadithia-azapentalene (26) as the major product (39%). This behaviour parallels that of compound (20) upon nitration and can be formulated analogously as a nitroso-dediazoniation (Scheme 1; NO^+ for NO_2^+). Appreciable quantities of the nitration products (21) (6%) and (22) (11%) were also produced along with the main product (26). The nitromethylenedithiole (22) must arise by nitro-dediazoniation of the substrate (20) (Scheme 1) rather than by *N*-oxidation of the major product (26), since we have already shown [3] that the oxadithia-azapentalene (26), when subjected to the nitrosation conditions, does not give a detectable amount of the nitromethylenedithiole (22).

Diazo-coupling.—We have previously shown [2] that 1-aryl-5-t-butyl-6,6a-dithia-1,2-diazapentalenes couple with arenediazonium tetrafluoroborates to give 3-arylazo-derivatives (29) in which the aryl groups are identical. Reaction proceeded more efficiently in ethanol, a more basic solvent, than in acetonitrile. Further studies of coupling reactions in which the aryl groups in the dithiadiazapentalene and the arenediazonium tetrafluoroborate are different, now show that diazonium ions exchange reversibly between the 6,6a-dithia-1,2-diazapentalene nucleus and a solution of diazonium ions. The following reactions were carried out in acetonitrile. (*A*) The 1-*p*-methoxyphenyldithiadiazapentalene (17) reacted with benzenediazonium tetrafluoroborate (2 : 1 molar ratio) to give the 1-phenyldithiadiazapentalene (1) almost quantitatively. (*B*) The 1-phenyldithiadiazapentalene (1) reacted incompletely with *p*-methoxybenzenediazonium tetrafluoroborate (3 : 1 molar ratio) to give the 1-*p*-methoxyphenyldithiadiazapentalene (17) (38%); much starting material (53%) was recovered. (*C*) The 1-phenyldithiadiazapentalene (1) reacted with *p*-nitrobenzenediazonium tetrafluoroborate (2 : 1 molar ratio) to give both the 1-*p*-nitrophenyldithiadiazapentalene (10) (69%) and its 3-*p*-nitrophenylazo-substitution product (30) (15%). We propose that the diazo-coupling reactions of 1-aryl-6,6a-dithia-1,2-diazapentalenes proceed according to Scheme 3. Reactions (*A*) and (*B*) are the reverse of one another, and involve the interconversion of the starting dithiadiazapentalene (31) [(*A*), $Ar^1 = p$-MeO·C_6H_4; (*B*), Ar^1 = Ph] and the 'exchanged' dithiadiazapentalene (33) [(*A*), Ar^2 = Ph; (*B*) $Ar^2 = p$-MeO·C_6H_4] *via* the intermediate (32) which acts as a 'turntable'. In reaction (*A*) formation of the 'exchanged' dithiadiazapentalene (33; Ar = Ph) is favoured because the *p*-methoxybenzenediazonium ion is more stable and less electrophilic than the benzenediazonium ion which, moreover, is present in excess. In reaction (*B*) the *p*-methoxybenzenediazonium ion succeeds in displacing the benzenediazonium ion to a limited extent by virtue of its concentration effect on the equilibrium. In reaction (*C*) the 'exchanged' dithiadiazapentalene (33; $Ar^2 = p$-NO_2·C_6H_4) is again favoured but further reaction occurs to give the 3-*p*-nitrophenylazo-substitution product (35; $Ar^2 = p$-NO_2·C_6H_4) *via* the intermediate (34; $Ar^2 = p$-NO_2·C_6H_4). It is not clear why reactions (*A*) and (*B*) do not produce the symmetrical and the unsymmetrical substitution



SCHEME 3

products (35) and (36) in detectable amounts. A possible reason is that the hydrogen at C-1′ in the intermediates (34; Ar^2 = Ph) and (32; $Ar^1 = p$-MeO·C_6H_4, Ar^2 = Ph) is too weakly acidic to be removed by the acetonitrile, in which proton activity is high. The intermediate (34; $Ar^2 = p$-NO_2·C_6H_4), however, is more acidic by virtue of increased electron withdrawal at C-1′ by the two *p*-nitrophenylazo-groups.

Position of Substitution.—Compounds (3) and (10) have previously been prepared by an unambiguous synthesis.[2] Structures were assigned to the substitution products (4), (6), and (7) on the basis of a comparison of their ^{1}H n.m.r. spectra with that of their precursor (1).[2] The spectra of compounds (4), (6), and (7) each showed an AB pair of doublets (*J ca* 6.7 Hz) arising from the 4-H,5-H interaction, and two multiplets (3 H and 2 H) arising from the 1-phenyl substituent, but they lacked a singlet corresponding to that from 3-H (δ 8.49) in the spectrum of compound (1). The substituents in compounds (4), (6), and (7) therefore occupy position 3.

The spectrum of the nitrosation product (24) also consisted of an AB pattern (J 6.6 Hz) and two multiplets (3 H and 2 H). This is consistent with initial attack of the precursor (1) at position 3.

The dibromo-derivative (5) is the product of further bromination of both monobromo-compounds (2) and (4), and its ^{1}H n.m.r. spectrum shows only an AB (J 6.7 Hz) and an AA'BB' pattern of signals. Each of these facts separately establishes structure (5) for the dibromination product from compound (1). Structures (13) and (14) assigned to the products of formylation of compounds (8) and (10), respectively, rest on the fact that the aldehydes (13) and (14) are also formed [1] from the oxadithiapentalene (19) by diazo-coupling and rearrangement. The dinitro-derivative obtained from the nitration of the dithiadiazapentalene (8) must be compound (16), since it was also formed nearly quantitatively by coupling of the nitromethylenedithiole (23) with *p*-nitrobenzenediazonium tetrafluoroborate.

The spectra of compounds (11), (15), and (25) contain only one low-field singlet, therefore substitution of their precursor (8) must have occurred at either position 3 or 4. We assume that position 3 has been substituted, by analogy with the formation of the related compounds (4), (7), and (24), respectively. Similar reasoning by analogy indicates structure (12) for the product of bromination of both compounds (9) and (11).

EXPERIMENTAL

^{1}H N.m.r. spectra were determined at 100 MHz. Solutions were 0.4M in deuteriochloroform, unless otherwise stated. Tetramethylsilane was used as internal reference and J values were measured 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 1-*p*-substituted phenyl group in compounds (5), (12), and (16) are the four most intense signals in the AA'BB' pattern. 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. Other experimental procedures are described in Part 20.

Bromination of 6,6a-*Dithia*-1,2-*diazapentalenes*.— 1-*Phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (1). A solution of bromine (10 mmol) in carbon tetrachloride (10 ml) was added to a solution of 1-phenyl-6,6a-dithia-1,2-diazapentalene [2] (1.10 g, 5 mmol) in carbon tetrachloride (150 ml). The mixture was stirred at room temperature for 10 min, poured into water, and extracted with ether. The extracts were washed with water (× 3), dried, and evaporated. Chromatography [silica (60 × 2.2 cm)] of the residue with petroleum–benzene (4 : 1) gave successively homogeneous red eluates, two-component red eluates, and orange eluates. Rechromatography of the residue from the two-component red eluates gave a further quantity of homogeneous red eluates and more of the orange eluates. The combined red eluates afforded 3-*bromo*-1-p-*bromophenyl*-6,6a-*dithia*-1,2-*diazapentalene* (5) (244 mg, 13%), reddish brown needles from hexane, m.p. 146—147° (Found: C, 31.8; H, 1.6; N, 7.3. $C_{10}H_6Br_2N_2S_2$ requires C, 31.8; H, 1.6; N, 7.4%); *m/e* 376, 368, and 380 (M^+); δ 7.48 and 7.57 (2 H, 2 *m*-protons of 1-Ar), 7.63 and 7.72 (2 H, 2 *o*-protons of 1-Ar), 7.99 (1 H, d, $J_{4.5}$ 6.7 Hz, 4-H), and 9.33 (1 H, d, $J_{5.4}$ 6.7 Hz, 5-H). The combined orange eluates yielded 3-*bromo*-1-*phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (4) (1 008 mg, 67%), orange-red spars from hexane, m,p. 97—99° (Found: C, 40.4; H, 2.4; N, 9.4. $C_{10}H_7BrN_2S_2$ requires C, 40.1; H, 2.4; N, 9.4%); *m/e* 298 and 300 (M^+); δ 7.24—7.53 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.69—7.80 (2 H, m, 2 *o*-protons of 1-Ph), 7.92 (1 H, d, $J_{4.5}$ 6.7 Hz, 4-H), and 9.32 (1 H, d, $J_{5.4}$ 6.7 Hz, 5-H).

1-*Phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (8). The procedure was identical with that of the preceding experiment, with 1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene [2] (1.38 g, 5 mmol) in place of compound (1). The initial red eluates yielded 3-*bromo*-1-p-*bromophenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (12) (291 mg, 13%), red prisms from hexane, m.p. 143.5—144.5° (Found: C, 39.1; H, 3.3; N, 6.5. $C_{14}H_{14}Br_2N_2S_2$ requires C, 38.7; H, 3.3; N, 6.5%); *m/e* 432, 434, and 436 (M^+); δ 1.47 (9 H, Bu^t), 7.45 and 7.54 (2 H, 2 *m*-protons of 1-Ar), 7.59 and 7.68 (2 H, 2 *o*-protons of 1-Ar), and 7.84 (1 H, 4-H). The succeeding orange eluates gave 3-*bromo*-1-*phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (11) (1 396 mg, 79%), orange-red needles from hexane, m.p. 104—105.5° (Found: C, 47.3; H, 4.2; N, 7.7. $C_{14}H_{15}BrN_2S_2$ requires C, 47.3; H, 4.3; N, 7.9%); *m/e* 354 and 356 (M^+); δ 1.47 (9 H, Bu^t), 7.21—7.48 (3 H, m, 2 *m*- + *p*-protons of 1 Ph), 7.71—7.83 (2 H, m, 2 *o*-protons of 1-Ph), and 7.82 (1 H, 4-H).

1-p-*Bromophenyl*-6,6a-*dithia*-1,2-*diazapentalene* (2). A solution of bromine (2 mmol) in carbon tetrachloride (2 ml) was added to a solution of 1-*p*-bromophenyl-6,6a-dithia-1,2-diazapentalene [2] (299 mg, 1 mmol) in carbon tetrachloride (30 ml). The mixture was stirred at room temperature for 10 min before being poured into water and extracted with ether. Chromatography [silica (60 × 2.2 cm)] of the residue from the washed (× 3), dried, and evaporated extracts with petroleum–benzene (4 : 1) gave red eluates which yielded 3-bromo-1-*p*-bromophenyl-6,6a-dithia-1,2-diazapentalene (5) (280 mg, 74%).

1-p-*Bromophenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (9). The procedure was identical with that of the preceding experiment, with 1-*p*-bromophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene [2] (355 mg, 1 mmol) in place of compound (2). 3-Bromo-1-*p*-bromophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (12) (420 mg, 97%) was obtained.

3-*Bromo*-1-*phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (4). Bromination of 3-bromo-1-phenyl-6,6a-dithia-1,2-diazapentalene (299 mg, 1 mmol) and collection of the product were effected by the procedure for the bromination of compound (2). Chromatography [silica (60 × 2.2 cm)] with petroleum–benzene (4 : 1) gave successively red eluates which yielded 3-bromo-1-*p*-bromophenyl-6,6a-dithia-1,2-diazapentalene (5) (85 mg, 23%), and orange eluates from which starting material (73 mg, 37%) was recovered.

3-*Bromo*-1-*phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (11). The procedure was identical with that of the preceding experiment, with 3-bromo-1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (355 mg, 1 mmol) in place of compound (4). 3-Bromo-1-*p*-bromophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (12) (226 mg, 52%) and starting material (99 mg, 28%) were isolated.

Formylation of 6,6a-*Dithia*-1,2-*diazapentalenes*.—1-*Phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (1). A solution of phosphoryl chloride (3.07 g, 1.82 ml, 20 mmol) in dimethylformamide (10 ml) was added dropwise during 15 min to a

stirred solution of 1-phenyl-6,6a-dithia-1,2-diazapentalene (440 mg, 2 mmol) in dimethylformamide (10 ml), and the resulting solution was heated at 60 °C for 2 h. The cooled solution was poured into aqueous M-sodium hydroxide (200 ml), and the mixture was extracted with benzene. The extracts were washed with water (× 5), dried, and evaporated, and the residue was chromatographed [silica (40 × 2.2 cm)]. Elution with benzene gave pale pink eluates which were discarded. Subsequent elution with benzene–ether (9 : 1) brought through orange eluates which afforded 1-phenyl-6,6a-dithia-1,2-diazapentalene-3-carbaldehyde (6) [1] (74 mg, 15%), δ (C_6D_6)* 6.92—7.18 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.55—7.65 (2 H, m, 2 *o*-protons of 1-Ph), 8.42 (1 H, d, $J_{5,4}$ 6.8 Hz, 5-H), 9.10 (1 H, d, $J_{4,5}$ 6.8 Hz, 4-H), and 10.06 (1 H, CHO).

1-*Phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (8). The procedure was identical with that of the preceding experiment, with 1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (552 mg, 2 mmol) in place of compound (1). Chromatography was performed with alumina (40 × 2.2 cm). Elution with benzene–petroleum (1 : 1) gave orange eluates from which starting material (190 mg, 34%) was recovered. Continued elution with benzene–ether (9 : 1) brought through orange eluates which yielded 1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene-3-carbaldehyde (13) [1] (345 mg, 57%), δ (C_6D_6) 1.35 (9 H, Bu^t), 7.00—7.25 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.66—7.77 (2 H, m, 2 *o*-protons of 1-Ph), 9.34 (1 H, 4-H), and 10.19 (1 H, CHO).

1-p-*Nitrophenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (10). A solution of phosphoryl chloride (3.07 g, 1.82 ml, 20 mmol) in dimethylformamide (10 ml) was added dropwise during 15 min to a stirred solution of 1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene [2] (642 mg, 2 mmol) in dimethylformamide (150 ml). The resulting mixture was heated at 60 °C for 1 h and then at 80 °C for 1 h before being cooled and poured into aqueous M-sodium hydroxide (200 ml). The mixture was extracted with benzene, and the residue from the washed (× 5), dried, and evaporated extracts was chromatographed [alumina (50 × 2.8 cm)]. Elution with benzene gave red eluates from which starting material (171 mg, 27%) was recovered. Subsequent elution with benzene–ether (9 : 1) brought through orange eluates which afforded 1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene-3-carbaldehyde (14) [1] (125 mg, 18%). Attempted formylation of 1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene (3) [2] (530 mg, 2 mmol) under the conditions of the foregoing experiment resulted in complete decomposition of the starting material.

Nitration of 6,6a-*Dithia*-1,2-*diazapentalenes*.—The following general procedure was used. Concentrated nitric acid (0.5 ml) was added to a solution of the 6,6a-dithia-1,2-diazapentalene (5 mmol) in acetic acid (150 ml), and the solution was kept at room temperature for 2 min before being diluted with water and extracted with benzene. The extracts were washed with water (× 2), saturated sodium hydrogen carbonate solution (× 2), and water (× 2), dried, and evaporated. In two reactions a modified general procedure was used in which a solution of the 6,6a-dithia-1,2-diazapentalene (1 mmol) in acetic acid (150 ml) was treated with concentrated nitric acid (0.1 ml). Subsequent work-up varied and is described for each reaction.

* The ^{1}H n.m.r. spectrum of compound (6) in $CDCl_3$ (ref. 1) shows a two-proton singlet at δ 9.19 owing to accidental equivalence of 4-H and 5-H.

1-*Phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (1). Chromatography [alumina (40 × 2.8 cm)] with benzene–petroleum (2 : 1) gave pale yellow eluates which were discarded. Subsequent elution with benzene brought through red eluates, the residue from which was rechromatographed [silica (60 × 2.2 cm)]. Elution with benzene–petroleum (1 : 1) gave orange-red eluates which afforded 1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene (3) [2] (160 mg, 12%). Continued elution with benzene brought through orange eluates which yielded 3-*nitro*-1-*phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (7) (638 mg, 48%), red prisms from benzene–cyclohexane, m.p. 151—151.5° (Found: C, 45.4; H, 2.6; N, 15.4. $C_{10}H_7N_3O_2S_2$ requires C, 45.3; H, 2.7; N, 15.8%); *m/e* 265 (M^+); δ 7.40—7.58 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.83—7.94 (2 H, m, 2 *o*-protons of 1-Ph), 9.05 (1 H, d, $J_{4,5}$ 6.7 Hz, 4-H), and 9.17 (1 H, d, $J_{5,4}$ 6.7 Hz, 5-H).

1-*Phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (8). Chromatography [alumina (40 × 2.8 cm)] with benzene–petroleum (2 : 1) gave pale yellow eluates which were discarded. Continued elution with benzene brought through a two-component red fraction, and subsequent elution with benzene–ether (4 : 1) gave orange-red eluates. Rechromatography [silica (60 × 2.2 cm)] of the residue from the red fraction gave successively 1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (10) [2] (120 mg, 7.5%) [from orange-red benzene–petroleum (1 : 1) eluates] and 3-*nitro*-1-*phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (15) (889 mg, 55%) (from orange benzene eluates), red prisms from cyclohexane, m.p. 114—116° (Found: C, 52.6; H, 4.7; N, 13.1. $C_{14}H_{15}N_3O_2S_2$ requires C, 52.3; H, 4.7; N, 13.1%); *m/e* 321 (M^+); δ 1.51 (9 H, Bu^t), 7.32—7.50 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.80—7.95 (2 H, m, 2 *o*-protons of 1-Ph), and 8.98 (1 H, 4-H). The orange-red benzene–ether eluates yielded 3-*nitro*-1-p-*nitrophenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (16) (174 mg, 9.5%), red needles from benzene–cyclohexane (1 : 1), m.p. 230—231° (Found: C, 46.1; H, 4.0; N, 15.4. $C_{14}H_{14}N_4O_4S_2$ requires C, 45.9; H, 3.8; N, 15.3%); *m/e* 366 (M^+); δ 1.54 (9 H, Bu^t), 7.96 and 8.05 (2 H, 2 *o*-protons of 1-Ar), 8.27 and 8.36 (2 H, 2 *m*-protons of 1-Ar), and 9.09 (1 H, 4-H).

3,4-*Dimethyl*-1-*phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (20).[2] Chromatography [alumina (35 × 2.8 cm)] with benzene gave red eluates which afforded 3,4-dimethyl-1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene (21) [2] (213 mg, 15%). Continued elution with ether–ethanol (99 : 1) brought through yellow eluates which yielded 4-methyl-3-(1-nitroethylidene)-3*H*-1,2-dithiole (22) [3,4] (330 mg, 35%).

1-p-*Nitrophenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (10). The modified general procedure was used. Chromatography [alumina (50 × 2.2 cm)] with benzene gave red eluates from which starting material (222 mg, 69%) was recovered. Subsequent elution with benzene–ether (4 : 1) brought through orange eluates which afforded 3-nitro-1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (16) (91 mg, 25%).

3-*Nitro*-1-*phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (15). The modified general procedure was used. Chromatography [alumina (50 × 2.2 cm)] with benzene gave starting material only (311 mg, 97%).

Synthesis of 3-*Nitro*-1-*p*-*nitrophenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (16) *by Coupling of* 3-*Nitromethylene*-5-*t*-*butyl*-3H-1,2-*dithiole* (23) *with* p-*Nitrobenzenediazonium*

[4] J. G. Dingwall, A. R. Dunn, D. H. Reid, and K. O. Wade, *J.C.S. Perkin I*, 1972, 1360.

Tetrafluoroborate (with A. S. INGRAM).—A solution of *p*-nitrobenzenediazonium tetrafluoroborate (1.78 g, 7.5 mmol) in acetonitrile (50 ml) was added to a solution of the dithiole (23)[5] (1.09 g, 5 mmol) in acetonitrile (150 ml). The resulting solution deposited a red solid and was kept at room temperature for 1 h before being diluted with water and extracted with benzene. The extracts were washed with water, dried, and evaporated, and the residue was chromatographed [alumina (30 × 2.4 cm)] with benzene. The orange-red eluates yielded 3-nitro-1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (1.68 g, 96%).

Nitrosation of 6,6a-*Dithia*-1,2-*diazapentalenes*.—The following general procedure was used. Sodium nitrite (690 mg, 10 mmol) was added to a stirred solution of the dithiadiazapentalene (5 mmol) in acetonitrile (75 ml) and acetic acid (75 ml) at room temperature. The mixture was stirred for 15 min, a second portion of sodium nitrite (345 mg, 5 mmol) was added, and the mixture was stirred for a further 15 min before being diluted with water and extracted with benzene. The extracts were washed successively with water (× 2), saturated aqueous sodium hydrogen carbonate (× 2), and water, dried, and evaporated. Subsequent chromatographic analysis of the residue varied and is described for each reaction.

1-*Phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (1). Chromatography [alumina (40 × 2.8 cm)] with benzene–petroleum (1 : 1) gave pale yellow eluates which were discarded. Continued elution with benzene brought through a two-component red fraction, and subsequent elution with benzene–ether (4 : 1) gave orange-yellow eluates. Rechromatography [silica (55 × 2.2 cm)] of the residue from the red fraction gave successively 1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene (3)[2] (16 mg, 1.2%) [from benzene–petroleum (1 : 1) eluates] and 3-nitro-1-phenyl-6,6a-dithia-1,2-diazapentalene (7) (85 mg, 6.4%) (from benzene eluates). The orange-yellow eluates furnished 3-*phenylazo*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (24) (624 mg, 50%), yellowish brown needles from benzene–cyclohexane, m.p. 138.5—139° (Found: C, 48.3; H, 2.7; N, 16.9; S, 25.9. $C_{10}H_7N_3OS_2$ requires C, 48.2; H, 2.8; N, 16.9; S, 25.7%); *m/e* 249 (M^+); δ ($CDCl_3$) 7.46—7.58 (3 H, m, 2 *m*- + *p*-protons of Ph), 7.95—8.08 (2 H, m, 2 *o*-protons of Ph), and 9.42 (2 H, 4- and 5-H); δ (C_6D_6) 7.10—7.20 (3 H, m, 2 *m*- + *p*-protons of Ph), 7.90—8.00 (2 H, m, 2 *o*-protons of Ph), 8.24 (1 H, d, $J_{5,4}$ 6.6 Hz, 5-H), and 8.87 (1 H, d, $J_{4,5}$ 6.6 Hz, 4-H).

1-*Phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (8). Chromatography was carried out according to the method of the preceding experiment and gave successively 1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (10)[2] (24 mg, 1.5%), 3-nitro-1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (15) (70 mg, 4.4%), and 3-*phenylazo*-5-*t*-*butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (25) (1.32 g, 87%), fine orange-yellow needles from cyclohexane, m.p. 156—156.5° (Found: C, 55.3; H, 5.1; N, 14.1. $C_{14}H_{15}N_3OS_2$ requires C, 55.1; H, 5.0; N, 13.8%); *m/e* 305 (M^+); δ($CDCl_3$) 1.54 (9 H, Bu^t), 7.45—7.59 (3 H, m, 2 *m*- + *p*-protons of Ph), 7.92—8.04 (2 H, m, 2 *o*-protons of Ph), and 9.32 (1 H, 4-H); δ(C_6D_6) 1.13 (9 H, Bu^t), 7.10—7.32 (3 H, m, 2 *m*- + *p*-protons of Ph), 7.97—8.06 (2 H, m, 2 *o*-protons of Ph), and 9.18 (1 H, 4-H). When a solution of the oxadithia-azapentalene (25) (610 mg, 2 mmol) in acetonitrile (50 ml) and acetic acid (50 ml) was treated with successive portions of sodium nitrite (4 + 2 mmol) under the conditions used for the nitrosation of the dithiadiazapentalene (8), no trace of the nitro-compound (15) was detected and starting material (601 mg, 99%) was recovered.

3,4-*Dimethyl*-1-*phenyl*-6,6a-*dithia*-1,2-*diazapentalene* (20). Chromatography [alumina (50 × 2.8 cm)] with benzene–petroleum (2 : 1) gave pale orange eluates which were discarded. Subsequent elution with benzene–petroleum (3 : 1) gave red eluates which afforded 3,4-dimethyl-1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene (21) (87 mg, 6%). Continued elution with benzene–ether (4 : 1) brought through yellow eluates from which 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (26)[3,4] (336 mg, 39%) was obtained. Elution finally with ether–ethanol (99 : 1) gave yellow eluates which yielded 4-methyl-3-(1-nitroethylidene)-3*H*-1,2-dithiole (22)[3,4] (102 mg, 11%).

Coupling of 1-*Aryl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalenes with Arenediazonium Tetrafluoroborates in Acetonitrile*.—The following general procedure was used. The arenediazonium tetrafluoroborate (4 mmol, unless otherwise stated) was added to a solution of the dithiadiazapentalene (2 mmol) in acetonitrile (75 ml), and the resulting 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 (× 3), dried, and evaporated. Subsequent work-up varied and is described for each reaction.

1-p-*Methoxyphenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (17)[2] *with benzenediazonium tetrafluoroborate*. Chromatography [alumina (35 × 2.2 cm)] with petroleum–benzene (2 : 1) gave orange eluates which afforded 1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (8) (540 mg, 98%).

1-*Phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (8) *with* p-*methoxybenzenediazonium tetrafluoroborate*. A larger quantity (6 mmol) of the tetrafluoroborate was used. Chromatography [alumina (35 × 2.2 cm)] with petroleum–benzene (2 : 1) gave orange eluates from which starting material (295 mg, 53%) was recovered. Continued elution with petroleum–benzene (1 : 1) gave orange eluates which yielded 1-*p*-methoxyphenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (17) (231 mg, 38%).

1-*Phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene* (8) *with* p-*nitrobenzenediazonium tetrafluoroborate*. Chromatography [alumina (40 × 2.2 cm)] with benzene–petroleum (2 : 1) gave pale orange eluates which were discarded. Subsequent elution with benzene brought through red eluates which afforded 1-*p*-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (10) (440 mg, 69%). Continued elution with benzene–ether (9 : 1) gave brownish red eluates from which 1-*p*-nitrophenyl-3-*p*-nitrophenylazo-5-t-butyl-6,6a-dithia-1,2-diazapentalene (30)[2] (144 mg, 15%) was obtained.

We thank the Carnegie Trust for the Universities of Scotland for a Postgraduate Research Studentship (to R. M. C.), and the S.R.C. for financial support.

[6/1751 *Received*, 16*th September*, 1976]

[5] D. H. Reid and R. G. Webster, unpublished data.