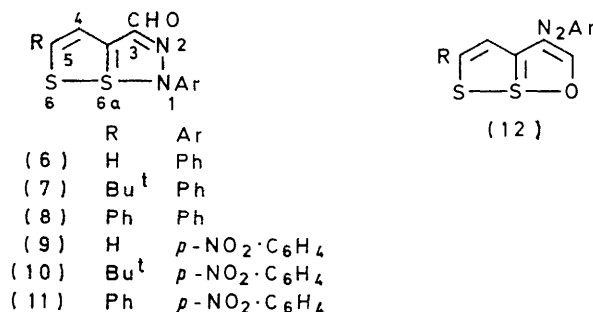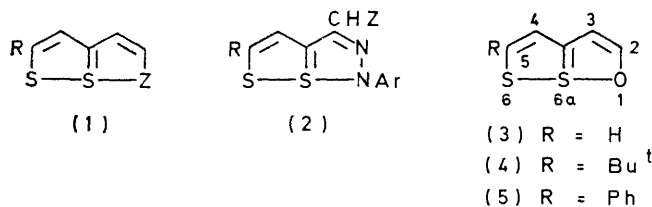# Studies of Heterocyclic Compounds. Part XX.[1] Substitution of 1-Oxa-6,-6a-dithiapentalenes with Arenediazonium Fluoroborates: Rearrangement into 6,6a-Dithia-1,2-diazapentalenes [2]

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

1-Oxa-6,6a-dithiapentalenes unsubstituted at position 3 couple with arenediazonium fluoroborates with accompanying rearrangement. 1-Oxa-6,6a-dithiapentalene and its 5-t-butyl and 5-phenyl derivatives gave 1-aryl-3-formyl-6,6a-dithia-1,2-diazapentalenes and the corresponding 5-substituted analogues, respectively. 1-Oxa-6,6a-dithiapentalenes in which the reactive position 3 is blocked, couple with p-nitrobenzene-diazonium fluoroborate with accompanying deformylation. 3,4-Dimethyl- and 3-methyl-5-phenyl-1-oxa-6,6a-dithiapentalene gave 3,4-dimethyl-1-p-nitrophenyl- and 3-methyl-1-p-nitrophenyl-5-phenyl-6,6a-dithia-1,2-diazapentalene, respectively, and 4,5-dihydro-3H-1-oxa-7,7a-dithiacyclopent[cd]indene gave 6,7-dihydro-2-p-nitrophenyl-5H-2a,3-dithia-1,2-diazacyclopent[cd]indene. 4,5,6,7-Tetrahydro-2-t-butyl-8-oxa-1,8a-dithia-cyclopent[a]indene reacted with p-nitrobenzenediazonium fluoroborate (i) in acetonitrile to give 5-(1-p-nitro-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalen-3-yl)pentanoic acid, and (ii) in methanol to give methyl 5-(1-p-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalen-3-yl)pentanoate. These results are accounted for by a previously proposed mechanism of electrophilic substitution of 1-oxa-6,6a-dithiapentalenes and related heterocyclic systems.

WE have reported briefly [2] that 1-oxa-6,6a-dithia-pentalenes (1; Z = O), 6a-thiathiophthens (1; Z = S), and 1,6a-dithia-6-azapentalenes (1; Z = NMe) couple

(1)

(2)

(3) R = H
(4) R = Bu^t
(5) R = Ph

(6) H Ph
(7) Bu^t Ph
(8) Ph Ph
(9) H p-NO$_2$·C$_6$H$_4$
(10) Bu^t p-NO$_2$·C$_6$H$_4$
(11) Ph p-NO$_2$·C$_6$H$_4$

(12)

with arenediazonium fluoroborates with accompanying rearrangement into 6,6a-dithia-1,2-diazapentalenes (2), a new class of hypervalent heterocyclic compound. Depending on the heteroatom Z, the primary product (2) may react further *in situ* to give a more stable, isolable product. We now give detailed results of studies of the diazo coupling reactions of 1-oxa-6,6a-dithiapentalenes. These fall into two categories, depending on whether the reactive position 3 in the oxadithiapentalene is free or blocked by an alkyl substituent.

We studied first the behaviour of three oxadithia-pentalenes (3)—(5) which are unsubstituted at positions 3 and 4. These compounds coupled readily with benzenediazonium fluoroborate in acetonitrile to give the 3-formyl-6,6a-dithia-1,2-diazapentalenes (6)—(8), respectively, in 53—74% yield. Compounds (3)—(5) reacted faster with the more electrophilic p-nitro-benzenediazonium fluoroborate and gave the aldehydes (9)—(11) in 75—98% yield. The diazo coupling

[1] Part XIX, R. M. Christie and D. H. Reid, *J.C.S. Perkin I*, 1976, 228.
[2] Preliminary communication, R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Chem. Comm.*, 1973, 92.

products possess the 6,6a-dithia-1,2-diazapentalene structures (6)—(11) rather than the unrearranged 3-arylazo-1-oxa-6,6a-dithiapentalene structures (12): they show strong i.r. carbonyl absorption in the range 1 670—1 688 cm⁻¹, and their ^{1}H n.m.r. spectra (CDCl₃) show formyl proton singlets in the range δ 10.02—10.12.

We have recently proposed [3] that the electrophilic substitution of 6a-thiathiophthens and related hypervalent heterocyclic compounds proceeds by way of intermediate 6π-electron cations, such as 1,2-dithiolium and 1,2-oxathiolium. On the basis of this mechanism the aldehydes (6)—(11) may be envisaged as arising *via* the dithiolium intermediate (13) (Scheme 1).

$$(3)-(5) \longrightarrow (13) \longrightarrow (6)-(11)$$

SCHEME 1
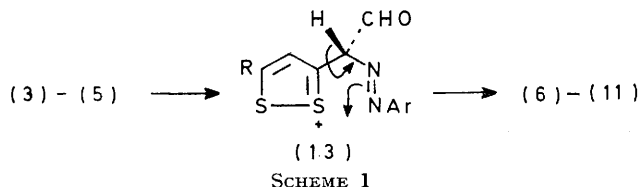
A consideration of the foregoing mechanism and of the high reactivity of position 3 in the oxadithiapentalene system prompted us to examine the diazo coupling reactions of oxadithiapentalenes blocked at position 3. Thus compounds (14)—(16) reacted smoothly with *p*-

	R¹	R²	R³		R¹	R²	R³
(14)	H	Me	Me	(17)	H	Me	Me
(15)	H	[CH₂]₃		(18)	H	[CH₂]₃	
(16)	Ph	H	Me	(19)	Ph	H	Me
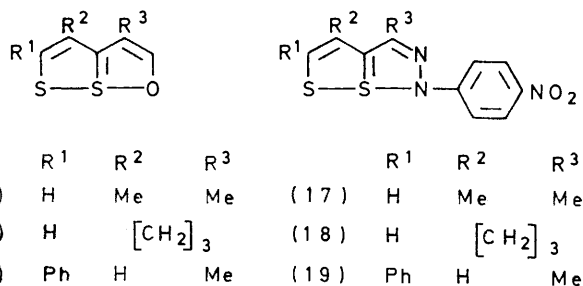
nitrobenzenediazonium fluoroborate in acetonitrile, with concomitant deformylation, to give the dithiadiazapentalenes (17)—(19),[1] respectively, in 70—83% yield. These findings are accommodated by an extension (Scheme 2) of our electrophilic substitution mechanism,

$$(14)-(16) \longrightarrow (20) \longrightarrow (17)-(19)$$
$$+ H^+ + HCO_2H$$

Ar = *p*-NO₂·C₆H₄

SCHEME 2
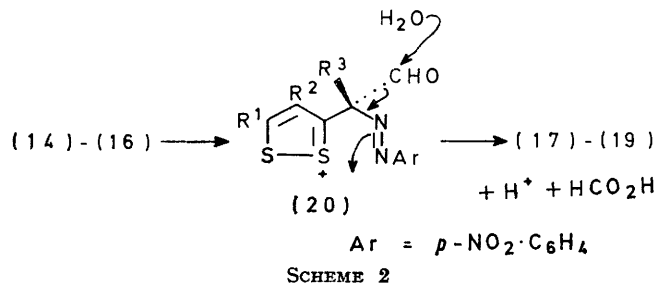
in which the dithiolium intermediate (20) undergoes nucleophilic attack by traces of water in the acetonitrile. It was not possible to establish the presence of the resulting formic acid, owing to the difficulty of detecting it in the presence of solvent, reactants, and products. However, the fate of the expelled carbonyl fragment was

established in the following related reactions. Treatment of the tetrahydro-8-oxa-1,8a-dithiacyclopent[*a*]-indene (21) with *p*-nitrobenzenediazonium fluoroborate in acetonitrile gave the carboxylic acid (23) (85%) *via* the intermediate (22) (Scheme 3). When methanol was

Ar = *p*-NO₂·C₆H₄

(23) R = H
(24) R = Me

SCHEME 3
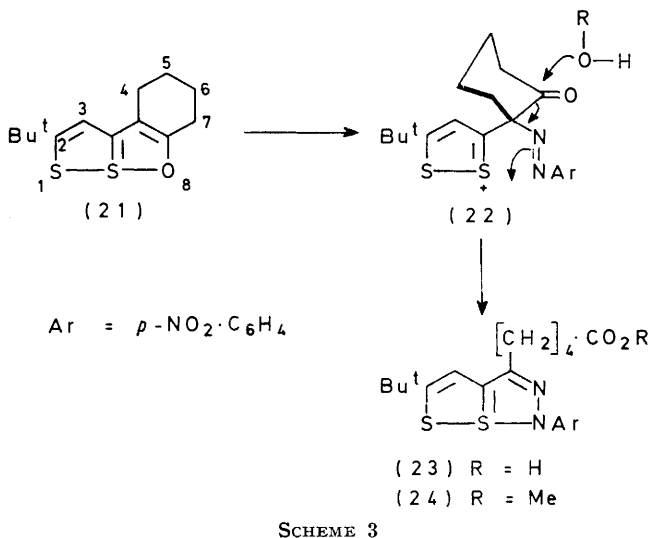
used in place of acetonitrile the corresponding methyl ester (24) was obtained (93%), as required by the proposed mechanism.

We have not found any evidence for electrophilic substitution elsewhere than at position 3 in the oxadithiapentalene system. Diazo-coupling at position 4 would involve 1,2-oxathiolium intermediates of the type (25). We suggest that the lack of reactivity of position 4 depends, at least in part, on two factors: (*a*) the 1,2-

(25)

(26)
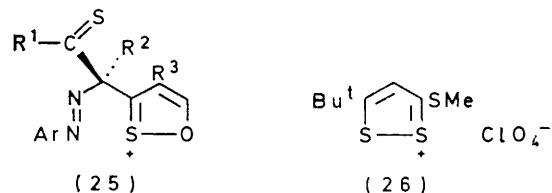
oxathiolium system may be less aromatic than the 1,2-dithiolium system; (*b*) formation of an oxatholium intermediate (25) also involves the formation of a thiocarbonyl group in a relatively unstable situation.

The oxadithiacyclopentindene (21), hitherto unknown, was prepared (43%) by the condensation of 3-methyl-thio-5-t-butyl-1,2-dithiolium perchlorate (26) with the enolate of 2-oxocyclohexane carboxylic acid.

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, and refer to solids dispersed in

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

KBr discs. ¹H N.m.r. spectra were determined at 100 MHz with a Varian HA 100 spectrometer. 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-nitrophenyl group in compounds (9)—(11), (23), and (24) are the four most intense signals in the AA'BB' pattern. 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, unless otherwise indicated. Solvent mixtures are described in ratios by volume. Criteria used in the identification of products included m.p.s, t.l.c. behaviour, and n.m.r. and mass spectra. 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.

4,5,6,7-*Tetrahydro*-2-*t*-*butyl*-8-*oxa*-1,8a-*dithiacyclopent*[a]-*indene* (21).—(i) 2-*Oxocyclohexanecarboxylic acid.* The following modification of the published method of preparation [4] gives reproducible results in large-scale work. Cyclohexanone (49 g, 52 ml, 0.5 mol) was added to a suspension of sodium amide in ether, prepared by dissolving sodium (14 g, 0.61 g atom) in liquid ammonia (500 ml) and replacing the ammonia by ether (500 ml) in the usual manner. The mixture was boiled for 30 min, then kept at ca. 35 °C while dry carbon dioxide was bubbled through for 3 h. The mixture was poured into a slurry of ice and an excess of 2M-hydrochloric acid, and the resulting mixture was extracted with ether (5 × 300 ml). The combined ethereal solutions were extracted with an excess of a saturated solution of sodium carbonate. The ice-cold carbonate extracts were acidified with 2M-hydrochloric acid, then extracted with ether (5 × 300 ml). Evaporation of the dried extracts gave 2-oxocyclohexanecarboxylic acid (29 g, 41%).

(ii) *Condensation of* 2-*oxocyclohexanecarboxylic acid with* 3-*methylthio*-5-*t*-*butyl*-1,2-*dithiolium perchlorate* (26). The oxo-acid (15.6 g, 110 mmol) was dissolved in 0.2M-sodium ethoxide in ethanol (500 ml). The perchlorate (26) [3] (15.25 g, 50 mmol) was added, and the resulting solution was heated at 50 °C for 15 min, cooled, and poured into water. The mixture was extracted with ether (× 3), and the extracts were washed with water (× 3), dried, and evaporated. Chromatography [alumina (50 × 2.8 cm)] of the residue with petroleum–benzene (3 : 1) gave pale yellow eluates which were discarded. Continued elution with benzene–petroleum (2 : 1) brought through red eluates. Subsequent elution with benzene–ether (4 : 1) yielded homogeneous yellow eluates. Rechromatography [alumina (50 × 2.8 cm)] of the residue from the red eluates with benzene–petroleum (2 : 1) brought through red eluates which were discarded, and further elution with benzene–ether (4 : 1) yielded yellow eluates. The combined yellow eluates afforded the *oxadithiacyclopentindene* (21) (5.46 g, 43%), yellow crystals, m.p. 69.5—70° (Found: C, 61.6; H, 7.4. C₁₃H₁₈OS₂ requires C, 61.4; H, 7.1%); *m/e* 254 (*M*⁺);

* The assignments of the signals at δ 2.52 and 2.68 are tentative and may require to be interchanged.

⁴ H. D. Gardner, W. H. Perkin, and H. Watson, *J. Chem. Soc.*, 1910, 1764.

$\lambda_{\text{max.}}$ 434infl (log ε 4.11), 420 (4.13), and 227 nm (4.29); δ 1.38 (9 H, Buᵗ), 1.83 (4 H, m, 5- + 6-H₂), 2.52 (2 H, m, 4-H₂ *), 2.68 (2 H, m, 7-H₂ *), and 6.94 (1 H, 3-H).

Coupling of 1-*Oxa*-6,6a-*dithiapentalenes with Benzenediazonium Fluoroborate.*—1-*Oxa*-6,6a-*dithiapentalene* (3). A solution of benzenediazonium fluoroborate (1.92 g, 10 mmol) in acetonitrile (50 ml) was added to a solution of 1-oxa-6,6a-dithiapentalene [5] (720 mg, 5 mmol) in acetonitrile (150 ml). The red solution was kept at room temperature for 1 h, diluted with water, and extracted with ether. The extracts were washed with water (× 3), dried, and evaporated. Chromatography [silica (30 × 2.8 cm)] of the residue with benzene gave orange eluates which afforded 1-*phenyl*-6,6a-*dithia*-1,2-*diazapentalene*-3-*carbaldehyde* (6) (704 mg, 57%), red needles (from cyclohexane–benzene), m.p. 139.5—140° (Found: C, 53.2; H, 3.2; N, 11.2. C₁₁H₈N₂OS₂ requires C, 53.2; H, 3.3; N, 11.3%); *m/e* 248 (*M*⁺); $\lambda_{\text{max.}}$ 475 (log ε 4.36), 346 (3.97), 312 (4.02), 243infl (4.33), and 234 nm (4.38); $\nu_{\text{max.}}$ 1 670 cm⁻¹ (C=O); δ 7.25—7.57 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.83—7.93 (2 H, m, 2 *o*-protons of 1-Ph), 9.19 (2 H, 4- and 5-H), and 10.07 (CHO).

5-*t*-*Butyl*-1-*oxa*-6,6a-*dithiapentalene* (4). The procedure was identical with that of the preceding experiment, with 5-t-butyl-1-oxa-6,6a-dithiapentalene [3] (1.00 g, 5 mmol) in place of compound (3), and chromatography was performed with alumina (30 × 2.8 cm). 1-*Phenyl*-5-*t*-*butyl*-6,6a-*dithia*-1,2-*diazapentalene*-3-*carbaldehyde* (7) (1.14 g, 74%) was obtained as orange prisms (from hexane), m.p. 111.5—112.5° (Found: C, 59.4; H, 5.2; N, 9.4. C₁₅H₁₆N₂OS₂ requires C, 59.2; H, 5.3; N, 9.2%); *m/e* 304 (*M*⁺); $\lambda_{\text{max.}}$ 474 (log ε 4.13), 348 (4.04), 319 (3.95), 273 (4.08), and 235 nm (4.40); $\nu_{\text{max.}}$ 1 688 cm⁻¹ (C=O); δ 1.49 (9 H, Buᵗ), 7.35—7.50 (3 H, m, 2 *m*- + *p*-protons of 1-Ph), 7.78—7.86 (2 H, m, 2 *o*-protons of 1-Ph), 9.09 (1 H, 4-H), and 10.02 (CHO).

5-*Phenyl*-1-*oxa*-6,6a-*dithiapentalene* (5). The procedure was identical with that of the preceding experiment, with 5-phenyl-1-oxa-6,6a-dithiapentalene[6] (1.10 g, 5 mmol) in place of compound (4). 1,5-*Diphenyl*-6,6a-*dithia*-1,2-*diazapentalene*-3-*carbaldehyde* (8) (860 mg, 53%) was obtained as orange-red needles (from cyclohexane), m.p. 154.5—155° (Found: C, 62.8; H, 3.8; N, 8.7. C₁₇H₁₂N₂OS₂ requires C, 62.9; H, 3.7; N, 8.6%); *m/e* 324 (*M*⁺); $\lambda_{\text{max.}}$ 492 (log ε 4.24), 356infl (3.87), 315 (4.30), 239 (4.54), and 205 nm (4.52); $\nu_{\text{max.}}$ 1 682 cm⁻¹ (C=O); δ 7.37—7.45 (6 H, m, 2 *m*- + *p*-protons of 1- and 5-Ph), 7.80—7.88 (4 H, m, 2 *o*-protons of 1- and 5-Ph), 9.38 (1 H, 4-H), and 10.04 (1 H, CHO).

Coupling of 1-*Oxa*-6,6a-*dithiapentalenes with* p-*Nitrobenzenediazonium Fluoroborate.*—1-*Oxa*-6,6a-*dithiapentalene* (3). A solution of *p*-nitrobenzenediazonium fluoroborate (1.775 g, 7.5 mmol) in acetonitrile (50 ml) was added to a solution of 1-oxa-6,6a-dithiapentalene (720 mg, 5 mmol) in acetonitrile (150 ml). The resulting solution became red, deposited a solid, and was kept at room temperature for 30 min before being filtered. Recrystallisation of the solid from benzene gave 1-p-*nitrophenyl*-6,6a-*dithia*-1,2-*diazapentalene*-3-*carbaldehyde* (9) (1.246 g) as small red needles, m.p. 275—276.5° (Found: C, 45.0; H, 2.7; N, 14.5. C₁₁H₇N₃O₃S₂ requires C, 45.0; H, 2.4; N, 14.3%); *m/e* 293

⁵ D. H. Reid and R. G. Webster, *J.C.S. Perkin I*, 1972, 1447.
⁶ J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc.* (C), 1968, 2543.

(M^+); $\lambda_{max.}$ 488, 357, 320br, 269infl, 244, and 218 nm; *
$\nu_{max.}$ 1 674 cm^{-1} (C=O); δ † 8.02 and 8.11 (2 H, 2 o-protons
of 1-Ar), 8.32 and 8.41 (2 H, 2 m-protons of 1-Ar), 9.23 (1 H,
d, $J_{4,5}$ 6.5 Hz, 4-H), 9.39 (1 H, d, $J_{5,4}$ 6.5 Hz, 5-H), and
10.12 (1 H, CHO). The reaction filtrates were diluted
with water and extracted with benzene, and the washed and
dried extracts were combined with the mother liquors from
the foregoing recrystallisation. Evaporation and chro-
matography [silica (15 × 2.8 cm)] of the residue with
benzene–ether (19 : 1) afforded more (192 mg) of the
aldehyde (total yield 1.438 g, 98%).

5-t-Butyl-1-oxa-6,6a-dithiapentalene (4). A solution of p-
nitrobenzenediazonium fluoroborate (1.775 g, 7.5 mmol) in
acetonitrile (50 ml) was added to a solution of 5-t-butyl-
1-oxa-6,6a-dithiapentalene (1.00 g, 5 mmol) in acetonitrile
(150 ml). The mixture was kept at room temperature for
30 min, diluted with water, and extracted with benzene.
The extracts were washed with water (× 3), dried, and
evaporated. Chromatography [alumina (35 × 2.8 cm)] of
the residue with benzene–ether (3 : 1) gave red eluates
which yielded 1-p-nitrophenyl-5-t-butyl-6,6a-dithia-1,2-diaza-
pentalene-3-carbaldehyde (10) (1.59 g, 91%), orange-red
needles (from benzene–cyclohexane), m.p. 187—187.5°
(Found: C, 51.8; H, 4.4; N, 12.0. $C_{15}H_{15}N_3O_2S_2$ requires
C, 51.9; H, 4.3; N, 12.0%); m/e 349 (M^+); $\lambda_{max.}$ 487 (log ε
4.34), 361 (4.26), 315 (4.01), 282 (4.04), 246infl (4.19), and
219 nm (4.38); $\nu_{max.}$ 1 680 cm^{-1} (C=O); δ 1.53 (9 H, Bu^t),
7.90 and 7.99 (2 H, 2 o-protons of 1-Ar), 8.24 and 8.33 (2 H,
2 m-protons of 1-Ar), 9.24 (1 H, 4-H), and 10.04 (1 H,
CHO).

5-Phenyl-1-oxa-6,6a-dithiapentalene (5). The procedure
was identical with that of the preceding experiment, with
5-phenyl-1-oxa-6,6a-dithiapentalene (1.10 g, 5 mmol) in
place of compound (4). 1-p-Nitrophenyl-5-phenyl-6,6a-
dithia-1,2-diazapentalene-3-carbaldehyde (11) (1.39 g, 75%)
was obtained as deep red prisms (from benzene), m.p.
214.5—215° (Found: C, 55.1; H, 3.0; N, 11.4. $C_{17}H_{11}N_3$-
O_3S_2 requires C, 55.3; H, 3.0; N, 11.4%); m/e 369 (M^+);
$\lambda_{max.}$ 506 (log ε 4.36), 370 (4.12), 328 (4.33), 221infl (4.43),
and 204 nm (4.54); $\nu_{max.}$ 1 670 cm^{-1} (C=O); δ † 7.50 (3 H,
m, 2 m- + p-protons of 5-Ph), 7.90 (2 H, m, 2 o-protons of
5-Ph), 7.96 and 8.05 (2 H, 2 o-protons of 1-Ar), 8.30 and
8.39 (2 H, 2 m-protons of 1-Ar), 9.58 (1 H, 4-H), and 10.10
(1 H, CHO).

3,4-Dimethyl-1-oxa-6,6a-dithiapentalene (14). A solution
of p-nitrobenzenediazonium fluoroborate (2.37 g, 10 mmol)
in acetonitrile (50 ml) was added to a solution of 3,4-
dimethyl-1-oxa-6,6a-dithiapentalene [3] (860 mg, 5 mmol) in
acetonitrile (150 ml). The red solution was kept at room
temperature for 45 min, diluted with water, and extracted
with benzene. The residue from the washed (× 3), dried,
and evaporated extracts was chromatographed [alumina
(35 × 2.8 cm)] with benzene. The red eluates yielded
3,4-dimethyl-1-p-nitrophenyl-6,6a-dithia-1,2-diazapentalene
(17) [1] (1.22 g, 83%).

4,5-Dihydro-3H-1-oxa-7,7a-dithiacyclopent[cd]indene (15).

* log ε Values were not determined owing to low solubility.
† Spectrum obtained for a saturated solution by using ‘Com-
puter of Averaged Transients;’ J value approximate.

The procedure was identical with that of the preceding
experiment, with compound (15) [7] (920 mg, 5 mmol) in
place of compound (14). 6,7-Dihydro-2-p-nitrophenyl-5H-
2a,3-dithia-1,2-diazacyclopent[cd]indene (18) [1] (1.21 g, 80%)
was obtained.

3-Methyl-5-phenyl-1-oxa-6,6a-dithiapentalene (16).—The
procedure was identical with that of the two preceding
experiments. The oxadithiapentalene [6] (1.25 g, 5 mmol)
gave 3-methyl-1-p-nitrophenyl-5-phenyl-6,6a-dithia-1,2-
diazapentalene (19) [1] (1.25 g, 70%).

Reaction of 4,5,6,7-Tetrahydro-2-t-butyl-8-oxa-1,8a-dithia-
cyclopent[a]indene (21) with p-Nitrobenzenediazonium Fluoro-
borate.—(a) In acetonitrile. A solution of p-nitrobenzene
diazonium fluoroborate (2.37 g, 10 mmol) in acetonitrile
(50 ml) was added to a solution of compound (21) (1.27 g,
5 mmol) in acetonitrile (200 ml). The mixture was stirred
at room temperature for 45 min, diluted with water, and
extracted with benzene (× 2). The extracts were washed
with water (× 2) before being extracted with aqueous
0.1M-sodium hydroxide (300 ml). The red alkaline extracts
were washed with benzene, then acidified with 2M-hydro-
chloric acid. The resulting mixture was extracted with
benzene (× 2), and the extracts were washed with water
(× 2), dried, and evaporated. 5-(1-p-Nitrophenyl-5-t-butyl-
6,6a-dithia-1,2-diazapentalen-3-yl)pentanoic acid (23) (1.79 g,
85%) was obtained as small deep red needles [from cyclo-
hexane–benzene (2 : 1)], m.p. 146—150° (Found: C, 54.0;
H, 5.5; N, 10.3. $C_{19}H_{23}N_3O_4S_2$ requires C, 54.1; H, 5.5;
N, 10.0%); m/e 421 (M^+); $\lambda_{max.}$ 504, 348, 339, 259, and
225 nm; * $\nu_{max.}$ 1 713 cm^{-1} (C=O); δ 1.48 (9 H, Bu^t), 1.92
(4 H, m, 3- + 4-H$_2$), 2.49 (2 H, t, 2-H$_2$), 3.10 (2 H, t, 5-H$_2$),
7.77 (1 H, 4'-H), 7.83 and 7.92 (2 H, 2 o-protons of 1'-Ar),
and 8.10 and 8.19 (2 m-protons of 1'-Ar).

(b) In methanol. p-Nitrobenzenediazonium fluoroborate
(3.56 g, 15 mmol) was added to a solution of compound (21)
(1.27 g, 5 mmol) in methanol (200 ml), and the mixture was
stirred at room temperature for 1 h. It was then diluted
with water and extracted with benzene (× 2), and the
extracts were washed with water (× 2), dried, and evapor-
ated. Chromatography [silica (35 × 2.8 cm)] with benzene
gave pale orange eluates which were discarded. Continued
elution with benzene–ether (99 : 1) brought through red
eluates which afforded methyl 5-(1-p-nitrophenyl-5-t-butyl-
6,6a-dithia-1,2-diazapentalen-3-yl)pentanoate (24) (2.03 g,
93%), deep red spars (from cyclohexane), m.p. 130—131°
(Found: C, 55.2; H, 5.6; N, 9.8. $C_{20}H_{25}N_3O_4S_2$ requires
C, 55.1; H, 5.8; N, 9.7%); m/e 435 (M^+); $\lambda_{max.}$ 506 (log ε
4.40), 346sh (4.16), 338 (4.19), 258 (4.03), and 225 nm (4.49);
$\nu_{max.}$ 1 728 cm^{-1} (C=O); δ 1.48 (9 H, Bu^t), 1.87 (4 H, m,
3- + 4-H$_2$), 2.43 (2 H, t, 2-H$_2$), 3.07 (2 H, t, 5-H$_2$), 3.67
(3 H, CO$_2$Me), 7.77 (1 H, 4'-H), 7.79 and 7.88 (2 H, 2 o-
protons of 1'-Ar), and 8.06 and 8.15 (2 m-protons of 1'-Ar).

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