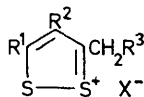
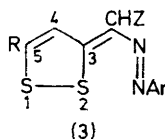
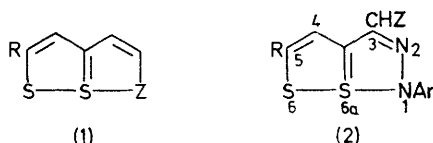


Studies of Heterocyclic Compounds. Part XIX.¹ Synthesis of 6,6a-Dithia- and 6,6a-Diselena-1,2-diazapentalenes

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- and 1-aryl-6,6a-diselena-1,2-diazapentalenes, two new classes of hypervalent heterocyclic compound, have been synthesised by the reaction of 3-methyl(ene)-1,2-dithiolium and 3-methyl(ene)-1,2-diselenolium salts, respectively, with arenediazonium fluoroborates. 1-Aryl-5-t-butyl-6,6a-dithia-1,2-diazapentalenes obtained from 3-methyl-5-t-butyl-1,2-dithiolium perchlorate were accompanied by small amounts of their 3-aryloxy-substitution products, which were subsequently produced in high yield by reaction of the 1-aryl-5-t-butyl-6,6a-dithia-1,2-diazapentalenes with the corresponding arenediazonium fluoroborates. The results of ¹H n.m.r. spectral studies and of X-ray crystallographic studies by other workers are discussed in relation to structure.

PRELIMINARY studies² have shown that the reactions of 6a-thiathiophthens (1; Z = S), 1-oxa-6,6a-dithiapentalenes (1; Z = O), and 1,6a-dithia-6-azapentalenes



	R ¹	R ²	R ³	X
(4)	H	H	H	ClO ₄
(5)	Bu ^t	H	H	ClO ₄
(6)	H	Me	Me	ClO ₄
(7)	H	[CH ₂] ₃		ClO ₄
(8)	Ph	H	Me	ClO ₄
(9)	Ph	H	H	ClO ₄
(10)	H	Ph	H	ClO ₄
(11)	H	Ph	Ph	Br

(1; Z = NMe) with arenediazonium fluoroborates involve substitution with rearrangement into 6,6a-dithia-1,2-diazapentalenes (2), a previously unknown class of heterocyclic compound. It seemed appropriate to study the reactivity of simple 6,6a-dithia-1,2-diazapentalenes

¹ Part XVIII, D. H. Reid and R. G. Webster, *J.C.S. Perkin I*, 1975, 2097.

² Preliminary communication, R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Chem. Comm.*, 1973, 92.

as an accompaniment to further studies of the diazo-coupling reactions. Also, we wished to obtain structurally simple 6,6a-dithia-1,2-diazapentalenes for crystallographic studies, since at the beginning of our work the bicyclic dithiadiazapentalene structure had not yet been established and the 3-aryloxy-substitution products (3) was a feasible alternative. This paper describes a synthesis of 1-aryl-6,6a-dithia- and 1-aryl-6,6a-diselena-1,2-diazapentalenes and some diazo-coupling reactions of 1-aryl-5-t-butyl-6,6a-dithia-1,2-diazapentalenes. It also discusses the significance of ¹H n.m.r. spectral data and X-ray crystallographic data in relation to structure.

Synthesis of 1-Aryl-6,6a-dithia- and 1-Aryl-6,6a-diselena-1,2-diazapentalenes.—The acidity of the methyl(ene) group in 3-methyl(ene)-1,2-dithiolium salts has been employed in the synthesis of 6a-thiathiophthens,³ 1-oxa-6,6a-dithiapentalenes,^{3a,d,4} 1,6a-dithia-6-azapentalenes,^{3e} 1,6a-dithia-6-selenapentalenes,^{3a} and 1-oxa-6,6a-dithia-2-azapentalenes.^{3d,4} We have found that the dithiolium salts (4)—(11) also react smoothly with arenediazonium fluoroborates in aqueous ethanol at room temperature to give the orange or red 1-aryl-6,6a-dithia-1,2-diazapentalenes (12)—(35) directly. This synthesis has wide scope, since a variety of 3-methyl(ene)-1,2-dithiolium salts^{3a,b,d,e} and arenediazonium fluoroborates⁵ are readily available. The hitherto unknown dithiolium salt (11) was prepared by established procedures.³

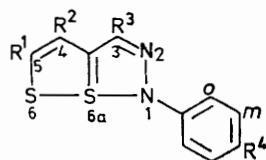
The 5-t-butyl-6,6a-dithia-1,2-diazapentalenes (13),

³ (a) J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc. (C)*, 1968, 2543; (b) J. G. Dingwall, D. H. Reid, and K. O. Wade, *ibid.*, 1969, 913; (c) G. Duguay, D. H. Reid, K. O. Wade, and R. G. Webster, *ibid.*, 1971, 2829; (d) J. G. Dingwall, A. R. Dunn, D. H. Reid, and K. O. Wade, *J.C.S. Perkin I*, 1972, 1360; (e) J. G. Dingwall, A. S. Ingram, D. H. Reid, and J. D. Symon, *ibid.*, 1973, 2351.

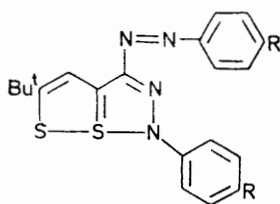
⁴ R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Perkin I*, 1974, 722.

⁵ A. Roe, *Organic Reactions*, 1949, 5, 193.

(21), (26), (30), (34), and (35) obtained from 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (5) were accompanied by small amounts of their 3-aryloxy-substitution



	R ¹	R ²	R ³	R ⁴
(12)	H	H	H	H
(13)	Bu ^t	H	H	H
(14)	H	Me	Me	H
(15)	H	[CH ₂] ₃	H	H
(16)	Ph	H	Me	H
(17)	Ph	H	H	H
(18)	H	Ph	H	H
(19)	H	Ph	Ph	H
(20)	H	H	H	NO ₂
(21)	Bu ^t	H	H	NO ₂
(22)	H	Me	Me	NO ₂
(23)	H	[CH ₂] ₃	H	NO ₂
(24)	Ph	H	Me	NO ₂
(25)	H	H	H	MeCO
(26)	Bu ^t	H	H	MeCO
(27)	H	Me	Me	MeCO
(28)	H	[CH ₂] ₃	H	MeCO
(29)	H	H	H	MeO
(30)	Bu ^t	H	H	MeO
(31)	H	Me	Me	MeO
(32)	H	[CH ₂] ₃	H	MeO
(33)	H	H	H	Br
(34)	Bu ^t	H	H	Br
(35)	Bu ^t	H	H	Me



- (36) R = H
 (37) R = NO₂
 (38) R = MeCO
 (39) R = MeO
 (40) R = Br
 (41) R = Me

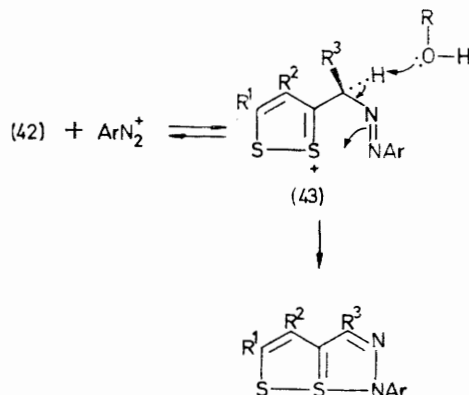
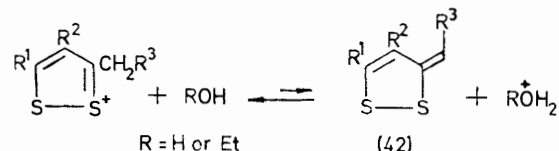
products (36)—(41),* respectively. These minor products were subsequently obtained in high yield by reaction of the primary products (13), (26), (30), (34), and (35) with the corresponding arenediazonium fluoroborates in ethanol.

* Electrophilic substitution of 1-aryl-6,6a-dithia-1,2-diazapentalenes occurs at position 3 (R. M. Christie and D. H. Reid, unpublished work.)

Arenediazonium fluoroborates react with 3-methyl(ene)-1,2-dithiolium salts most satisfactorily in hydrogen-bonding solvents (H₂O or ROH). These solvents assist the reaction (see Scheme) initially by deprotonating the 3-methyl(ene)-1,2-dithiolium salt to give the corresponding 3-methylene-1,2-dithiole (42), and subsequently by deprotonating the dithiolium intermediate (43). A similar intermediate (43; R³ = arylazo) is formed † and deprotonated in the diazo-coupling reactions of 1-aryl-5-t-butyl-6,6a-dithia-1,2-diazapentalenes leading to compounds (36)—(41). The role of the solvent is illustrated by the reaction of compound (13) with benzenediazonium fluoroborate which, in ethanol, gave the 3-aryloxy-derivative (36) in good yield (74%) together with some starting material (14%), but with acetonitrile as solvent the yields were 10 and 88%, respectively. The reactions of compound (30) with *p*-methoxybenzenediazonium fluoroborate in ethanol and acetonitrile gave results which paralleled the foregoing (see Experimental section).

We have also established a satisfactory route to 1-aryl-6,6a-diselena-1,2-diazapentalenes by using 3-methyl(ene)-1,2-diselenolium salts in place of dithiolium salts in the foregoing synthesis. 3,5-Dimethyl- (44)^{3a} and 3-ethyl-4-methyl-1,2-diselenolium perchlorate (45)^{3a} gave the purple diselenadiazapentalenes (46)—(50) in modest yields (19—42%).

Structure and ¹H N.m.r. Spectra of 1-Aryl-6,6a-dithia-1,2-diazapentalenes.—Four-electron three-centre bonds are characteristically (ca. 5—15%) longer than the

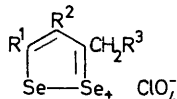


corresponding two-electron covalent bonds. An X-ray crystallographic structure determination⁶ of 1-phenyl-5-t-butyl-6,6a-dithia-1,2-diazapentalene (13) shows that

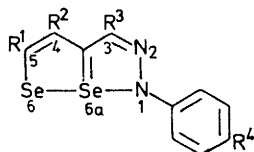
† See ref. 4 for a discussion of the mechanism of the electrophilic substitution of 6a-thiathiophthens and related hypervalent heterocyclic systems.

⁶ L. P. Darro, L. K. Hansen, A. Hordvik, and K. Tomren, unpublished data; we thank Professor Hordvik for permission to disclose data for compound (13).

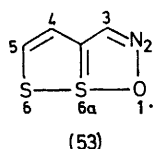
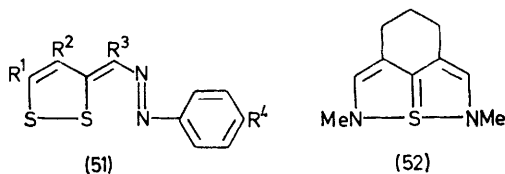
both the S-S (2.426 Å) and the S-N (1.841 Å) distances are significantly greater than the two-electron covalent S-S (*ca.* 2.08 Å) and S-N (*ca.* 1.75 Å) bond lengths, respectively. These data support the bicyclic formulation for 6,6a-dithia-1,2-diazapentalenes, involving four-electron three-centre bonding in the S-S-N sequence, rather than the 3-arylazomethylene-1,2-dithiole structure



	R ¹	R ²	R ³
(44)	Me	H	H
(45)	H	Me	Me



	R ¹	R ²	R ³	R ⁴
(46)	Me	H	H	H
(47)	H	Me	Me	H
(48)	Me	H	H	NO ₂
(49)	H	Me	Me	NO ₂
(50)	Me	H	H	MeO



(51). The S-N bond in 1-phenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (13) is shorter and therefore stronger than the S-N bonds (1.901 and 1.948 Å) in compound (52),⁷ whereas the S-S bond is longer and weaker than those (2.363 Å) in 6a-thiathiophthen (1; R = H, Z = S).⁸

¹H N.m.r. chemical shifts of ring protons in 6,6a-dithia-1,2-diazapentalenes (Table) occur in the range found for protons in other four-electron three-centre bonded structures, for example in 6a-thiathiophthen (1; R = H, Z = S) [2(5)-H, δ 9.18; 3(4)-H, δ 7.96],^{3a} in 1-oxa-6,6a-dithia-2-azapentalene (53) (5-H, δ 9.41; 4-H, δ 8.23; 3-H, δ 9.20),^{3d} and in 6-methyl-1,6a-dithia-6-

azapentalene (1; R = H, Z = NMe) (2-H, δ 8.86; 3-H, δ 7.45; 4-H, δ 7.05).^{3e}

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. Solutions were 0.4M in deuteriochloroform, unless otherwise stated, with tetramethylsilane as internal reference. *J* Values were measured on the 100 Hz scale. Unless otherwise stated δ values refer to singlet absorptions. Mass spectra were obtained with an A.E.I. MS902 spectrometer. Column chromatography was carried out with Spence grade H alumina. 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°.

3-Benzyl-4-phenyl-1,2-dithiolium Bromide (11) (with J. G. DINGWALL).—Hydrogen bromide in acetic acid (50% w/v; 6.75 ml, 42 mmol) was added to a solution of hydroxymethylene dibenzyl ketone⁹ (5.97 g, 25 mmol) in acetic acid (50 ml), followed immediately by hydrogen disulphide¹⁰ (1.5 ml). The solution was heated at 70–75 °C for 5 min, decanted from precipitated gummy sulphur, cooled, and diluted gradually with much ether. The resulting solid was filtered off and washed with carbon disulphide followed by ether. **3-Benzyl-4-phenyl-1,2-dithiolium bromide** (6.70 g, 77%) was obtained as pale yellow plates [from acetic acid (addition of ethyl acetate)], m.p. 164–174° (decomp.); δ (CF₃CO₂H; 60 MHz) 4.59 (2 H, CH₂Ph), 7.64 (5 H, CH₂Ph), 7.4–8.2 (5 H, m, 4-Ph), and 10.13 (1 H, 5-H) (Found: C, 54.7; H, 4.0. C₁₆H₁₃BrS₂ requires C, 55.0; H, 3.7%).

Synthesis of 1-Aryl-6,6a-dithia-1,2-diazapentalenes: Coupling of 3-Methyl(ene)-1,2-dithiolium Salts with Arenediazonium Fluoroborates.—The majority of the 6,6a-dithia-1,2-diazapentalenes were prepared by one of the following procedures.

Procedure A. A solution of benzenediazonium fluoroborate (1.005 g, 5.25 mmol) in water (50 ml) was added to a solution of the dithiolium salt (5 mmol) in ethanol (120 ml), and the mixture was stirred at room temperature for 40 min, diluted with water, and extracted with benzene (× 2). The extracts were washed with water (× 3), dried, and evaporated. The residue was chromatographed twice (alumina: 50 × 2.8 cm; 30 × 2.8 cm) with petroleum-benzene (2:1) (orange or red eluates) before being recrystallised.

Procedure B. A solution of *p*-nitrobenzenediazonium fluoroborate (1.245 g, 5.25 mmol) in ethanol (75 ml) and water (75 ml) was added to a solution of the dithiolium salt (5 mmol) in ethanol (120 ml). The mixture was stirred at room temperature for 1 h, diluted with water and extracted with benzene (× 2), and the extracts were washed with water (× 3), dried, and evaporated. The residue was chromatographed twice (alumina: 50 × 2.8 cm; 30 × 2.8 cm) with benzene (red eluates) before being recrystallised.

Procedure C. A solution of *p*-acetylbenzenediazonium

⁹ E. Benary and G. A. Bitter, *Ber.*, 1928, **61**, 1057.

¹⁰ F. Fehér, W. Laue, and G. Winkhaus, *Z. anorg. Chem.*, 1956, **288**, 113.

⁷ A. Hordvik and K. Julshamn, *Acta Chem. Scand.*, 1972, **26**, 343.

⁸ L. K. Hansen and A. Hordvik, *Acta Chem. Scand.*, 1973, **27**, 411.

fluoroborate (1.286 g, 5.5 mmol) in ethanol (100 ml) and water (50 ml) was added to a solution of the dithiolium salt (5 mmol) in ethanol (120 ml). The mixture was stirred at room temperature for 1 h, diluted with water, and extracted with ether ($\times 2$), and the extracts were washed with water ($\times 3$), dried, and evaporated. The residue was chromatographed twice (alumina: 50×2.8 cm; 30×2.8 cm) with

The following dithiadiazapentalenes were obtained from 3-methyl-1,2-dithiolium perchlorate (4) ^{3a} (procedure in parentheses): 1-phenyl-6,6a-dithia-1,2-diazapentalene (12) (345 mg, 31%) (A), red needles from hexane, m.p. 95–96°, λ_{\max} 483 (log ϵ 4.20), 289 (3.96), 250sh (4.23), 234 (4.42), and 203 nm (4.34), M^+ 220 (Found: C, 54.8; H, 3.6; N, 12.6; S, 29.4. $C_{10}H_8N_2S_2$ requires C, 54.5; H, 3.7; N, 12.7;

Chemical shifts (δ) in the 100 MHz 1H n.m.r. spectra of the 6,6a-dithia-1,2-diazapentalenes (12)—(35) and the 6,6a-diselena-1,2-diazapentalenes (46)—(50), in $CDCl_3$ (J in Hz)

	R ¹	R ²	R ³	<i>ortho</i> ^a	<i>meta</i> ^a	<i>para</i> R ⁴
(12)	9.31 (d) $J_{5,4} 6.6$	7.82 (d) ^b $J_{4,5} 6.6$	8.49 ^b	7.76—7.86 (m)	7.26—7.53 (m)	
(13)	1.44	7.68	8.36	7.68—7.81 (m)	7.20—7.46 (m)	
(14)	8.95 (q) $J_{5,4-Me} 0.8$	2.82 (d) $J_{4-Me,5} 0.8$	2.87	7.72—7.89 (m)	7.19—7.46 (m)	
(15)	8.92 (t) $J_{4,5-H_2} 0.9$	<i>c</i>	<i>c</i>	7.66—7.79 (m)	7.17—7.45 (m)	
(16)	<i>d</i>	7.89	2.65	<i>d</i>	<i>d</i>	<i>d</i>
(17)	<i>e</i>	8.08	8.49	<i>e</i>	<i>e</i>	<i>e</i>
(18)	9.15	7.48	8.42	7.74—7.86 (m)	7.21—7.54 (m)	
(19)	9.27	6.97	7.04 ^f	7.88—7.98 (m)	7.30—7.57 (m)	
(20) ^g	9.38 (d) $J_{5,4} 6.3$ ^h	7.94 (d) $J_{4,5} 6.3$ ^h	8.52	7.90, 7.99	8.25, 8.34	
(21) ^g	1.47	7.81	8.41	7.85, 7.94	8.22, 8.31	
(22) ^g	9.18	2.93	2.94	7.87, 7.96	8.22, 8.31	
(23) ^g	9.14	<i>i</i>	<i>i</i>	7.90, 7.99	8.27, 8.36	
(24)	7.45 (m) ^j 7.90 (m) ^k	8.08	2.76	7.86, 7.95	8.22, 8.31	
(25)	9.38 (d) $J_{5,4} 6.4$	7.91 (d) $J_{4,5} 6.4$	8.53	7.85, 7.94	8.01, 8.10	2.61
(26)	1.44	7.70	8.32	7.72, 7.81	7.90, 7.99	2.52
(27)	9.05 (q) $J_{5,4-Me} 0.7$	2.82 (d) $J_{4-Me,5} 0.7$	2.85	7.72, 7.81	7.89, 7.98	2.55
(28)	9.02 (t) $J_{4,5-H_2} 0.8$	<i>l</i>	<i>l</i>	7.73, 7.82	7.90, 7.99	2.55
(29)	9.18 (d) $J_{5,4} 6.7$	7.75 (d) ^b $J_{4,5} 6.7$	8.42 ^b	7.63, 7.72	6.89, 6.98	3.80
(30)	1.42	7.62	8.33	7.61, 7.70	6.87, 6.96	3.79
(31)	8.87 (q) $J_{5,4-Me} 0.8$	2.82 (d) $J_{4-Me,5} 0.8$	2.88	7.62, 7.71	6.88, 6.97	3.80
(32)	8.82 (t) $J_{4,5-H_2} 0.8$	<i>m</i>	<i>m</i>	7.62, 7.71	6.87, 6.96	3.79
(33)	9.26 (d) $J_{5,4} 6.6$	7.81 (d) ^b $J_{4,5} 6.6$	8.45 ^b	7.61, 7.70	7.46, 7.55	
(34)	1.44	7.70	8.36	7.61, 7.70	7.45, 7.54	
(35)	1.43	7.66	8.35	7.60, 7.69	7.15, 7.24	2.33
(46)	2.72 (d) $J_{5-Me,4} 0.9$	7.75 (q)	8.48 ^b	7.75—7.84 (m)	7.30—7.45 (m)	
(47)	9.72br	2.94 (d) $J_{4-Me,5} 0.8$	2.96	7.78—7.90 (m)	7.23—7.46 (m)	
(48) ^g	2.78	8.13	8.51	7.85, 7.94	8.20, 8.29	
(49) ^g	10.15	3.03	3.04	7.94, 8.03	8.23, 8.32	
(50)	2.68 (d) $J_{5-Me,4} 0.9$	7.88 (q) ^b	8.44 ^b	7.67, 7.76	6.84, 6.93	3.78

* Signals assigned to the pairs of *ortho*- and *meta*-protons of the *para*-substituted 1-phenyl group in compounds (20)—(35) and (48)—(50) are the four most intense signals in the AA'BB' pattern. ^b Further weak splitting; 3-H weakly coupled to 4-H (J ca. 0.3 Hz). ^c 2.08 (quint), 6-H₂; 3.02 (m), 5-H₂; 3.08 (t), 7-H₂. ^d 7.17—7.49 (m), 4 *m*- + 2 *p*-protons of 1- and 5-Ph; 7.67—7.91 (m), 4 *o*-protons of 1- and 5-Ph. ^e 7.34—7.54 (m), 4 *m*- + 2 *p*-protons of 1- and 5-Ph; 7.77—7.94 (m), 4 *o*-protons of 1- and 5-Ph. ^f Signal weakly split. ^g Compound sparingly soluble; spectrum recorded by accumulation. ^h Approximate value; see footnote g. ⁱ 2.20 (m), 6-H₂; 3.15 (m), 5- and 7-H₂. ^j 2 *m*- and *p*-protons of 5-Ph. ^k 2 *o*-protons of 5-Ph. ^l 2.12 (quint), 6-H₂; 3.06br (t), 5-H₂; 3.10br (t), 7-H₂. ^m 2.08 (quint), 6-H₂; 3.03br (t), 5-H₂; 3.09br (t), 7-H₂.

benzene-ether (4 : 1) (red eluates) before being recrystallised.

Procedure D. This was identical with procedure C, except that *p*-methoxybenzenediazonium fluoroborate (1.220 g, 5.5 mmol) was used in place of *p*-acetylbenzenediazonium fluoroborate, and chromatography was carried out with benzene (red eluates).

Procedure E. This was identical with procedure C, except that *p*-bromobenzenediazonium fluoroborate (1.489 g, 5.5 mmol) was used in place of *p*-acetylbenzenediazonium fluoroborate, and chromatography was carried out with petroleum-benzene (3 : 1) (orange or red eluates).

S, 29.1%); 1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene (20) (321 mg, 24%) (B), orange-red prisms from benzene-cyclohexane, m.p. 198—199°, λ_{\max} 495 (log ϵ 4.27), 339sh (4.13), 327 (4.20), 251 (4.10), 226 (4.44), and 205 nm (4.38), M^+ 265 (Found: C, 45.1; H, 2.7; N, 15.4. $C_{10}H_7N_2O_2S_2$ requires C, 45.3; H, 2.7; N, 15.8%); 1-*p*-acetylphenyl-6,6a-dithia-1,2-diazapentalene (25) (238 mg, 18%) (C), orange-red plates from benzene-cyclohexane (1 : 1), m.p. 180—180.5°, λ_{\max} 492 (log ϵ 4.22), 305 (4.36), 248infl (4.09), 227 (4.38), and 205 nm (4.35), ν_{\max} (KBr) 1 680 cm^{-1} (C=O), M^+ 262 (Found: C, 54.9; H, 3.9; N, 10.6. $C_{12}H_{10}N_2OS_2$ requires

C, 54.9; H, 3.8; N, 10.7%); 1-*p*-methoxyphenyl-6,6a-dithia-1,2-diazapentalene (29) (350 mg, 28%) (D), orange-red spars from hexane, m.p. 110—110.5°, λ_{\max} 486 (log ϵ 4.14), 329infl (3.52), 297 (3.97), 248sh (4.27), 234 (4.41), and 216 nm (4.22), M^+ 250 (Found: C, 52.9; H, 4.0; N, 11.5. $C_{11}H_{10}N_2OS_2$ requires C, 52.8; H, 4.0; N, 11.2%); 1-*p*-bromophenyl-6,6a-dithia-1,2-diazapentalene (33) (324 mg, 22%) (E), orange-red needles from hexane, m.p. 126—127°, λ_{\max} 484 (log ϵ 4.17), 292 (4.07), 253 (4.24), 231 (4.38), and 204 nm (4.36), M^+ 298 and 300 (Found: C, 40.0; H, 2.2; N, 9.3. $C_{10}H_7BrN_2S_2$ requires C, 40.1; H, 3.4; N, 9.4%).

The following dithiadiazapentalenes were obtained from 3-ethyl-4-methyl-1,2-dithiolium perchlorate (6):^{3e} 3,4-dimethyl-1-phenyl-6,6a-dithia-1,2-diazapentalene (14) (1.116 g, 90%) (A), red needles from cyclohexane, m.p. 136—137°, λ_{\max} 498 (log ϵ 4.12), 293 (4.00), 254sh (4.18), 235 (4.41), and 203 nm (4.39), M^+ 248 (Found: C, 58.1; H, 4.9; N, 11.2. $C_{12}H_{12}N_2S_2$ requires C, 58.0; H, 4.9; N, 11.3%); 3,4-dimethyl-1-*p*-nitrophenyl-6,6a-dithia-1,2-diazapentalene (22) (1.392 g, 95%) (B), fine dark red needles from benzene, m.p. 208.5—209°, λ_{\max} 513 (log ϵ 4.31), 349sh (4.11), 339 (4.19), 258 (4.12), 228 (4.45), and 202 nm (4.44), M^+ 293 (Found: C, 49.3; H, 4.0; N, 13.9. $C_{12}H_{11}N_3O_2S_2$ requires C, 49.1; H, 3.8; N, 14.3%); 1-*p*-acetylphenyl-3,4-dimethyl-6,6a-dithia-1,2-diazapentalene (27) (1.439 g, 99%) (C), red needles from benzene-cyclohexane (1:1), m.p. 158—160°, λ_{\max} 509 (log ϵ 4.25), 314 (4.38), 254 (4.11), 229 (4.38), and 205 nm (4.37), ν_{\max} (KBr) 1 664 cm^{-1} (C=O), M^+ 290 (Found: C, 58.1; H, 4.9; N, 9.4. $C_{14}H_{14}N_2OS_2$ requires C, 57.9; H, 4.9; N, 9.7%); 1-*p*-methoxyphenyl-3,4-dimethyl-6,6a-dithia-1,2-diazapentalene (31) (1.378 g, 99%) (D), fine red needles from cyclohexane, m.p. 153—153.5°, λ_{\max} 505 (log ϵ 4.16), 335infl (3.49), 301 (4.05), 256sh (4.23), 235 (4.44), and 207 nm (4.27), M^+ 278 (Found: C, 56.1; H, 5.2; N, 10.3. $C_{13}H_{14}N_2OS_2$ requires C, 56.1; H, 5.1; N, 10.1%).

The following dithiadiazapentalenes were obtained from 4,5,6,7-tetrahydrobenzo[*c*][1,2]dithiolium perchlorate (7):^{3d} 6,7-dihydro-2-phenyl-5H-2a,3-dithia-1,2-diazacyclopent[*cd*]indene (15) (1.246 g, 99%) (A), red needles from hexane, m.p. 100—100.5°, λ_{\max} 504 (log ϵ 4.17), 295 (4.02), 254sh (4.21), 230 (4.41), and 203 nm (4.34), M^+ 296 (Found: C, 59.8; H, 4.6; N, 10.5. $C_{13}H_{12}N_2S_2$ requires C, 60.0; H, 4.7; N, 10.8%); 6,7-dihydro-2-*p*-nitrophenyl-5H-2a,3-dithia-1,2-diazacyclopent[*cd*]indene (23) (1.287 g, 84%) (B), dark red prisms from benzene-cyclohexane (1:1), m.p. 236—238°, λ_{\max} * 525, 350sh, 342, 260, 225, and 203 nm, M^+ 305 (Found: C, 51.5; H, 3.6; N, 13.6. $C_{13}H_{11}N_3O_2S_2$ requires C, 51.5; H, 3.6; N, 13.8%); 2-*p*-acetylphenyl-6,7-dihydro-5H-2a,3-dithia-1,2-diazacyclopent[*cd*]indene (28) (1.389 g, 92%) (C), red needles from benzene-cyclohexane (1:1), m.p. 149—150°, λ_{\max} 519 (log ϵ 4.29), 315 (4.39), 257 (4.10), 225 (4.40), and 205 nm (4.41), ν_{\max} (KBr) 1 665 cm^{-1} (C=O), M^+ 302 (Found: C, 59.6; H, 4.7; N, 9.0. $C_{15}H_{14}N_2OS_2$ requires C, 59.6; H, 4.7; N, 9.3%); 6,7-dihydro-2-*p*-methoxyphenyl-5H-2a,3-dithia-1,2-diazacyclopent[*cd*]indene (32) (1.430 g, 99%) (D), dark red needles from hexane, m.p. 118.5—119.5°, λ_{\max} 515 (log ϵ 4.19), 338 (3.45), 302 (4.05), 253sh (4.22), 230 (4.42), and 205 nm (4.36), M^+ 290 (Found: C, 57.8; H, 4.9; N, 9.7. $C_{14}H_{14}N_2OS_2$ requires C, 57.9; H, 4.9; N, 9.7%).

The following dithiadiazapentalenes were obtained from 3-ethyl-5-phenyl-1,2-dithiolium perchlorate (8):^{3a} 3-methyl-1,5-diphenyl-6,6a-dithia-1,2-diazapentalene (16) (1.481 g,

96%) (A), fine dark red needles from cyclohexane, m.p. 108—109°, λ_{\max} 507 (log ϵ 4.29), 306 (4.10), 254sh (4.41), 238 (4.53), and 204 nm (4.57), M^+ 310 (Found: C, 65.6; H, 4.4; N, 8.9. $C_{17}H_{14}N_2S_2$ requires C, 65.8; H, 4.5; N, 9.0%); 3-methyl-1-*p*-nitrophenyl-5-phenyl-6,6a-dithia-1,2-diazapentalene (24) (1.536 g, 87%) (B), dark red needles from benzene, m.p. 218—219°, λ_{\max} * 521, 350sh, 342, 227, and 206 nm, M^+ 355 (Found: C, 57.4; H, 3.6; N, 11.5. $C_{17}H_{13}N_3O_2S_2$ requires C, 57.5; H, 3.7; N, 11.8%).

The following dithiadiazapentalenes were also obtained from the dithiolium salts indicated: 1,5-diphenyl-6,6a-dithia-1,2-diazapentalene (17) (1.064 g, 72%) [(A), from the salt (9)^{3a}], red plates from benzene-cyclohexane, m.p. 163—163.5°, λ_{\max} 504 (log ϵ 4.29), 302 (4.13), 251sh (4.45), 237 (4.57), and 204 nm (4.63), M^+ 296 (Found: C, 64.9; H, 4.1; N, 9.6. $C_{16}H_{12}N_2S_2$ requires C, 64.8; H, 4.1; N, 9.5%); 1,4-diphenyl-6,6a-dithia-1,2-diazapentalene (18) (1.157 g, 78%) [(A), from the salt (10)^{3a}], red needles from cyclohexane, m.p. 111.5—112.5°, λ_{\max} 491 (log ϵ 4.14), 299 (4.11), 280 (4.13), 257infl (4.21), 233 (4.43), and 205 nm (4.44), M^+ 296 (Found: C, 64.9; H, 4.1; N, 9.5. $C_{16}H_{12}N_2S_2$ requires C, 64.8; H, 4.1; N, 9.5%); 1,3,4-triphenyl-6,6a-dithia-1,2-diazapentalene (19) (1.775 g, 96%) [(A), from the salt (11)], dark red prisms from cyclohexane, m.p. 207—208.5°, λ_{\max} 500 (log ϵ 4.11), 323infl (3.97), 293 (4.23), 250infl (4.37), 229 (4.44), and 206 nm (4.54), M^+ 372 (Found: C, 71.1; H, 4.4; N, 7.3. $C_{22}H_{16}N_2S_2$ requires C, 71.0; H, 4.3; N, 7.5%).

*Reactions of 3-Methyl-5-*t*-butyl-1,2-dithiolium Perchlorate (5) with Arenediazonium Fluoroborates.*—Reactions were carried out and the product mixtures were collected according to procedures A—E. Subsequent chromatographic purification methods varied and are given individually.

(a) *With benzenediazonium fluoroborate.* Procedure A was used. The product was chromatographed (alumina; 50 × 2.8 cm) with petroleum-benzene (2:1) which gave orange eluates, and then with benzene which brought through red eluates. Rechromatography (alumina; 30 × 2.8 cm) of the residue from the orange eluates gave 1-phenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (13) (616 mg, 45%), red plates from hexane, m.p. 115—115.5°, λ_{\max} 483 (log ϵ 4.23), 285sh (3.96), 260infl (4.15), 234 (4.39), and 202 nm (4.43), M^+ 276 (Found: C, 61.0; H, 6.0; N, 10.4; S, 23.6. $C_{14}H_{16}N_2S_2$ requires C, 60.8; H, 5.8; N, 10.1; S, 23.2%). Rechromatography (alumina; 30 × 2.8 cm) of the residue from the red eluates afforded 1-phenyl-3-phenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (36) (189 mg, 10%), dark red prisms from cyclohexane, m.p. 183—184°, λ_{\max} 488 (log ϵ 4.20), 424 (4.34), 302infl (4.05), 285 (4.12), 250 (4.37), 238 (4.38), 224infl (4.34), and 201 nm (4.52), M^+ 380 (Found: C, 63.3; H, 5.4; N, 14.5. $C_{20}H_{20}N_4S_2$ requires C, 63.1; H, 5.3; N, 14.7%).

(b) *With *p*-nitrobenzenediazonium fluoroborate.* Procedure B was used. The product was chromatographed (alumina; 50 × 2.8 cm) with benzene, which gave red eluates, and then with benzene-ether (9:1) which brought through brownish-red eluates. Rechromatography (alumina; 30 × 2.8 cm) of the residue from the red eluates yielded 1-*p*-nitrophenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (21) (557 mg, 37%), dark red spars from benzene, m.p. 267—268°, λ_{\max} 498 (log ϵ 4.35), 343sh (4.10), 331 (4.17), 255 (4.07), 225 (4.41), and 205 nm (4.43), M^+ 321 (Found: C, 52.2; H, 4.7; N, 12.8. $C_{14}H_{15}N_3O_2S_2$ requires C, 52.3; H, 4.7; N, 13.1%). Rechromatography (alumina; 30 × 2.8 cm) of the residue from the brownish red eluates afforded

* Intensities not determined owing to low solubility.

1-*p*-nitrophenyl-3-*p*-nitrophenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (37) (105 mg, 4.5%), small reddish brown needles from benzene, m.p. 296—297°, λ_{max} * 481, 310infr, 292 br, 251br, 222, and 200 nm, M^+ 470 (Found: C, 50.8; H, 3.8; N, 17.9. $\text{C}_{20}\text{H}_{18}\text{N}_6\text{O}_4\text{S}_2$ requires C, 51.1; H, 3.9; N, 17.9%).

(c) With *p*-acetylbenzenediazonium fluoroborate. Procedure C was used. The product was chromatographed (alumina; 50 × 2.8 cm) with benzene-ether (4 : 1) which gave red eluates, and then with ether-benzene (2 : 1), which brought through brownish-red eluates. Rechromatography (alumina; 30 × 2.8 cm) of the residue from the red eluates afforded 1-*p*-acetylphenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (26) (477 mg, 30%), orange plates from cyclohexane, m.p. 140—141°, λ_{max} 490 (log ϵ 4.31), 307 (4.37), 252 (4.07), 227 (4.32), and 209 nm (4.33), ν_{max} (KBr) 1 680, ν_{max} (CHCl₃) 1 688 cm⁻¹ (C=O), M^+ 318 (Found: C, 60.6; H, 5.6; N, 8.9. $\text{C}_{16}\text{H}_{18}\text{N}_2\text{OS}_2$ requires C, 60.4; H, 5.7; N, 8.8%). Rechromatography (alumina; 30 × 2.8 cm) of the residue from the brownish-red eluates gave 1-*p*-acetylphenyl-3-*p*-acetylphenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (38) (213 mg, 9.2%), dark red needles from benzene-cyclohexane, m.p. 234—235°, λ_{max} 444 (log ϵ 4.47), 288 (4.42), 251 (4.26), 218infr (4.35), and 205 nm (4.43), ν_{max} (KBr) 1 673 and 1 683, ν_{max} (CHCl₃) 1 690 cm⁻¹ (C=O), M^+ 464 (Found: C, 62.2; H, 5.3; N, 12.0. $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_2\text{S}_2$ requires C, 62.1; H, 5.2; N, 12.1%).

(d) With *p*-methoxybenzenediazonium fluoroborate. Procedure D was used. The product was chromatographed (alumina; 50 × 2.8 cm) with benzene which gave orange-red eluates, and subsequently with benzene-ether (4 : 1) which brought through brownish-red eluates. Rechromatography (alumina; 30 × 2.8 cm) of the residue from the orange-red eluates gave 1-*p*-methoxyphenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (30) (1.161 g, 76%), orange-red plates from hexane, m.p. 144—144.5°, λ_{max} 488 (log ϵ 4.22), 296 (3.94), 254infr (4.19), 233 (4.39), and 209 nm (4.31), M^+ 306 (Found: C, 58.9; H, 6.3; N, 9.5. $\text{C}_{15}\text{H}_{18}\text{N}_2\text{OS}_2$ requires C, 58.8; H, 5.9; N, 9.2%). Rechromatography (alumina; 30 × 2.8 cm) of the residue from the brownish red eluates afforded 1-*p*-methoxyphenyl-3-*p*-methoxyphenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (39) (60 mg, 2.7%), reddish-brown needles from hexane, m.p. 110—111.5°; λ_{max} 489infr (log ϵ 4.29), 444infr (4.39), 434 (4.41), 332br (4.16), 246infr (4.37), 230 (4.41), and 207 nm (4.42), M^+ 440 (Found: C, 59.8; H, 5.8; N, 12.8. $\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_2\text{S}_2$ requires C, 60.0; H, 5.5; N, 12.7%).

(e) With *p*-bromobenzenediazonium fluoroborate. Procedure E was used. The product was chromatographed (alumina; 50 × 2.8 cm) with petroleum-benzene (3 : 1) which gave orange-red eluates, and subsequently with benzene which brought through brownish red eluates. Rechromatography (alumina; 30 × 2.8 cm) of the residue from the orange-red eluates gave 1-*p*-bromophenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (34) (730 mg, 41%), orange-red needles from hexane, m.p. 163.5—165°, λ_{max} 485 (log ϵ 4.28), 289sh (4.05), 267 (4.21), 231 (4.32), and 204 nm (4.42), M^+ 354 and 356 (Found: C, 47.4; H, 4.5; N, 7.9. $\text{C}_{14}\text{H}_{15}\text{BrN}_2\text{S}_2$ requires C, 47.3; H, 4.3; N, 7.9%). Rechromatography (alumina; 30 × 2.8 cm) of the residue from the brownish-red eluates afforded 1-*p*-bromophenyl-3-*p*-bromophenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (40) (398 mg, 15%), fine red needles from cyclohexane, m.p. 217.5—220°, λ_{max} 490sh (log ϵ 4.29), 433 (4.44), 310vbr (4.13), 286infr (4.17), 260 (4.41), 222 (4.24), and 201 nm

(4.55), M^+ 536, 538, and 540 (Found: C, 44.7; H, 3.6; N, 10.4. $\text{C}_{20}\text{H}_{18}\text{Br}_2\text{N}_4\text{S}_2$ requires C, 44.6; H, 3.4; N, 10.4%).

(f) With toluene-*p*-diazonium fluoroborate. The procedure was identical with the procedure (a), with toluene-*p*-diazonium fluoroborate (1.086 g, 5.25 mmol) in place of benzenediazonium fluoroborate. This gave successively 5-*t*-butyl-1-*p*-tolyl-6,6a-dithia-1,2-diazapentalene (35) (988 mg, 68%), orange-red plates from hexane, m.p. 129.5—130.5°, λ_{max} 481 (log ϵ 4.21), 288infr (3.96), 257 (4.18), 234 (4.38), and 206 nm (4.38), M^+ 290 (Found: C, 62.2; H, 6.1; N, 9.8. $\text{C}_{15}\text{H}_{18}\text{N}_2\text{S}_2$ requires C, 62.0; H, 6.2; N, 9.7%), and 5-*t*-butyl-1-*p*-tolyl-3-*p*-tolylazo-6,6a-dithia-1,2-diazapentalene (41) (138 mg, 6.8%), reddish brown spars from cyclohexane, m.p. 167.5—170°, λ_{max} 487infr (log ϵ 4.24), 426 (4.39), 312 (4.12), 287 (4.11), 251 (4.39), 242infr (4.38), 224 (4.38), and 204 nm (4.49), M^+ 408 (Found: C, 64.6; H, 6.1; N, 13.8. $\text{C}_{22}\text{H}_{24}\text{N}_4\text{S}_2$ requires C, 64.7; H, 5.9; N, 13.7%).

*Coupling Reactions of 1-Aryl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalenes with Arenediazonium Fluoroborates: General Procedure.*—The arenediazonium fluoroborate (4 mmol, unless otherwise stated) was added to a solution of the 1-aryl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (2 mmol) in ethanol (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 (× 4), and the extracts were washed with water (× 3), dried, and evaporated. Subsequent work-up varied and is described for each reaction.

(a) 1-Phenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (13) with benzenediazonium fluoroborate. Chromatography (alumina; 40 × 2.2 cm) with petroleum-benzene (3 : 1) gave orange eluates from which starting material (79 mg, 14%) was recovered. Continued elution with benzene gave red eluates which afforded 1-phenyl-3-phenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (36) (558 mg, 74%). Repetition of the reaction with acetonitrile as solvent in place of ethanol gave starting material (486 mg, 88%) and compound (36) (79 mg, 10%).

(b) 1-*p*-Acetylphenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (26) with *p*-acetylbenzenediazonium fluoroborate. Chromatography (alumina; 30 × 2.2 cm) with benzene-ether (4 : 1) gave red eluates from which starting material (42 mg, 6.6%) was recovered. Continued elution with benzene-ether (1 : 1) gave brownish red eluates which yielded 1-*p*-acetylphenyl-3-*p*-acetylphenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (38) (835 mg, 90%).

(c) 1-*p*-Methoxyphenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (30) with *p*-methoxybenzenediazonium fluoroborate. A larger quantity (6 mmol) of the fluoroborate was used. Chromatography (alumina; 35 × 2.2 cm) with petroleum-benzene (1 : 1) gave orange-red eluates from which starting material (18 mg, 2.9%) was recovered. Continued elution with benzene gave brownish red eluates which afforded 1-*p*-methoxyphenyl-3-*p*-methoxyphenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (39) (785 mg, 89%). Repetition of the reaction with acetonitrile as solvent in place of ethanol gave starting material (286 mg, 47%) and compound (39) (65 mg, 7.4%).

(d) 1-*p*-Bromophenyl-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (34) with *p*-bromobenzenediazonium fluoroborate. Chromatography (alumina; 40 × 2.2 cm) with petroleum-benzene (3 : 1) gave orange-red eluates containing starting material (32 mg, 9%). Continued elution with benzene gave brownish red eluates which afforded 1-*p*-bromophenyl-3-*p*-bromophenylazo-5-*t*-butyl-6,6a-dithia-1,2-diazapentalene (40) (827 mg, 77%).

* See footnote on page 232.

(e) *5-t-Butyl-1-p-tolyl-6,6a-dithia-1,2-diazapentalene* (35) with *toluene-p-diazonium fluoroborate*. Chromatography (alumina; 40×2.2 cm) with petroleum-benzene (3:1) gave orange eluates containing starting material (107 mg, 17%). Continued elution with benzene gave red eluates which yielded *5-t-butyl-1-p-tolyl-3-p-tolylazo-6,6a-dithia-1,2-diazapentalene* (41) (623 mg, 76%).

Synthesis of 1-Aryl-6,6a-diselena-1,2-diazapentalenes:

Coupling of 3-Methyl(ene)-1,2-diselenolium Salts with Arene-diazonium Fluoroborates.—Procedures A', B', and D' were used, which were identical with procedures A, B, and D, respectively, except that diselenolium salts (5 mmol) were used in place of dithiolium salts. Solutions of 1-aryl-6,6a-diselena-1,2-diazapentalenes are purple or deep violet. The following diselenadiazapentalenes were obtained (procedure in parentheses): *5-methyl-1-phenyl-6,6a-diselena-1,2-diazapentalene* (46) (533 mg, 33%) [(A'), from the salt (44)^{3d}], purple needles from hexane, m.p. 109–110°, λ_{\max} 529 (log ϵ 4.17), 340vbr (3.54), 280 (4.19), 250 (4.47), 212 (4.41), and 202 nm (4.42), principal mass spectral peaks at m/e 328 and 330 (Found: C, 40.5; H, 3.1; N, 8.7. $C_{11}H_{10}N_2Se_2$ requires C, 40.3; H, 3.1; N, 8.5%); *3,4-dimethyl-1-phenyl-6,6a-diselena-1,2-diazapentalene* (47) (700 mg, 41%) [(A'), from the salt (45)^{3d}], purple needles from hexane, m.p. 82–83°, λ_{\max} 542 (log ϵ 4.14), 345infl (3.39), 286 (4.22), 251 (4.46), and 202 nm (4.48), principal mass spectral peaks at m/e 342 and 344 (Found: C, 41.8; H, 3.6;

N, 8.0; Se, 46.7. $C_{12}H_{12}N_2Se_2$ requires C, 42.1; H, 3.5; N, 8.2; Se, 46.2%); *5-methyl-1-p-nitrophenyl-6,6a-diselena-1,2-diazapentalene* (48) (361 mg, 19%) [(B'), from the salt (44)], violet needles from benzene-cyclohexane, m.p. 225–227°, λ_{\max} 543 (log ϵ 4.34), 346br (4.20), 277infl (4.00), 244 (4.35), 220 (4.36), and 203 nm (4.50), principal mass spectral peaks at m/e 373 and 375 (Found: C, 35.2; H, 2.5; N, 11.2. $C_{11}H_9N_3O_2Se_2$ requires C, 35.4; H, 2.4; N, 11.3%); *3,4-dimethyl-1-p-nitrophenyl-6,6a-diselena-1,2-diazapentalene* (49) (804 mg, 42%) [(B'), from the salt (45)], fine violet needles from benzene-cyclohexane, m.p. 207–208°, λ_{\max} 561 (log ϵ 4.24), 361sh (4.11), 350 (4.15), 286 (4.01), 266infl (4.06), 242 (4.27), and 203 nm (4.40), principal mass spectral peaks at m/e 387 and 389 (Found: C, 37.1; H, 2.9; N, 10.8. $C_{12}H_{11}N_3O_2Se_2$ requires C, 37.2; H, 2.9; N, 10.9%); *1-p-methoxyphenyl-5-methyl-6,6a-diselena-1,2-diazapentalene* (50) (451 mg, 25%) [(D'), from the salt (44)], purple plates from hexane, m.p. 121–122.5°, λ_{\max} 541 (log ϵ 4.23), 348br (3.69), 289 (4.15), 249 (4.46), and 216 nm (4.36), principal mass spectral peaks at m/e 358 and 360 (Found: C, 40.2; H, 3.5; N, 8.1. $C_{12}H_{12}N_2OSe_2$ requires C, 40.2; H, 3.4; N, 7.8%).

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