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Studies of Heterocyclic Compounds. Part XI.[1] 1-Oxa-6,6a-dithia-2-azapentalenes, 1-Oxa-6,6a-diselena-2-azapentalenes, and 3-Nitromethylene-3*H*-1,2-dithioles

By **J. G. Dingwall, A. R. Dunn, D. H. Reid,* and K. O. Wade,** Department of Chemistry, The Purdie Building, The University, St. Andrews, Scotland

Nitrosation of 3-alkyl-1,2-dithiolium salts gives 1-oxa-6,6a-dithia-2-azapentalenes (3-nitrosomethylene-3*H*-1,2-dithioles) in excellent yield. 3-Alkyl-1,2-diselenolium salts likewise afford 1-oxa-6,6a-diselena-2-azapentalenes (3-nitrosomethylene-3*H*-1,2-diselenoles), a new class of heterocyclic compounds. Attempted nitration of 2-t-butyl-6a-thiathiophthen with tetranitromethane gave 3-formyl-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene and a small amount of 5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene. 2-Phenyl-6a-thiathiophthen behaved analogously. 3,4-Dimethyl-6a-thiathiophthen and 4,5-dihydro-3*H*-benzo[*cd*][6a]thiathiophthen gave products of partial desulphurisation, nitration, and nitrosation in low yield. The significance of ^{1}H n.m.r. spectral data is discussed in relation to structure of the reaction products.

3-ALKYL-1,2-DITHIOLIUM salts (1)—(5) condense readily with *NN*-dimethylthioformamide in boiling acetic anhydride [2-4] by virtue of the acidity [5] of the methylene group adjacent to the ring. The resulting Vilsmeier salts (6), when treated with sodium hydrogen sulphide, sodium hydrogen selenide, sodium hydroxide, or aliphatic amines, afford 6a-thiathiophthens (7; X = S),[2,3] 1,6a-dithia-6-selenapentalenes (7; X = Se),[2] 1-oxa-6,6a-dithiapentalenes (7; X = O),[2] or 6,6a-dithia-1-azapentalenes (7; X = NR),[4] respectively. This paper

[1] Part X, D. H. Reid, *J. Chem. Soc.* (*C*), 1971, 3187.
[2] J. G. Dingwall, S. McKenzie, and D. H. Reid, *J. Chem. Soc.* (*C*), 1968, 2543.
[3] J. G. Dingwall, D. H. Reid, and K. O. Wade, *J. Chem. Soc.* (*C*), 1969, 913.
[4] D. H. Reid and J. D. Symon, *Chem. Comm.*, 1969, 1314.
[5] D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *J. Chem. Soc.*, 1962, 5104.

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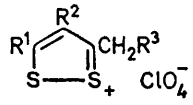
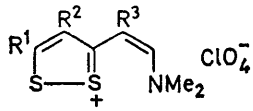
describes further exploitation of 3-alkyl-1,2-dithiolium and -1,2-diselenolium salts for the synthesis of analogues of 6a-thiathiophthens, and related results of attempts to nitrate 6a-thiathiophthens.

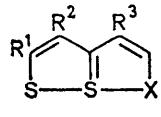
Brief treatment of the dithiolium salts (1)—(5) with sodium nitrite in acetic acid–acetonitrile gave the 1-oxa-6,6a-dithia-2-azapentalenes (8)—(12) in excellent yield.





(6)

	R^1	R^2	R^3
(1)	H	H	H
(2)	Bu^t	H	H
(3)	Ph	H	H
(4)	H	Me	Me
(5)	H	$-[CH_2]_3-$	



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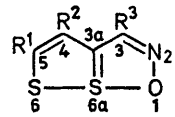
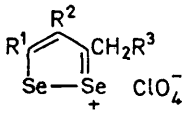
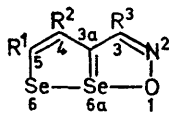


	R^1	R^2	R^3
(8)	H	H	H
(9)	Bu^t	H	H
(10)	Ph	H	H
(11)	H	Me	Me
(12)	H	$-[CH_2]_3-$	
(13)	Bu^t	H	CHO
(14)	Ph	H	CHO
(15)	Ph	H	Bz

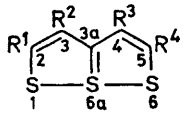
Ready access to this class of compounds is thereby provided. Several members had previously been obtained [6-8] in attempts to nitrate and nitrosate 6a-thiathiophthens. Extension of the nitrosation procedure to the diselenolium salts (16)—(18) also afforded the





	R^1	R^2	R^3
(16)	Me	H	H
(17)	Ph	H	H
(18)	H	Me	Me

	R^1	R^2	R^3
(19)	Me	H	H
(20)	Ph	H	H
(21)	H	Me	Me

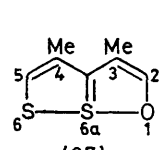


	R^1	R^2	R^3	R^4
(22)	Bu^t	H	H	H
(23)	Ph	H	H	H
(24)	H	Me	Me	H
(25)	H	$-[CH_2]_3-$		H
(26)	Ph	H	H	Ph

stable 1-oxa-6,6a-diselena-2-azapentalenes (19)—(21), members of a new class of heterocyclic compounds.

Concurrently with this work we studied the nitration of 6a-thiathiophthens as part of an investigation of the reactivity of 6a-thiathiophthens. We wished to nitrate under non-acidic conditions, since 6a-thiathiophthens are labile towards acid and undergo partial desulphurisation to form 1-oxa-6,6a-dithiapentalenes (7; X = O).[9-11] We decided, therefore, to use tetranitromethane in the presence of an excess of pyridine.[12]

2-t-Butyl-6a-thiathiophthen (22) reacted with tetranitromethane to give the aldehyde (13) (46%), resulting from partial desulphurisation and *nitrosation*, together with a small quantity (7%) of the previously described 1-oxa-6,6a-dithia-2-azapentalene (9). 2-Phenyl-6a-thiathiophthen (23) behaved in a similar manner, and gave a mixture of the aldehyde (14) (36%) and the azapentalene (10) (8%). The i.r. spectra of compounds (13) and (14) support their formulation as aldehydes [ν(C=O) (KBr): (13), 1669; (14), 1677 cm^{-1}] rather than 3-nitroso-1-oxa-6,6a-dithiapentalenes [*cf.* ketone (15) [6,8]]. Nitrosation by tetranitromethane is unprecedented. Formation of the aldehydes (13) and (14) recalls the formation of the



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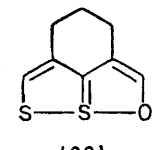
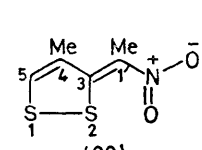


(28)



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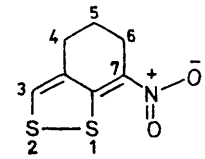

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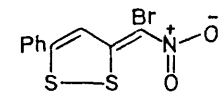

(31)

ketone (15) upon treatment of 2,5-diphenyl-6a-thiathiophthen (26) with nitric acid in acetic acid.[6,8] We suggest that oxidative desulphurisation occurs first, producing the 1-oxa-6,6a-dithiapentalene, together with nitrosonium ion or its equivalent which subsequently nitrosates the 1-oxa-6,6a-dithiapentalene or unchanged 6a-thiathiophthen. The minor products probably arise by further oxidation of the aldehydes (13) and (14), and decarboxylation of the resulting carboxylic acids.

The 3,4-disubstituted 6a-thiathiophthens (24) and (25) both reacted with tetranitromethane to give three products in low yield. There was no indication of

[6] R. J. S. Beer, D. Cartwright, R. J. Gait, R. A. W. Johnstone, and S. D. Ward, *Chem. Comm.*, 1968, 688.
[7] R. J. S. Beer and R. J. Gait, *Chem. Comm.*, 1970, 328.
[8] R. J. S. Beer, D. Cartwright, R. J. Gait, and D. Harris, *J. Chem. Soc.* (*C*), 1971, 963.
[9] F. Arndt, E. Aron, C. Martius, and R. Schwarz, *Rev. Fac. Sci. Univ. Istanbul, Ser. A*, 1948, **13**, 57.
[10] O. Coulibaly and Y. Mollier, *Bull. Soc. chim. France*, 1969, 3208.
[11] H. Behringer, H. Reimann, and M. Ruff, *Angew. Chem.*, 1960, **72**, 415.
[12] W. M. Weaver, in ' The Chemistry of the Nitro- and the Nitroso-groups. Part 2,' ed. H. Feuer, Interscience, New York and London, 1970, p. 1.

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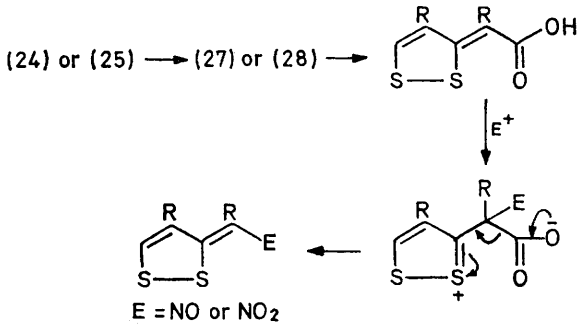
nitration or nitrosation at position 2 (5). 3,4-Dimethyl-6a-thiathiophthen (24) gave 3,4-dimethyl-1-oxa-6,6a-dithiapentalene (27) (6%), 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (11) (1·5%), and 4-methyl-3-(1-nitroethylidene)-3*H*-1,2-dithiole (29) (10%). The bridged 6a-thiathiophthen (25) gave correspondingly a mixture of compounds (28) (4%), (12) (10%), and (30) (4%). We suggest that the products (29), (30), (11), and (12) arise by the following sequence of reactions (see Scheme): oxidative desulphurisation gives the



SCHEME

1-oxa-6,6a-dithiapentalene (27) or (28); further oxidation gives the corresponding carboxylic acid; nitro- and nitroso-decarboxylation finally gives the 3-nitromethylene-3*H*-1,2-dithiole (29) or (30) and the azapentalene (11) or (12). The readiness of 6a-thiathiophthens to undergo oxidation at S(1) or S(6) and/or hydrolysis imposes a restriction on the type of electrophile and the conditions which may be used to effect substitution without concomitant oxidation or hydrolysis.

A recent determination of bond lengths in the nitro-compound (31) [13] and the 'nitroso'-compound (15) [14] reveals (i) that the S–S bond length (2·07 Å) in the nitro-compound is in the normal range for disulphides (*ca.* 2·08 Å), whereas the S–S distance (2·18 Å) in the 'nitroso'-compound is abnormally long, and is in the range of S–S bond lengths found in 6a-thiathiophthens; (ii) that the S–O distance (2·03 Å) in the 'nitroso'-compound is much shorter than that (2·37 Å) in the nitro-compound; (iii) that there is much greater bond length alternation in the nitro-compound than in the 'nitroso'-compound. It was concluded that there is little or no bonding interaction between oxygen and sulphur in the nitro-compound (31), but that the 'nitroso'-compound is best represented as a bicyclic structure (1-oxa-6,6a-dithia-2-azapentalene) (15) in which there is considerable π-electron delocalisation. A comparison of ^{1}H n.m.r. spectral data for the nitro- and 'nitroso'-compounds in the pairs (29), (11) and (30), (12) (see Table) supports this conclusion. The signal from the dithiole ring proton in compounds (11) and (12) occurs at much lower field than the signal from the dithiole ring proton in the corresponding nitro-compounds (29) and (30) (Δδ −1·03 and −1·22 p.p.m.). The signals from the substituents in the compounds (11) and (12) also occur at appreciably lower field than those from the substituents in the corresponding nitro-compounds (29) and (30) [δ(1′-Me) (29) − δ(3-Me) (11), −0·19; δ(4-Me) (29) − δ(4-Me) (11), −0·26 p.p.m.]. These chemical shift differences are attributed mainly to the effect of the larger ring-current resulting from more extensive π-electron delocalisation in the bicyclic azapentalenes (11) and (12).

TABLE [a]

Chemical shifts (δ) in the ^{1}H n.m.r. spectra of (A) the 1-oxa-6,6a-dithia-2-azapentalenes (8)—(14) and the 1-oxa-6,6a-diselena-2-azapentalenes (19)—(21), and (B) the 3-nitromethylene-3*H*-1,2-dithioles (29) and (30) (solutions in deuteriochloroform, *J*/Hz)

	Proton signals (δ/p.p.m.)		
	R^1	R^2	R^3
(A)			
(8)	9·41d $J_{5,4}$ 6·3	8·23d $J_{4,5}$ 6·3	9·20
(9)	1·50	8·04	9·08
(10)	7·42—7·54 m [b] 7·77—7·93 m [c]	8·31	9·08
(11)	9·07b	2·89	2·89
(12)	9·07b	*d*	*d*
(13)	1·59	9·22	10·39
(14)	7·50—7·62 m [b] 7·87—8·04 m [c]	9·54	10·46
(19)	2·78d $J_{5\text{-Me},4}$ 1·0	8·40q $J_{4,5\text{-Me}}$ 1·0	9·20
(20)	7·42—7·54 m [b] 7·76—7·92 m [c]	8·82	9·32
(21)	10·56q $J_{5,4\text{-Me}}$ 0·7	3·06d $J_{4\text{-Me},5}$ 0·7	3·01
(B)			
(29)	8·04, q, $J_{5,4\text{-Me}}$ 0·9, 5-H 2·70, 1′-Me 2·63, d, $J_{4\text{-Me},5}$ 0·9, 4-Me		
(30)	7·85, b, 3-H 2·90, m, 4-CH_2 + 6-CH_2 1·96, bm, 5-CH_2		

[a] Unless otherwise stated values refer to singlet absorptions. For multiplets d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, b = broad. [b] 2*m*- and *p*-protons of 5-Ph. [c] 2 *o*-Protons of 5-Ph. [d] 3·12 bt and 3·20 bt (α-CH_2 and α′-CH_2); 2·15 bqn (β-CH_2).

We provisionally formulate the diselenole derivatives also as bicyclic structures (19)—(21), in the absence of spectral or structural data.

The hitherto unknown dithiolium salt (5) was obtained by established procedures.[2] It was converted into the 6a-thiathiophthen (25) and the oxygen analogue (28), without isolation of the intermediate Vilsmeier salt (6; R^1 = H, R^{2}R^3 = [CH_2]$_3$), by a modification of a previously described procedure.[3]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were measured with a Unicam SP800 spectrophotometer. Light absorption data refer to solutions in cyclohexane; sh = shoulder, infl = inflection, br = broad. I.r. spectra were recorded with a Perkin-Elmer 621 spectrometer with 0·02M-chloroform solutions. ^{1}H N.m.r. spectra were obtained with a Perkin-Elmer R10 spectrometer operating at 60 MHz. Solutions were 0·3M in deuteriochloroform, unless otherwise stated. Chemical shifts (δ) are given in p.p.m. downfield from tetramethylsilane as internal reference. *J* Values were measured on the 100 Hz

[13] K. I. G. Reid and I. C. Paul, *J. Chem. Soc.* (*B*), 1971, 952.
[14] P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc.* (*B*), 1971, 946.

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scale. Unless otherwise stated (d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, b = broad) values refer to singlet absorptions. Mass spectra were obtained with an AEI MS902 spectrometer. T.l.c. was performed on silica gel G (Merck). Solvent mixtures are described in ratios of volumes. Solutions were dried over sodium sulphate and evaporated with a rotary evaporator. Criteria used in the identification of reaction products included t.l.c. behaviour, m.p.s, and n.m.r. and mass spectra.

Materials.—Light petroleum was of b.p. 40—60°. Perchloric acid refers to 70—72% (w/w) perchloric acid. Dimethylformamide was dried over calcium hydride for *ca.* 1 week, then distilled at 15 mmHg. The 1,2-diselenolium salts (16)—(18) were prepared [15] according to the procedure of Heath, Martin, and Stewart.[16]

4,5,6,7-*Tetrahydrobenzo*[c][1,2]*dithiolium Perchlorate* (5).—2-Hydroxymethylenecyclohexanone (6·3 g, 50 mmol), hydrogen disulphide [17] (3 ml), and perchloric acid (6·3 ml) were reacted in acetic acid (100 ml) as previously described.[2] 4,5,6,7-*Tetrahydrobenzo*[c][1,2]*dithiolium perchlorate* (5·51 g, 42%) was obtained as colourless needles, m.p. 111—112° (from acetic acid) (Found: C, 32·9; H, 3·6. $C_7H_9ClO_4S_2$ requires C, 32·8; H, 3·6%), δ(CF_3CO_2H) 2·01—2·20 (4H, m, 5- and 6-CH_2), 3·20—3·57 (4H, m, 4- and 7-CH_2), and 9·89 (1H, 3-H).

4,5-*Dihydro*-3H-*benzo*[cd][6a]*thiathiophthen* (25).—A mixture of phosphoryl chloride (0·92 ml, 10 mmol), the salt (5) (1·28 g, 5 mmol), and *NN*-dimethylthioformamide [18] (10 ml) was heated at 60° for 10 min. The solution was cooled to 0°, diluted with *NN*-dimethylformamide (20 ml), and treated with aqueous 2M-sodium hydrogen sulphide (25 ml). The resulting mixture was diluted with water and extracted with benzene. The extracts were washed thoroughly with water, dried, and evaporated, finally at 0·1 mmHg to remove residual *NN*-dimethylthioformamide. Chromatography of the residue on a column of silica gel (25 × 3·0 cm) with light petroleum–benzene (3 : 2) as eluant, gave red eluates which yielded 4,5-*dihydro*-3H-*benzo*[cd][6a]*thiathiophthen* as red plates (700 mg, 70%), m.p. 79·5—80° (from cyclohexane) (Found: C, 48·0; H, 4·1. $C_8H_8S_3$ requires C, 48·0; H, 4·0%), $\lambda_{max.}$ 492 (log ε 3·72), 460 (4·72), and 233 nm (4·33), δ 1·99 (2H, qn, $J_{4\text{-}CH_2,\ 3\text{- and }5\text{-}CH_2}$ 6·0 Hz, 4-CH_2), 2·99 (4H, t, $J_{3\text{- and }5\text{-}CH_2,4\text{-}CH_2}$ 6·0 Hz, 3- and 5-CH_2), and 8·78 (2H, 2- and 6-H).

4,5-*Dihydro*-3H-*benzo*[cd]-1-*oxa*-6,6a-*dithiapentalene* (28) (with M. G. Jackson).—A mixture of the salt (5) (1·28 g, 5 mmol), phosphoryl chloride (1·30 ml, 14 mmol), and *NN*-dimethylthioformamide (10 ml) was heated at 60° for 10 min. The solution was cooled to 0°, diluted with *NN*-dimethylformamide (50 ml), and treated with aqueous 2M-sodium hydroxide (60 ml). Work up as for the benzothiathiophthen (25) and chromatography on a column of silica gel (22 × 2·6 cm) with benzene as eluant gave red eluates. Further elution with benzene–ether (1 : 1) brought through orange eluates. The residue from the red eluates was rechromatographed on a column of alumina (25 × 2·6 cm) with benzene–light petroleum (3 : 1) to give red eluates which yielded 4,5-dihydro-3*H*-benzo[*cd*][6a]thiathiophthen (25) (157 mg, 16%). The residue from the orange eluates was rechromatographed (silica gel; 50 × 2·6 cm) with benzene–ether (4 : 1) and produced 4,5-*dihydro*-3H-*benzo*[cd]-1-*oxa*-6,6a-*dithiapentalene* (574 mg, 62%) as yellow needles, m.p. 103·5—104° (from cyclohexane) (Found: C, 52·4; H, 4·5. $C_8H_8OS_2$ requires C, 52·2; H, 4·3%), $\lambda_{max.}$ 448 (log ε 3·99), 428 (4·03), 407sh (3·82), 280sh (2·99), 230 (4·16), and 209sh nm (3·84), δ 1·88 (2H, bqn, 4-CH_2), 2·71 (2H, bt, 3- or 5-CH_2), 2·82 (2H, bt, 5- or 3-CH_2), 7·56 (1H, 6-H), and 9·33 (1H, 2-H).

Preparation of 1-*Oxa*-6,6a-*dithia*-2-*azapentalenes from* 3-*Alkyl*-1,2-*dithiolium Salts*.—The following general procedure was used (deviations are given in individual cases). Sodium nitrite (276 mg, 4 mmol) was added to a stirred solution of the dithiolium salt (2 mmol) in acetonitrile (25 ml) and acetic acid (25 ml). The resulting orange-yellow solution was stirred for 20 min before being diluted with water and extracted with benzene. The extracts were washed successively with water, saturated sodium hydrogen carbonate solution, and water, dried, and evaporated. The residue was chromatographed (alumina; 15 × 3·0 cm) with benzene. The residue from the yellow eluates was recrystallised from cyclohexane.

5-*t*-*Butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (9) *from* 3-*methyl*-5-*t*-*butyl*-1,2-*dithiolium perchlorate* (2). The dithiolium salt [3] (4 mmol) was treated with sodium nitrite (552 mg, 8 mmol) in acetonitrile–acetic acid (1 : 1, 100 ml). Chromatography with benzene–ether (9 : 1), and recrystallisation from light petroleum gave 5-*t*-*butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (690 mg, 86%) as orange needles, m.p. 73—74° (Found: C, 47·5; H, 5·6; N, 7·0. $C_8H_{11}NOS_2$ requires C, 47·8; H, 5·5; N, 7·0%), M^+ at *m/e* 201, $\lambda_{max.}$ 400 (log ε 3·80), 275 (3·58), 233 (4·45), and 200 nm (4·04).

5-*Phenyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (10) *from* 3-*methyl*-5-*phenyl*-1,2-*dithiolium perchlorate* (3).[2] The compound (10) (397 mg, 90%) was obtained as orange needles, m.p. 142—143° (lit.,[6] 131—132°) (Found: C, 54·1; H, 3·3; N, 6·5. Calc. for $C_{10}H_7NOS_2$: C, 54·2; H, 3·2; N, 6·3%), M^+ at *m/e* 221, $\lambda_{max.}$ 416 (log ε 3·97), 320 (3·99), 230 (4·46), and 209 nm (4·37).

3,4-*Dimethyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (11) *from* 3-*ethyl*-4-*methyl*-1,2-*dithiolium perchlorate* (4).[4] Benzene–ether (9 : 1) was used for chromatography. 3,4-*Dimethyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (220 mg, 64%) was obtained as orange-red needles, m.p. 127—128° (Found: C, 41·9; H, 4·3; N, 8·4. $C_6H_7NOS_2$ requires C, 41·6; H, 4·1; N, 8·1%), M^+ at *m/e* 173, $\lambda_{max.}$ 413 (log ε 3·78), 275sh (3·33), 231 (4·30), and 206 nm (3·95).

4,5-*Dihydro*-3H-*benzo*[cd]-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (12) *from* 4,5,6,7-*tetrahydrobenzo*[c][1,2]*dithiolium perchlorate* (5). The *compound* (12) (328 mg, 89%) formed orange-red plates, m.p. 95—96° (Found: C, 45·3; H, 3·9; N, 7·7. $C_7H_7NOS_2$ requires C, 45·4; H, 3·8; N, 7·6%), M^+ at *m/e* 185, $\lambda_{max.}$ 420 (log ε 3·73), 275sh (3·43), 233 (4·32), and 209 nm (4·01).

1-*Oxa*-6,6a-*dithia*-2-*azapentalene* (8) *from* 3-*Methyl*-1,2-*dithiolium Perchlorate* (1).—Sodium nitrite (276 mg, 4 mmol) was added to a stirred solution of the dithiolium salt [2] (433 mg, 2 mmol) in acetonitrile–acetic acid (1 : 1, 50 ml) at room temperature. The solution was stirred for 15 min, more sodium nitrite (276 mg, 2 mmol) was added, and stirring was continued for a further 15 min. The solution was diluted with water and extracted with benzene. The extracts were washed successively with water, saturated aqueous sodium hydrogen carbonate, and water, dried, and

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evaporated. The combined product from two such reactions (520 mg, 90%) was recrystallised from cyclohexane to give 1-*oxa*-6,6a-*dithia*-2-*azapentalene* as orange needles, m.p. 83—84° (Found: C, 33·1; H, 2·0; N, 9·5. $C_4H_3NOS_2$ requires C, 33·1; H, 2·1; N, 9·7%), M^+ at *m/e* 145, $\lambda_{max.}$ 402 (log ε 3·61), 270sh (3·47), 231 (4·30), and 207 nm (3·94).

5-*Methyl*-1-*oxa*-6,6a-*diselena*-2-*azapentalene* (19).—Sodium nitrite (690 mg, 10 mmol) was added to a stirred solution of 3,5-dimethyl-1,2-diselenolium perchlorate (16) (1·623 g, 5 mmol) in acetonitrile–acetic acid (1 : 1, 120 ml) at room temperature. The mixture was stirred for 2 min, poured into water, and extracted with benzene. The benzene extracts were washed with water (× 4), dried, and evaporated. Chromatography of the residue (silica gel; 12 × 3·0 cm) with benzene gave orange-brown eluates which yielded 5-*methyl*-1-*oxa*-6,6a-*diselena*-2-*azapentalene* (878 mg, 70%). Recrystallisation from light petroleum–benzene (9 : 1) gave light-sensitive brown crystals, m.p. 80—81° (Found: C, 23·5; H, 1·9; N, 5·3; Se, 62·3. $C_5H_5NOSe_2$ requires C, 23·8; H, 2·0; N, 5·5; Se, 62·4%), principal peaks at *m/e* 251, 253, and 255, $\lambda_{max.}$ 446 (log ε 3·78), 315sh (3·50), 253 (4·22), and 218 nm (4·07).

5-*Phenyl*-1-*oxa*-6,6a-*diselena*-2-*azapentalene* (20).—Sodium nitrite (690 mg, 10 mmol) was added to a stirred solution of 3-methyl-5-phenyl-1,2-diselenolium perchlorate (17) (1·933 g, 5 mmol) in acetonitrile–acetic acid (1 : 1, 120 ml) at room temperature. The mixture was stirred for 2 min, diluted with water, and extracted with benzene. The extracts were washed with water (× 4), dried, and evaporated. The residue was chromatographed (alumina; 20 × 3·0 cm) with benzene–ether (9 : 1). The orange-brown eluates gave 5-*phenyl*-1-*oxa*-6,6a-*diselena*-2-*azapentalene* (910 mg, 58%) which crystallised from cyclohexane–benzene (5 : 1) as light-sensitive brown needles, m.p. 132—133° (Found: C, 37·7; H, 2·2; N, 4·3; Se, 49·5. $C_{10}H_7NOSe_2$ requires C, 38·1; H, 2·2; N, 4·5; Se, 50·1%), principal peaks at *m/e* 313, 315, and 317, $\lambda_{max.}$ 458 (log ε 3·91), 354 (4·01), and 242 nm (4·41).

3,4-*Dimethyl*-1-*oxa*-6,6a-*diselena*-2-*azapentalene* (21).—The procedure was identical with that of the preceding experiment. From 3-ethyl-4-methyl-1,2-diselenolium perchlorate (18) (1·693 g, 5 mmol) 3,4-*dimethyl*-1-*oxa*-6,6a-*diselena*-2-*azapentalene* (790 mg, 68%) was obtained after chromatography with ether as brown needles, m.p. 128—129° (from cyclohexane) (Found: C, 26·9; H, 2·8; N, 5·3. $C_6H_7NOSe_2$ requires C, 27·0; H, 2·6; N, 5·3%), principal peaks at *m/e* 265, 267, and 269, $\lambda_{max.}$ 459 (log ε 3·82), 305br (3·40), 252 (4·33), and 217 nm (4·32).

Reaction of Tetranitromethane with 6a-*Thiathiophthens*.—*With* 2-*t-butyl*-6a-*thiathiophthen* (22). A solution of tetranitromethane (784 mg, 4 mmol) in benzene (20 ml) was added dropwise to a solution of 2-t-butyl-6a-thiathiophthen [19] (432 mg, 2 mmol) in benzene (20 ml) and pyridine (8 ml) at 50°. The resulting solution was boiled for 15 min, cooled, and poured into water. The mixture was extracted thrice with benzene and the extracts were washed with water, dried, and evaporated. The residue was chromatographed (alumina; 20 × 2·5 cm) with benzene–light petroleum (1 : 1) to give orange eluates from which 2-t-butyl-6a-thiathiophthen (27 mg, 6·3%) was recovered. Continued elution with benzene brought through a yellow band which yielded 5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene (9) (27 mg, 6·7%), m.p. 73·5—74° (Found: C, 47·6; H, 5·6; N, 7·2. Calc. for $C_8H_{11}NOS_2$: C, 47·8; H, 5·5; N, 7·0%), identical with the product obtained by nitrosation of 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (2). Subsequent elution with ether brought through a yellow-green band which gave 3-*formyl*-5-*t-butyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (13) (210 mg, 46%), red needles from light petroleum, m.p. 139—140° (Found: C, 47·1; H, 4·8; S, 28·1. $C_9H_{11}NO_2S_2$ requires C, 47·1; H, 4·8; S, 28·0%), M^+ at *m/e* 229, ν 1669 (C=O) cm^{-1}.

With 2-*phenyl*-6a-*thiathiophthen* (23). A solution of tetranitromethane (392 mg, 2 mmol) in benzene (10 ml) was added to a solution of 2-phenyl-6a-thiathiophthen [2] (236 mg, 1 mmol) in benzene (25 ml) and pyridine (4 ml) at 40°. The solution was boiled for 15 min, cooled, diluted with water, and thrice extracted with benzene. The extracts were washed with water, dried, and evaporated. Preparative t.l.c. of the residue (silica gel; 20 × 20 cm, 1 mm-layer thickness) with benzene gave two yellow bands. The faster-moving band gave, after extraction and evaporation, 3-*formyl*-5-*phenyl*-1-*oxa*-6,6a-*dithia*-2-*azapentalene* (14) (90 mg, 36%), red needles from cyclohexane, m.p. 174—175° (Found: C, 53·1; H, 2·7; S, 25·8. $C_{11}H_7NO_2S_2$ requires C, 53·0; H, 2·8; S, 25·7%), M^+ at *m/e* 249, ν 1677 (C=O) cm^{-1}. The second yellow band yielded 5-phenyl-1-oxa-6,6a-dithia-2-azapentalene (10) (18 mg, 8%), identical with the product obtained by nitrosation of 3-methyl-5-phenyl-1,2-dithiolium perchlorate (3).

With 3,4-*dimethyl*-6a-*thiathiophen* (24). A solution of tetranitromethane (1·96 g, 10 mmol) in benzene (50 ml) was added to a solution of 3,4-dimethyl-6a-thiathiophthen [20] (940 mg, 5 mmol) in benzene (125 ml) and pyridine (25 ml). The resulting solution was boiled for 15 min, cooled, diluted with water, and extracted with benzene (3 × 200 ml). The extracts were washed thrice with water, dried, and evaporated. The residue was chromatographed (alumina; 15 × 3·0 cm). The yellow eluates were collected in 500 ml fractions (× 6) and the composition was ascertained by t.l.c.: * (i) benzene; (ii)—(v), benzene–ether (9 : 1); (vi), ether. Fractions (i)—(iv) were combined and evaporated, and the residue was rechromatographed on a column of alumina (15 × 1·5 cm) with benzene–ether (9 : 1) as eluant. The eluates afforded 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (11) (12 mg, 1·5%). Rechromatography of the residue from fraction (v) (alumina; 15 × 1·5 cm) with benzene–ether (9 : 1) gave 3,4-dimethyl-1-oxa-6,6a-dithiapentalene [20] (27) (50 mg, 5·8%), M^+ at *m/e* 172. The residue from fraction (vi) was rechromatographed (alumina; 15 × 1·5 cm) with ether. The eluates yielded 4-*methyl*-3-(1-*nitroethylidene*)-3H-1,2-*dithiole* (29) (91 mg, 9·6%), orange needles from benzene, m.p. 191—192° (Found: C, 37·7; H, 3·9; N, 7·4. $C_6H_7NO_2S_2$ requires C, 38·0; H, 3·7; N, 7·0%), M^+ at *m/e* 189, $\lambda_{max.}$ 463 (log ε 4·31), 441 (4·20), 415sh (3·72), 293 (3·41), 241infl (3·84), and 215 nm (4·07).

With 4,5-*dihydro*-3H-*benzo*[cd][6a]*thiathiophthen* (25). The procedure was identical with that of the preceding experiment, but with 4,5-dihydro-3*H*-benzo[*cd*][6a]thiathiophthen (1 g, 5 mmol). The product was chromatographed (alumina; 25 × 3·0 cm) with benzene to give crimson eluates; continued elution with benzene–ether

* Compound (11) migrates more rapidly than compound (27) on alumina (column chromatography) but more slowly on silica (t.l.c.), with benzene–ether (9 : 1) as eluant.

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(9 : 1) gave yellow eluates; and final elution with ether brought through a strongly adsorbed yellow band. Rechromatography of the residue from the crimson eluates (alumina; 15 × 1·5 cm) with benzene–light petroleum (1 : 1) gave pale yellow eluates from which sulphur (87 mg) was isolated, and subsequently crimson eluates from which starting material (25) (50 mg, 5%) was recovered. The residue from the first yellow band contained two components (t.l.c.) * and was rechromatographed (alumina; 60 × 1·7 cm) with benzene–ether (9 : 1). The eluates yielded 4,5-dihydro-3*H*-benzo[*cd*]-1-oxa-6,6a-dithia-2-azapentalene (12) (93 mg, 10%) and subsequently 4,5-dihydro-3*H*-benzo[*cd*]-1-oxa-6,6a-dithiapentalene (28) (38 mg, 4·1%). The eluates from the strongly adsorbed yellow band were evaporated and the residue was rechromatographed (alumina; 15 × 1·5 cm) with ether. The yellow eluates yielded 5,6-*dihydro*-7-*nitro*-4H-*benzo*[c][1,2]*dithiole* (30) (34 mg, 3·9%), orange needles from benzene–cyclohexane (1 : 1), m.p. 213·5—214·5° (Found: C, 41·5; H, 3·7; N, 7·1. $C_7H_7NO_2S_2$ requires C, 41·8; H, 3·5; N, 7·0%), M^+ at *m/e* 201, $\lambda_{max.}$ 461 (log ε 4·34), 436 (4·24), 415sh (3·90), 289br (3·48), 244sh (3·83), and 218 nm (4·20).

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* Compound (12) migrates more rapidly than compound (28) on alumina but more slowly on silica, with benzene–ether (9 : 1) as eluant.

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