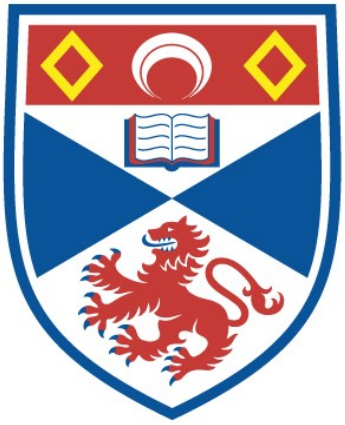
STUDIES OF 1,6,6A-TRITHIAPENTALENES AND RELATED SYSTEMS WITH SPECIAL REFERENCE TO NITROGEN ANALOGUES

Robert Matthews Christie

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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STUDIES OF 1,6,6a-TRITHIAPENTALENES AND RELATED SYSTEMS, WITH SPECIAL REFERENCE TO NITROGEN ANALOGUES

being a Thesis

presented by

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to the

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in application for

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To my wife, Linda

DECLARATION

I declare that this thesis is based on the results of experiments carried out by me, that it is of my own composition, and has not been submitted previously in application for a higher degree.

CERTIFICATE

I hereby certify that Robert Matthews Christie, B.Sc., has spent eleven terms at research work under my supervision, has fulfilled the conditions of the Resolution of the University Court, 1967 No. 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

UNIVERSITY CAREER

I entered the University of St. Andrews in October 1967, and subsequently graduated B.Sc. with First Class Honours in Chemistry in June 1971.

In October 1971, I was awarded a Carnegie Research Scholarship, and, from then until July 1974, I carried out the work which is embodied in this thesis in the Department of Chemistry, University of St. Andrews under the supervision of Dr. D.H. Reid.

ACKNOWLEDGEMENTS

I should like to express my gratitude to Dr. D.H. Reid for his advice and guidance, and for continued interest in this work.

I should also like to thank Professor Lord Tedder for making available laboratory facilities.

Thanks are also due to the technical staff of the Department of Chemistry for their valuable assistance and to Mrs. W. Pogorzelec, who prepared the typescript.

Finally, I should like to thank the Carnegie Trust for the Universities of Scotland for the award of a Research Scholarship which enabled me to carry out this research.

EXPLANATORY NOTE

This thesis is divided into three sections, Parts 1, 2 and 3. Each part is divided into a number of principal sections, each prefixed by a capital letter.

Part 1 consists of a review of the background literature relevant to the work embodied in this thesis.

Part 2 is a discussion of the results achieved in the course of the investigation.

Part 3 is devoted to a description of the experimental details and is complementary to Part 2.

Tables of nmr, ultraviolet and visible and mass spectral data are contained in Appendices A, B and C respectively.

Where reference is made to the chemical literature, this is indicated by a number in superscript, a key to which can be found at the end of the thesis. The structural formulae which have been reproduced for illustrative purposes have been assigned Arabic numerals, which correspond to the numbers which have been assigned to the relevant compounds in the text. The structure keys to Parts 1 and 2 are distinct. The structure key to Part 3 is the same as that for Part 2.

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SUMMARY

An attempted synthesis of 1,6-dimethyl-6a-thia-1,6-diazapentalene from 2,5-dimethylisothiazolium perchlorate was unsuccessful. In the course of the work it was found that 2,5-dimethylisothiazolium perchlorate reacts with methylamine to give a thiophen derivative, the structure of which was proved by synthesis. The mechanism of the rearrangement is discussed.

The reactions of 1,6,6a-trithiapentalenes, 1-oxa-6,6a-dithiapentalenes and 1,6a-dithia-6-azapentalenes with arenediazonium fluoroborates were studied, as part of a detailed investigation of the electrophilic substitution of 1,6,6a-trithiapentalenes and related systems. These reactions proceed by way of electrophilic attack at the 3(4)-position and rearrangement into derivatives of the 1,6a-dithia-5,6-diazapentalene system. When the substrate contains alkyl substituents at the 3- and 4-positions, formation of the 1,6a-dithia-5,6-diazapentalene involves displacement of a CHS, CHO or CHNMe group by the diazonium group. A mechanism accounting for the various features of the electrophilic substitution of 1,6,6a-trithiapentalenes and related systems is proposed. It is suggested that attack by an electrophile at the 3(4)-position of the 10π bicyclic substrate generates a 6π monocyclic intermediate.

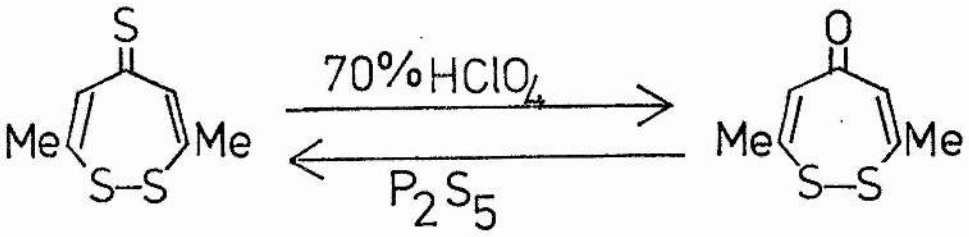
A general synthesis of 1,6a-dithia-5,6-diazapentalenes and 1,6a-diselena-5,6-diazapentalenes has been developed, involving the reaction of 3-methyl(ene)-1,2-dithiolium or 3-methyl(ene)-1,2-diselenolium salts with arenediazonium fluoroborates. The structure of 1,6a-dithia-5,6-diazapentalenes is discussed in the light of ^{1}H nmr, electronic and mass spectral data and X-ray crystal structure data, and is compared with the structures of 1,6,6a-trithiapentalenes and 1,6a-dithia-6-azapentalenes.

1,6a-Dithia-5,6-diazapentalenes undergo electrophilic substitution at the 4-position. Bromination, formylation and nitration give the 4-substituted 1,6a-dithia-5,6-diazapentalenes, whereas nitrosation is accompanied by rearrangement into derivatives of the 1-oxa-6,6a-dithia-2-azapentalene system. Methylation of 1,6a-dithia-5,6-diazapentalenes with methyl fluorosulphonate affords 5-(2-methylthiovinyl)-1,2,3-thiadiazolium fluorosulphonates, which react with methylamine to give 6a-thia-1,2,6-triazapentalenes. 6a-Thia-1,2,6-triazapentalenes are also obtained by the reaction of 1,6a-dithia-5,6-diazapentalenes with methylamine. Protonation of 1,6a-dithia-5,6-diazapentalenes in trifluoroacetic acid was studied by ^{1}H nmr spectroscopy. The structures of the protonated species are discussed.

1,6a-Dithia-5,6-diazapentalenes containing alkyl groups in the 3- and 4-positions are partially desulphurised by mercury(II)acetate to give 1-oxa-6a-thia-5,6-diazapentalenes. 1-Oxa-6a-thia-5,6-diazapentalenes couple with arenediazonium fluoroborates to give 6a-thia-1,2,5,6-tetraazapentalenes. Symmetrically substituted 6a-thia-1,2,5,6-tetraazapentalenes show real or time-averaged C_{2v} symmetry in solution and are formulated as bicyclic structures of the 1,6,6a-trithiapentalene type.

PART ONE

INTRODUCTION


S
Me
Me
S–S
70% HClO4
P2S5
O
Me
Me
S–S

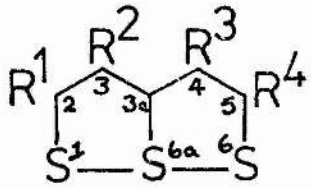
1 2


Me
Me
S—S—S

3


Me
Me
S—S—O

4


R1
R2
R3
R4
1
2
3
3a
4
5
6
6a
S
S
S

5

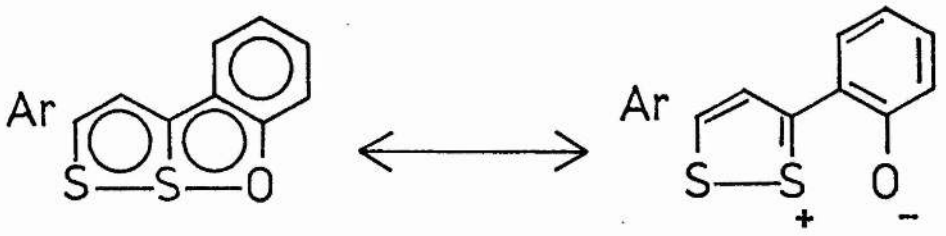
A. 1,6,6a-trithiapentalenes and related compounds

In recent years there has been considerable interest centred on the unusual structural features of the 1,6,6a-trithiapentalene system. In 1925, Arndt, Nachtwey and Pusch[1] isolated a compound from the reaction of heptane-2,4,6-trione with phosphorus pentasulphide, for which they proposed the 1,2-dithiepin-5-thione structure (1). Arndt and coworkers[2] presented supporting evidence for this structure when they showed that treatment of this product with 70% perchloric acid gave a compound, assigned the 1,2-dithiepin-5-one structure (2), from which the original compound could be recovered by thionation with phosphorus pentasulphide. In addition, Bothner-By and Traverso[3] demonstrated that the compound assigned structure (1) possessed C_{2v} symmetry by showing that its nmr spectrum consisted of two singlets with intensities in the ratio 3:1. Evidence for the 1,6,6a-trithiapentalene structure (3) was presented by Bezzi and coworkers[4,5] in 1958, when they established the correct geometry of the molecule by X-ray crystallography. Independently, Guillouzo[6] showed that the compound, for which structure (2) had been proposed, in fact had the 1-oxa-6,6a-dithiapentalene structure (4) from the carbonyl stretching frequency of the compound. Since then a large variety of related compounds have been synthesised and structural studies, especially X-ray crystallography, have contributed much to an understanding of the systems.

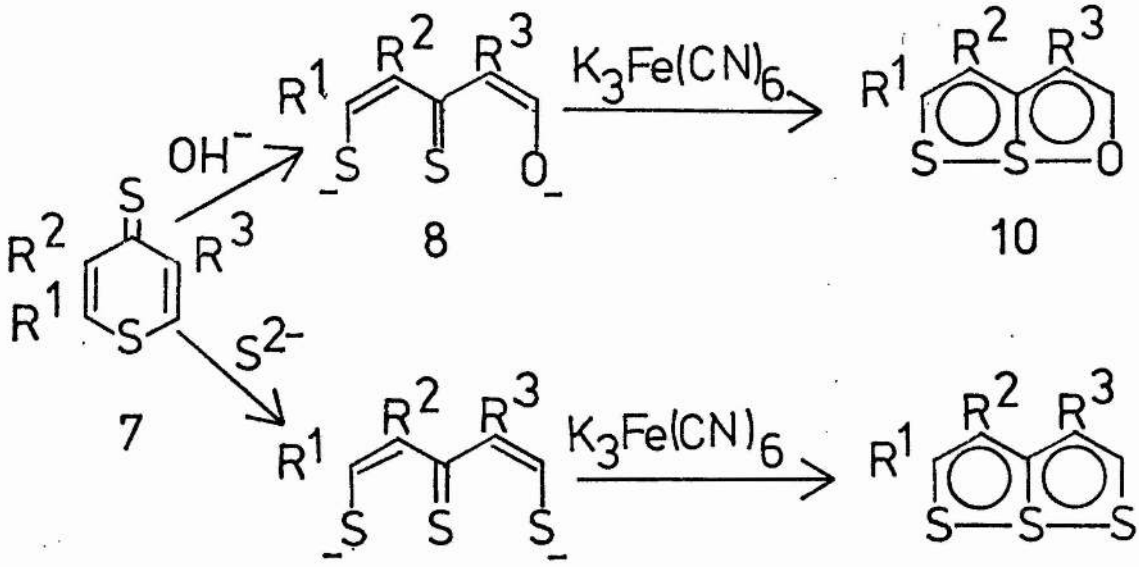
Reviews on 1,6,6a-trithiapentalenes and related compounds have been given by Breslow and Skolnik[7], Lozac'h and Vialle[8], Lozac'h[9,10], Beer[11,12], Klingsberg[13], and Reid[14].

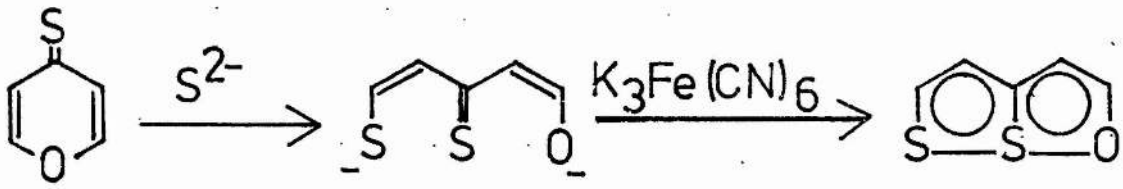
A general nomenclature for this series of compounds based on pentalene, suggested by Lozac'h[9,15], will be used throughout this thesis to formulate compounds for which there is evidence for a bicyclic structure. The name 6a-thiathiophthen has been commonly

applied to the three-sulphur compounds (5) but this has the disadvantage that it cannot be applied to many of the related compounds. Chemical abstracts indexes this system as [1,2]-dithiolo-[1,5-b][1,2]-dithiole-7-S^{IV}.

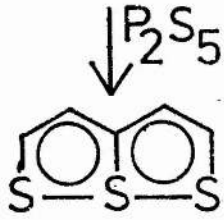

Ar
S—S—O
Ar
S—S
O

6


R1
R2
R3
K3Fe(CN)6
OH−
S2−
S
O
8
10
7
9
11


S
O
S2−
K3Fe(CN)6
S—S—O

14 15 12


P2S5
S—S—S

13

B. Synthesis of 1,6,6a-trithiapentalenes and related compounds

(a) 1,6,6a-trithiapentalenes and related compounds containing oxygen

These two classes of compound are considered together because the syntheses are often analogous and because in many cases, formation of trithiapentalenes involves the prior formation of oxadithiapentalenes. A large number of reactions lead to these systems and only those syntheses which are most general and which give good yields will be discussed.

(i) Interconvertibility of the sulphur and oxygen compounds

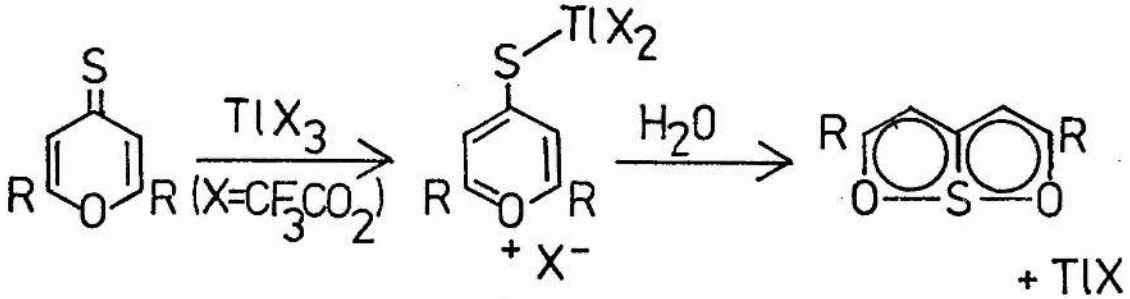
Many 1,6,6a-trithiapentalenes have been converted into 1-oxa-6 6a-trithiapentalenes by the action of strong acids. For example, 2,5-dimethyl-1,6,6a-trithiapentalene (3) reacts with 70% perchloric acid to form the corresponding oxygen compound (4)[2]. Mercury(II) acetate has also been used to effect this type of reaction[16]. The reverse process, thionation of oxadithiapentalenes, can be achieved in most cases by the action of phosphorus pentasulphide, although compounds such as (6), in which the oxygen is attached to a benzene ring resist the replacement of oxygen by sulphur[17,18].

(ii) From triketones

Arndt's original synthesis of 2,5-dimethyl-1,6,6a-trithiapentalene (3)[1] utilised the reaction of heptane-2,4,6-trione with phosphorus pentasulphide. Since then, several trithiapentalenes[18] have been prepared from triketones in this way.

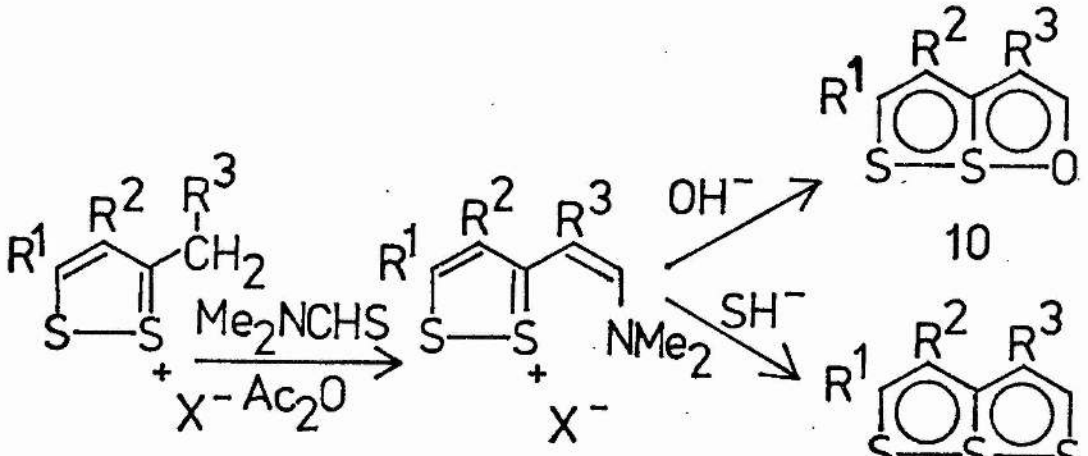
(iii) From 4H-thiopyran-4-thiones and 4H-pyran-4-thiones

4H-Thiopyran-4-thiones (7) are ring-opened by hydroxide or sulphide to the di-anions (8) or (9) which can be oxidised by potassium ferricyanide to give the corresponding oxadithiapentalenes (10) or trithiapentalenes (11)[19]. This method gives a good yield of 1,6,6a-trithiapentalene (13). In a similar reaction[20], treatment

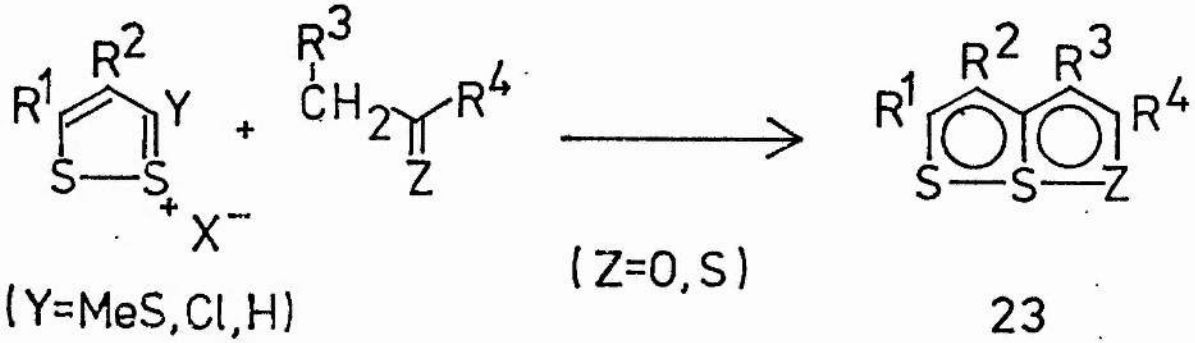


16 17 18

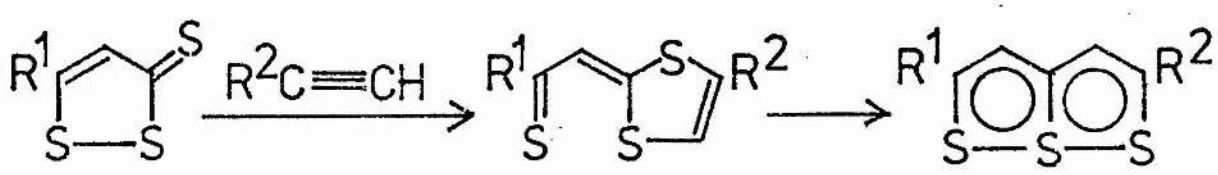
(a) R = H
(b) R = Me
(c) R = CO_2Et



19 20 10 11



21 22 23



24 25 26

of 4H-pyran-4-thione (14) with sulphide produces the di-anion (15) and subsequent oxidation affords 1-oxa-6,6a-dithiapentalene (12), which can be thionated with phosphorus pentasulphide to give compound (13) in good overall yield. An elegant synthesis of 1,6-dioxa-6a-thiapentalenes (18a)-(18c) involves the reaction of 4H-pyran-4-thiones (16a)-(16c) with thallium(III) trifluoroacetate[21]. Ring-opening of the resulting intermediates (17a)-(17c) is accompanied by loss of thallium(I) trifluoroacetate and formation of the dioxathiapentalenes.

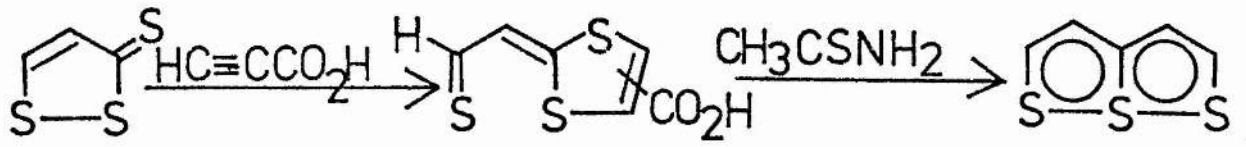
(iv) From 1,2-dithiolium salts

A versatile synthesis of 1,6,6a-trithiapentalenes and related compounds utilises the Vilsmeier salts (20) formed by the reaction of 3-methyl(ene)-1,2-dithiolium salts (19) with dimethylthioformamide in acetic anhydride[22,23]. The salts (20) react smoothly with hydroxide or hydrosulphide to give 1-oxa-6,6a-dithiapentalenes (10) or 1,6,6a-trithiapentalenes (11) respectively.

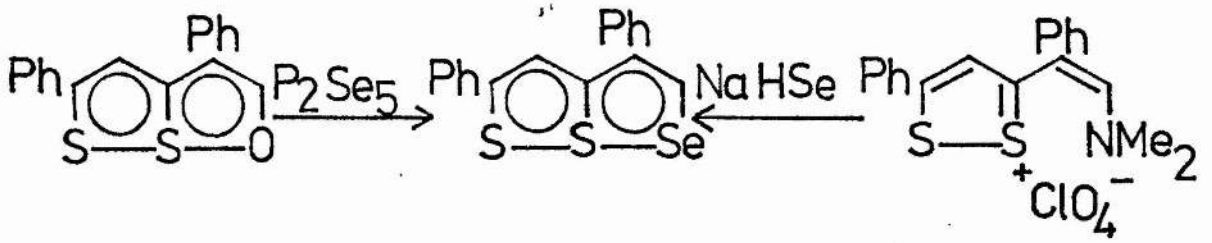
Another commonly employed synthetic scheme involves the reaction of 1,2-dithiolium salt (21) containing a group Y (MeS, Cl, H) in the 3-position which is eliminated (as MeS^-, Cl^-, H^-) after condensation at this 3-position with a methyl(ene) carbonyl or thiocarbonyl compound (22) to form an oxadithiapentalene or a trithiapentalene (23)[24-28].

(v) From 1,2-dithiole-3-thiones

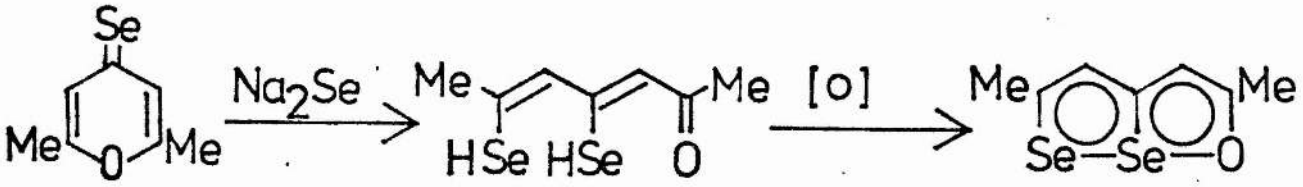
The reaction of 1,2-dithiole-3-thiones (24) with acetylenes gives the thiones (25) or under certain conditions the trithiapentalenes (26), which can also be obtained by the action of phosphorus pentasulphide on the isomeric compounds (25)[29,30]. A useful route to the parent trithiapentalene (13)[31] involves the reaction of 1,2-dithiole-3-thione (27) with propiolic acid, followed by treatment of the resulting mixture of carboxylic acids (28) with thioacetamide in boiling naphthalene.



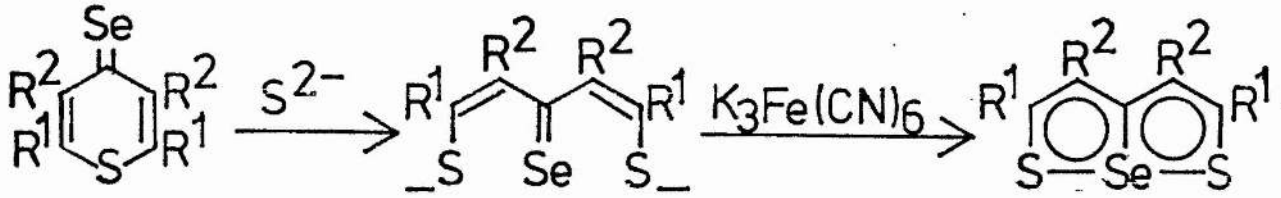
27 28 13



30 29 31

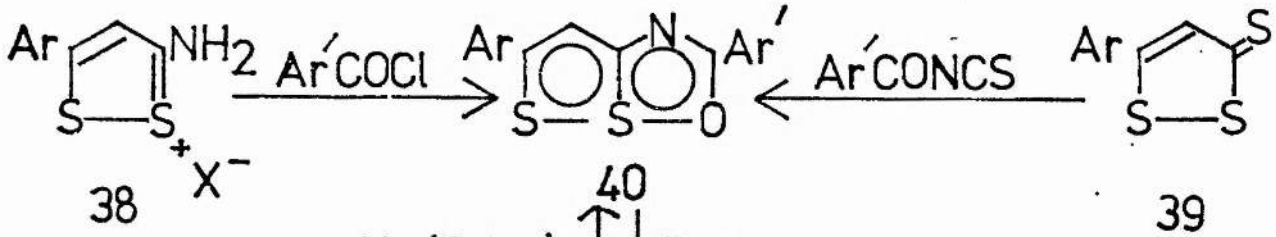


32 33 34

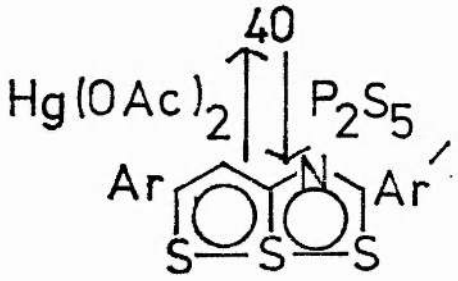


35 36 37

(a) $R^I = R^2 = H$
(b) $R^I = H \quad R^2 = Me$
(c) $R^I = Ph \quad R^2 = H$



38 39



41

(b) Selenium analogues of 1,6,6a-trithiapentalenes

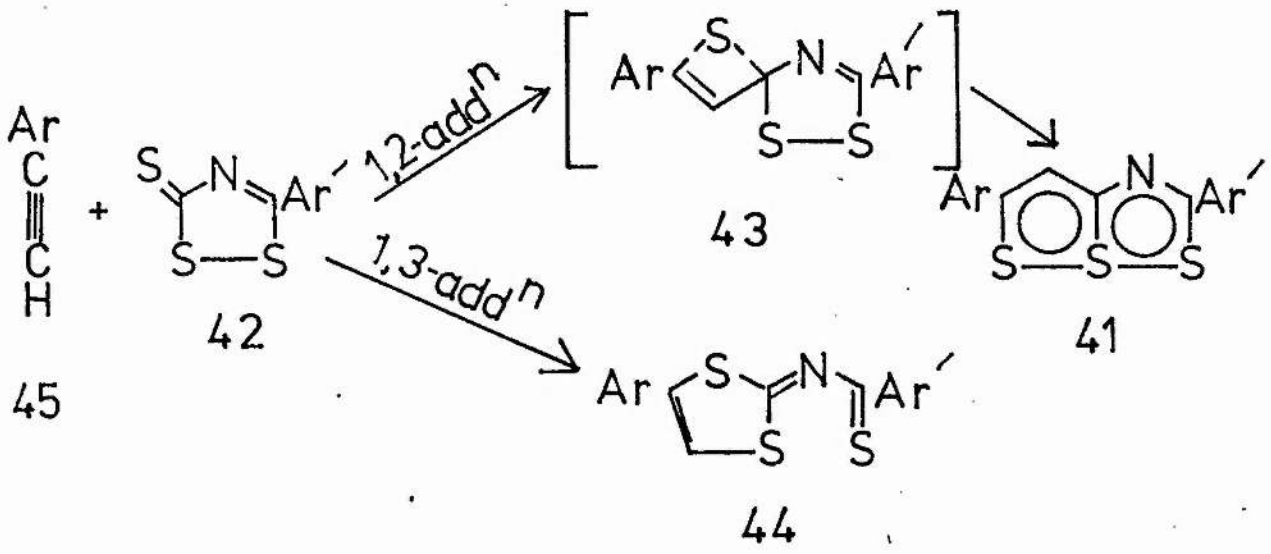
2,4-Diphenyl-1,6a-dithia-6-selenapentalene (29) has been obtained in two different ways: (i) by reaction of 3,5-diphenyl-1-oxa-6,6a-dithiapentalene (30) with phosphorus pentaselenide[32] and (ii) by treatment of the Vilsmeier salt (31) with sodium hydrogen selenide[22]. The reaction of 2,6-dimethyl-4H-pyran-4-selenoketone (32) with sodium selenide leads to compound (33)[33,34], which, on exposure to air, is oxidised to 2,5-dimethyl-1-oxa-6,6a-diselenapentalene (34). Reid has developed a synthesis of 1,6-dithia-6a-selenapentalenes (37a)-(37c)[35] which involves ring-opening of 4H-thiopyran-4-selenoketones (35a)-(35c) to give the di-anions (36a)-(36c) which are subsequently oxidised with potassium ferricyanide to give the dithiaselenapentalenes.

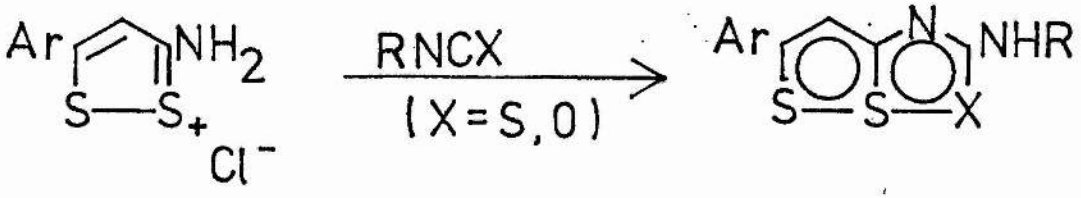
(c) Nitrogen analogues of 1,6,6a-trithiapentalenes

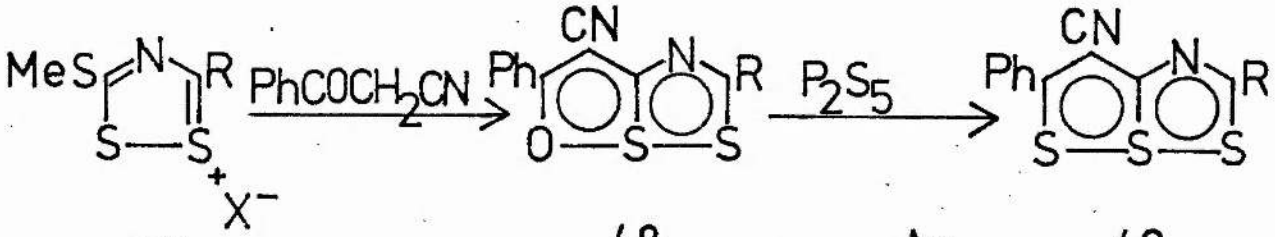
A number of compounds related to the 1,6,6a-trithiapentalene system in which up to four atoms have been replaced by nitrogen are known, and because this thesis is concerned mainly with nitrogen analogues, the synthesis of these compounds will be considered in detail.

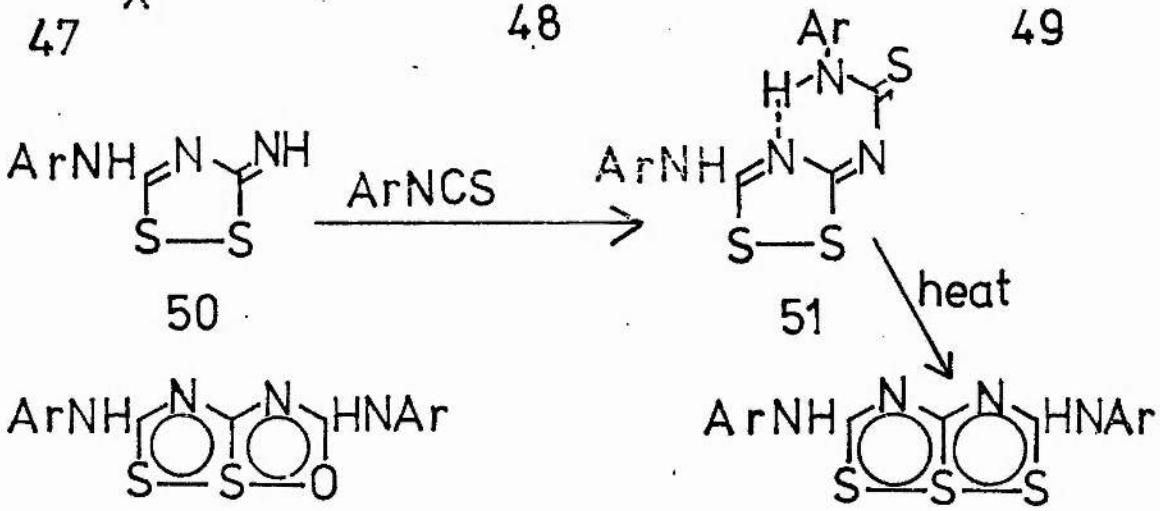
(i) Replacement of CH by nitrogen in the 3(4)-position

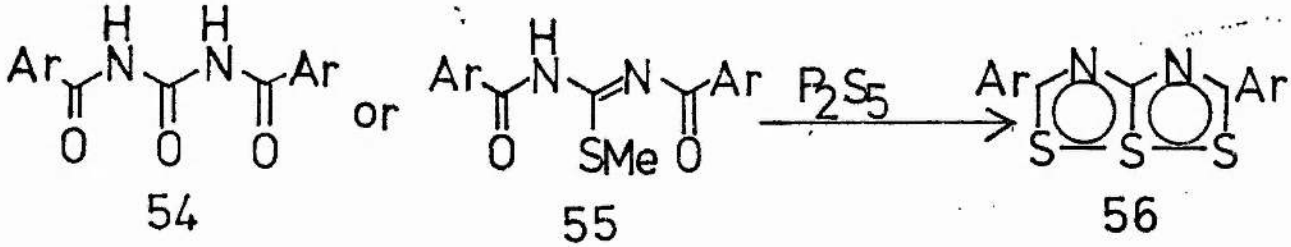
The 1-oxa-6,6a-dithia-3-azapentalene (40) has been obtained in two ways[36,37]: (i) by aroylation of the 3-amino-1,2-dithiolium salt (38) and (ii) by reaction of the 1,2-dithiole-3-thione (39) with an aroyl isothiocyanate. Treatment of compound (40) with phosphorus pentasulphide affords the 1,6,6a-trithia-3-azapentalene (41), and from this the oxygen compound can be regenerated by reaction with mercury(II) acetate. Lang and Vialle[36] have shown that the reaction of the 5-aryl-1,2,4-dithiazole-3-thione (42) with acetylenes gives two products, the thione (44) resulting from a 1,3-dipolar addition, and the trithiaazapentalene (41) which is obtained, it is suggested,


1,2-addn
1,3-addn
43
42
45
41
44


RNCX
(X=S,O)
38
46


PhCOCH2CN
P2S5
47
48
49


ArNCS
heat
50
51
53
52


or
P2S5
54
55
56

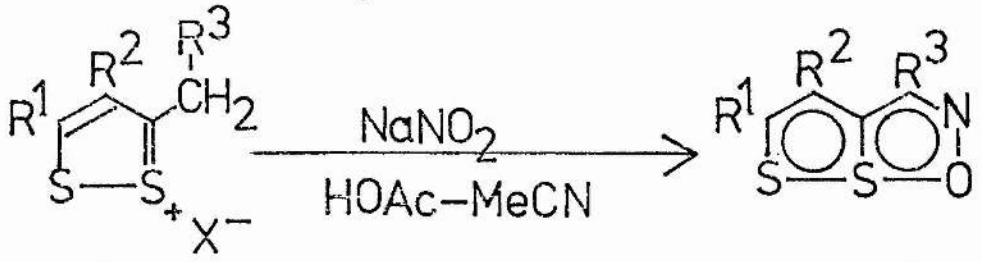
from a rearrangement of intermediate (43) formed by a 1,2-dipolar addition. Another synthesis of this type of compound involves the reaction of 3-amino-1,2-dithiolium salts (38) with aromatic and aliphatic isothiocyanates (X = S) or isocyanates (X = O). This produces the corresponding trithiaazapentalene or oxadithiaazapentalene (46) containing an arylamino or alkylamino group at the 2-position[38]. Treatment of the 3-methylthio-1,2,4-dithiazolium salt (47) with ω-cyanoacetophenone forms the 1-oxa-6,6a-dithia-4-azapentalene (48), from which the trithiaazapentalene (49) is obtained by reaction with phosphorus pentasulphide[38].

Arylisothiocyanates react with 5-imino-3-arylamino-1,2,4-dithiazoles (50) to give colourless products, formulated as the trans structures (51), stabilised by hydrogen bonding, which, on heating, isomerise to the 2,5-bis(arylamino)-1,6,6a-trithia-3,4-diazapentalenes (52)[39]. If an arylisocyanate is used, the corresponding oxygen compound (53) results. In a synthesis analogous to the synthesis of trithiapentalenes from triketones, N,N'-diaroylurea (54) reacts with phosphorus pentasulphide to give the trithiadiazapentalene (56), although in low yield[40,41]. Good yields are obtained, however, if the N,N'-diaroyl-S-methylisothioureas (55) are used.

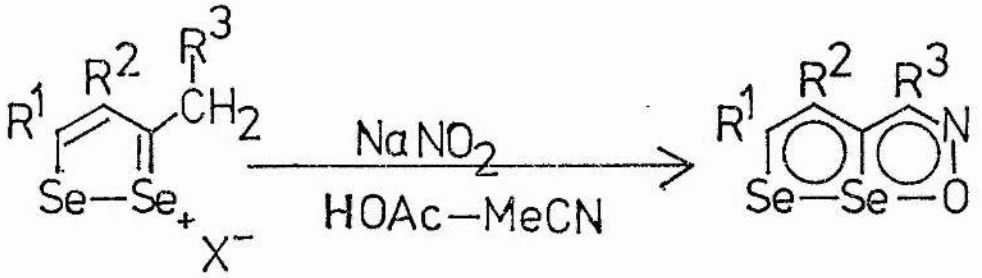
These systems are known only with aryl or arylamino substituents. The parent compounds are unknown.

(ii) Replacement of CH by nitrogen in the 2(5)-position

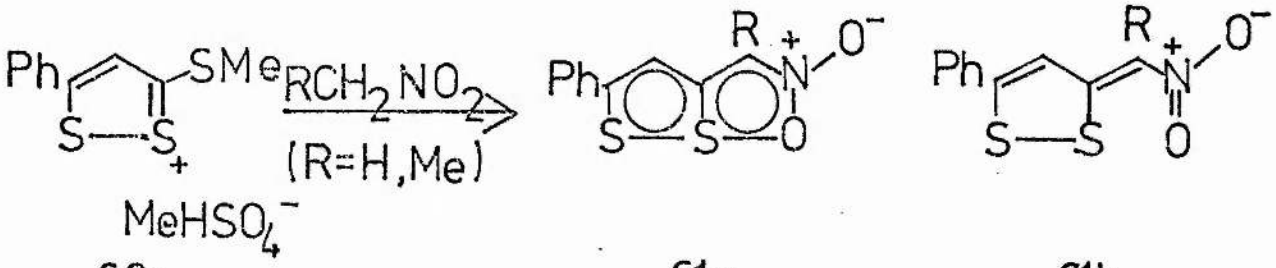
Treatment of 3-methyl(ene)-1,2-dithiolium salts (19) with sodium nitrite in acetic acid-acetonitrile gives the 1-oxa-6,6a-dithia-2-azapentalenes (57), and an extension of this procedure to the diselenolium salts (58) affords the analogous 1-oxa-6,6a-diselena-2-azapentalenes (59)[42]. Reaction of the dithiolium salt (60) with a nitroalkane leads to a compound which can be regarded as a 1-oxa-6,6a-dithia-2-azapentalene-2-oxide (61a) or as a 3-nitromethylene-3H-1,2-dithiole (61b)[43]. A large number of compounds based on systems (57) and (61) have been produced in nitrosations[44-46], and



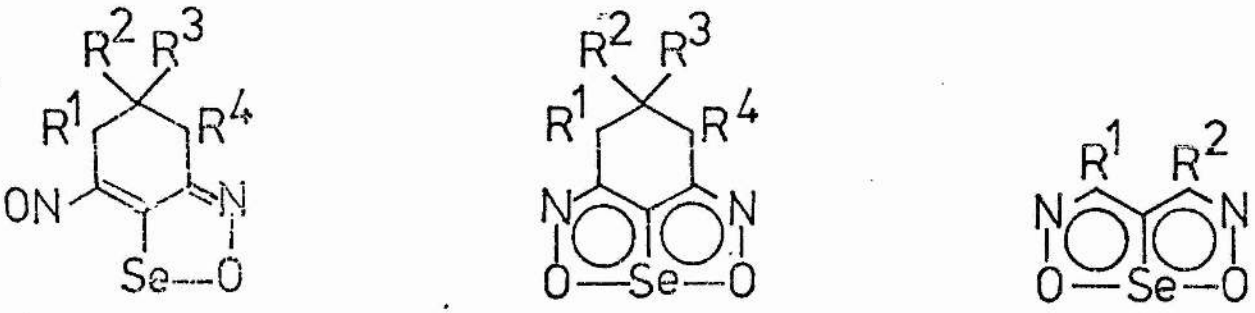
19 57



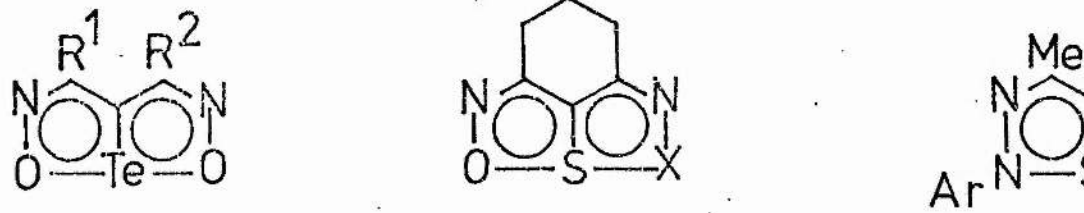
58 59



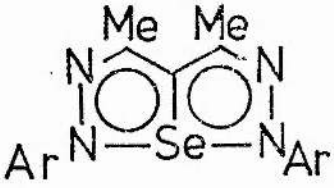
60 61a 61b



62 63 64



65 66 (X=O, S)



67

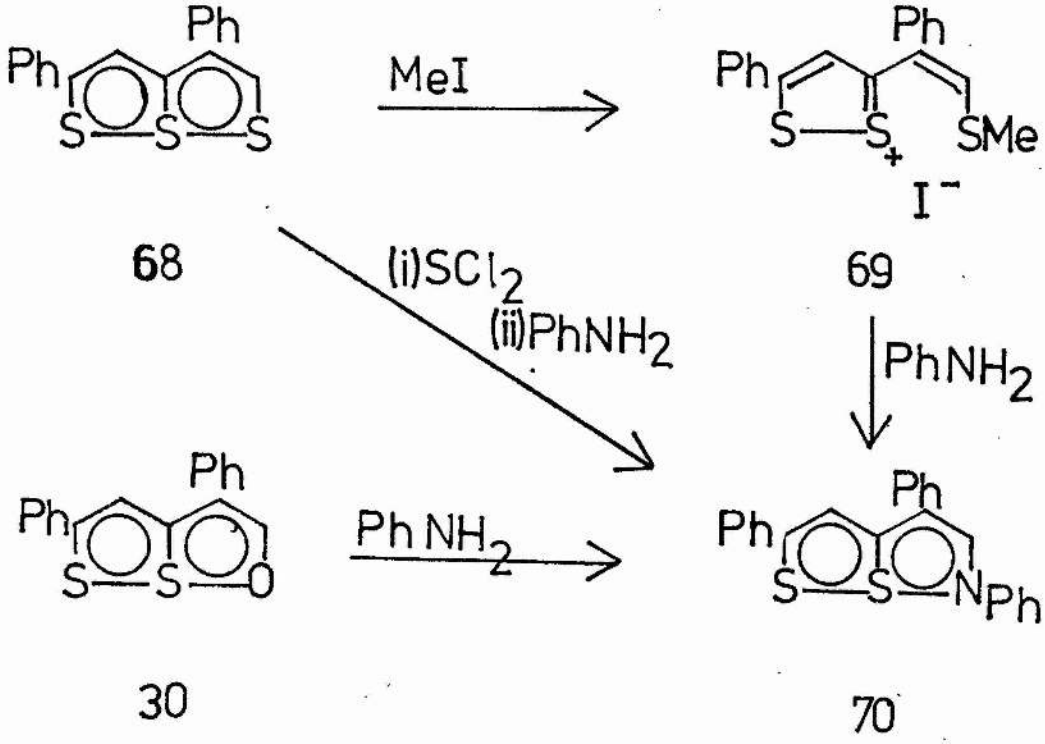
(Ar = 2,4-dinitrophenyl)

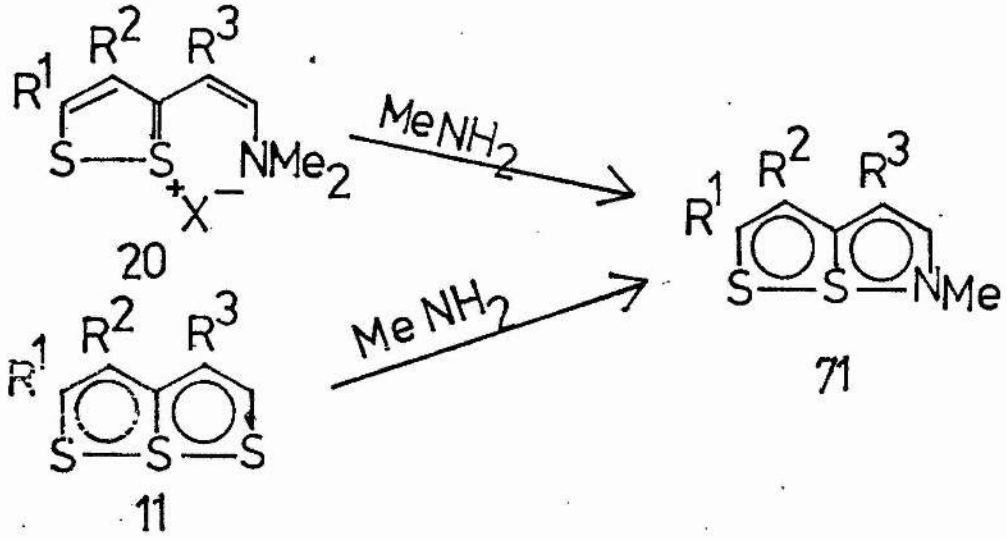
nitrations[42,44,45] of 1,6,6a-trithiapentalenes and related compounds and these will be discussed in a later section on electrophilic substitution reactions.

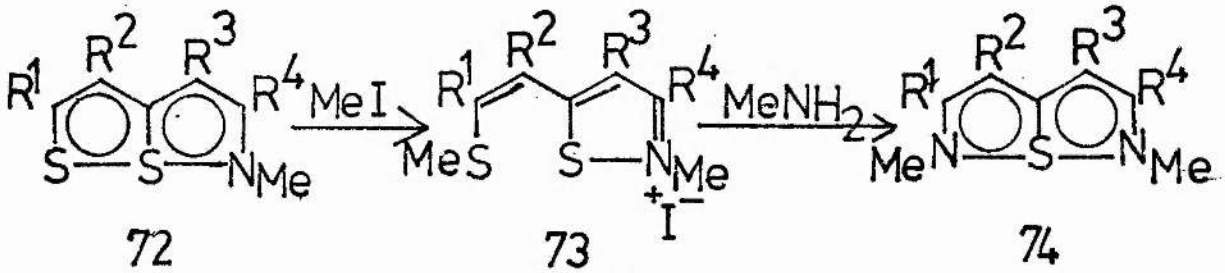
In 1949, King and Felton[47] isolated a series of red compounds from the reaction of dioximes of cyclohexane-1,3-diones with selenium dioxide for which they proposed structure (62). Vialle[48] repeated two of these reactions using symmetrical dioximes and demonstrated that the compounds were actually the bicyclic 1,6-dioxa-6a-selena-2,5-diazapentalenes (63), structures which King and Felton had discounted on the basis of strain considerations. A number of compounds of type (64) have now been made[48,49] including the parent compound (R^1=R^2=H). Vialle[49], in an extension of this procedure, has shown that tellurium dioxide reacts in the same way to give the 1,6-dioxa-6a-tellura-2,5-diazapentalenes (65), and Beer and Poole[50] have obtained an analogous sulphur compound (66, X=O) by treatment of the dioxime with sulphur dichloride. In the latter reaction the 1-oxa-6,6a-dithia-2,5-diazapentalene (66, X=S) was also isolated in small amount. Another variation of this type of synthesis[49] is the formation of the 6a-selena-1,2,5,6-tetraazapentalene (67) by the reaction of selenium dioxide with the bis(2,4-dinitrophenylhydrazone) of pentane-2;4-dione.

(iii) Replacement of the heteroatom by nitrogen in the 1(6)-position

Methylation of 2,4-diphenyl-1,6,6a-trithiapentalene (68) with methyl iodide[51] occurs at sulphur to give the salt (69) which reacts with aniline to form 2,4,6-triphenyl-1,6a-dithia-6-azapentalene (70). This compound is also obtained by reaction of aniline with the uncharacterised sulphur dichloride adduct of the trithiapentalene (68) or by treatment of the oxadithiapentalene (30) with aniline[51]. Ethylation of trithiapentalenes using triethyloxonium fluoroborate and reaction of the resulting salts with aniline leads to the same type of compound[52]. Reid and coworkers[53] have shown that



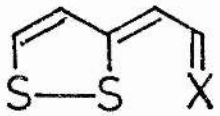




	R^1	R^2	R^3	R^4
(a)	H	H	H	H
(b)	H	Me	Me	H
(c)	H	$CH_2CH_2CH_2$		H
(d)	Me	H	H	Me

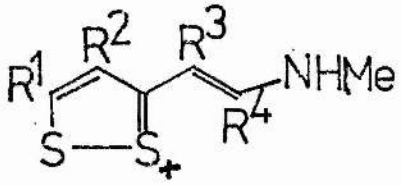
trithiapentalenes react with methylamine to give the dithiaaza-pentalenes (71). This synthesis provides a route to the simplest compound in this series (71, $R^1=R^2=R^3=H$) in good yield. 1,6a-Dithia-6-azapentalenes (71) have also been prepared by the reaction of the Vilsmeier salts (20) with methylamine[53,54]. Methylation of dithiaazapentalenes (72) yields the isothiazolium salts (73) which subsequently react with methylamine to give the 6a-thia-1,6-diazapentalenes (74)[55,56]. Four symmetrical derivatives of this system (74a)-(74d) have been prepared in this way.

75



76

(X= S, O, NR)



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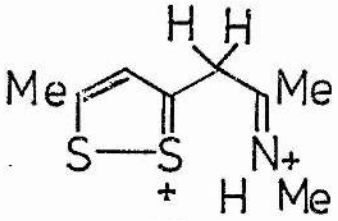

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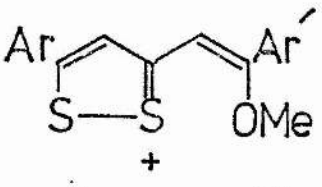

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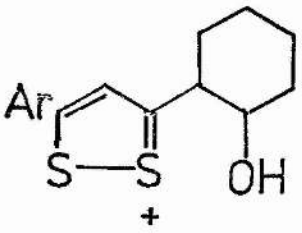

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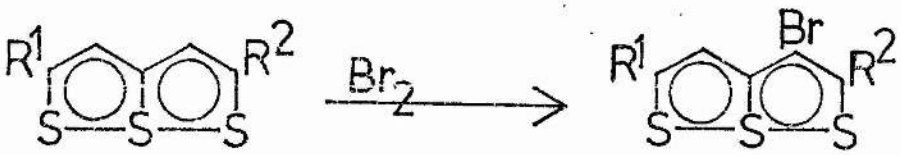
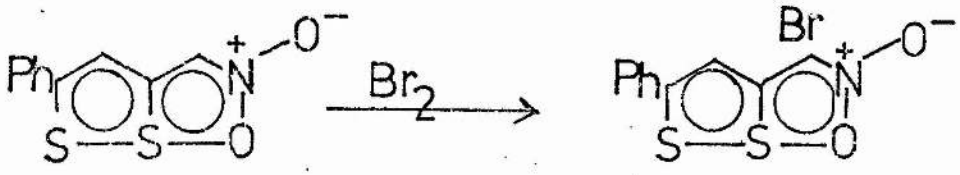


81 82

(a) R^1 = Ph, R^2 = Ph
(b) R^1 = Me, R^2 = Me
(c) R^1 = Ph, R^2 = Me
(d) R^1 = Ph, R^2 = SMe



83 84

C. Reactivity of 1,6,6a-trithiapentalenes and related compounds

(a) Carbonyl reactions

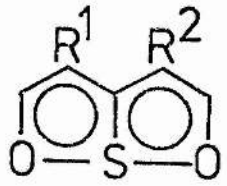
These compounds are formulated in this thesis as bicyclic structures (75) and not as monocyclic structures (76), since there is a degree of S--X interaction. These compounds can, however, undergo many of the usual carbonyl-type reactions. Oxadithiapentalenes, for example, form 2,4-dinitrophenylhydrazones[57,16], while trithiapentalenes are more inert[57] under the same conditions. This reflects the strong S--S interaction in the latter since thiocarbonyl compounds are normally observed to be more reactive than carbonyl compounds. The reactions involved in the interconversion of trithiapentalenes and oxadithiapentalenes [see B, (a), (i)] and the formation of dithiaazapentalenes from oxadithiapentalenes and trithiapentalenes [see B, (c), (iii)] are further examples of this carbonyl reactivity.

Trithiapentalenes may be methylated at sulphur [eg., compound (69)] using methyl iodide[51] or ethylated in the same way by triethyloxonium fluoroborate[52]. Methylation of dithiaazapentalenes by methyl iodide also occurs at sulphur to give the salts (73)[51,54-56]. In contrast, the nmr spectra of dithiaazapentalenes in trifluoroacetic acid show that protonation occurs mainly at nitrogen to give the species (77)[53], and in the case where $R^1=R^4=Me$, $R^2=R^3=H$, the C-protonated species (78) is also observed. Methylation of oxadithiapentalenes requires the more powerful methylating agent, methyl fluorosulphonate, and leads to the unstable salts (79)[58], while perchlorates (80) have been isolated from O-protonation of these systems[17,59].

(b) Substitution reactions

1,6,6a-Trithiapentalenes and related compounds undergo electrophilic substitution with a variety of reagents. Substitution occurs exclusively at the 3(4)-position in agreement with calculated

18a

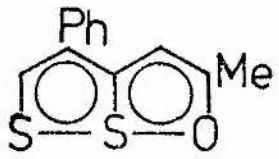


85

(a) R^I = Br, R^2 = Br

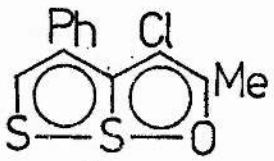
(b) R^I = I , R^2 = H

(c) R^I = I , R^2 = I



86

SCl_2



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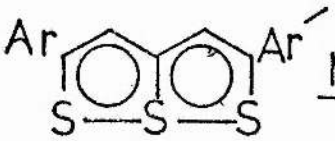
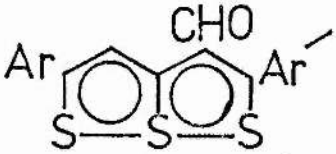


88

Me_2NCHO, $POCl_3$



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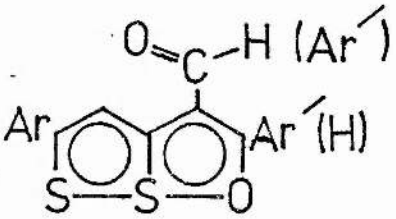
90

Me_2NCHO, $POCl_3$



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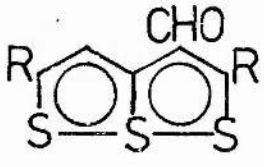
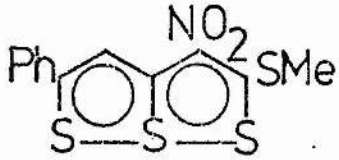
Me_2NCHS, $POCl_3$



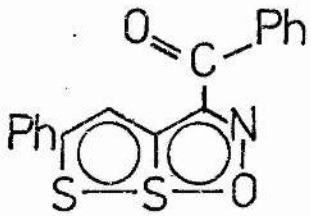
93

(a) R = H

(b) R = D



94



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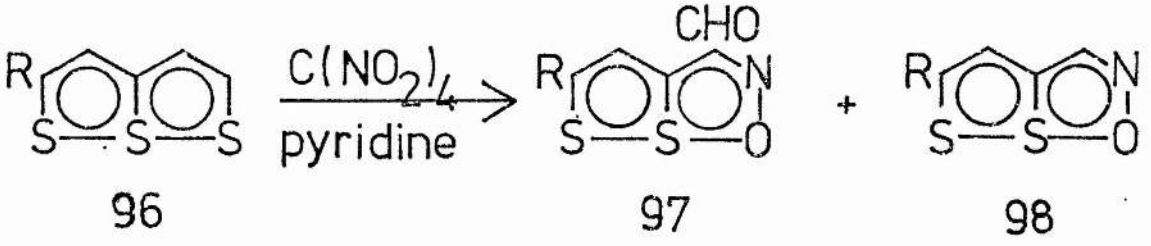
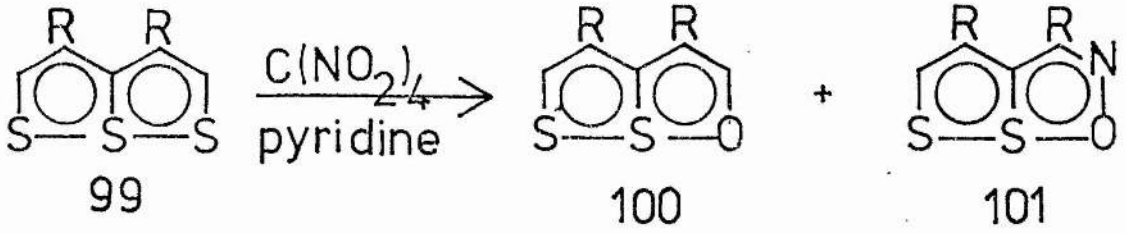
charge densities[60]. Bromination of the trithiapentalenes (81) proceeds smoothly, yielding the mono-bromo compounds (82)[44,45,61]. Similarly compound (83) gives the mono-substitution product (84)[43]. 1,6-Dioxa-6a-thiapentalene (18a) reacts with bromine to give the dibromo compound (85a) in high yield. Compound (18a) can be selectively mono-iodinated to afford compound (85b) or di-iodinated to give compound (85c), using iodine-silver acetate[21]. Reaction of the oxadithiapentalene (86) with sulphuryl chloride gave the chloro-compound (87), but an attempt to chlorinate the analogous trithia-pentalene in the same way was unsuccessful[24].

Vilsmeier-Haack formylation of 2,5-diaryl-1,6,6a-trithia-pentalenes (88) is achieved using dimethylformamide and phosphoryl chloride to give the 3-formyl compounds (89)[62,63,64], or using heptadeuteriodimethylformamide to give the corresponding deuterio-formyl compounds[64,65]. Formylation of the 2,5-diaryl-1-oxa-6,6a-dithiapentalene (90) affords a product, shown by nmr to be a mixture of oxadithiapentalenes (91)[66,67]. Reid and coworkers[68] have obtained 3-formyl-1,6,6a-trithiapentalene (93a) by treatment of the unsubstituted compound (92a) with dimethylthioformamide and phosphoryl chloride. In the same way, the 2,5-dideuterio compound (92b) gave the corresponding aldehyde (93b) in which both deuterium atoms were retained, proving unambiguously that formylation had occurred at the 3-position. 2-t-Butyl[68] and 2-phenyl-1,6,6a-trithiapentalene[23] are formylated at the 4-position.

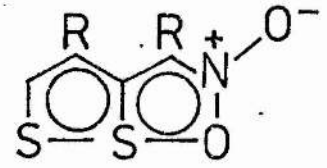
Nitration of the trithiapentalene (81d) with nitric acid gives the nitro compound (94)[44,45]. The 2,5-diphenyl compound (81a), however, leads to the nitrosation product (95), a derivative of the 1-oxa-6,6a-dithia-2-azapentalene system, when either nitric acid or copper(II) nitrate is used[44,45]. Similar results were obtained from attempted nitrations with tetranitromethane-pyridine[42]. The trithiapentalenes (96) gave two products: compound (97), the major product, resulting from nitrosation, and compound (98), the minor



96 97 98



99 100 101



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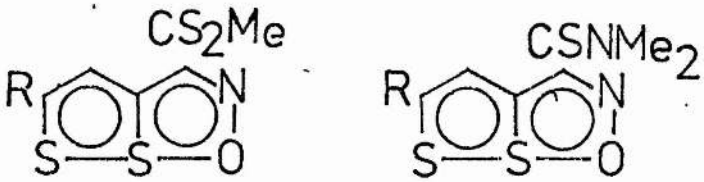

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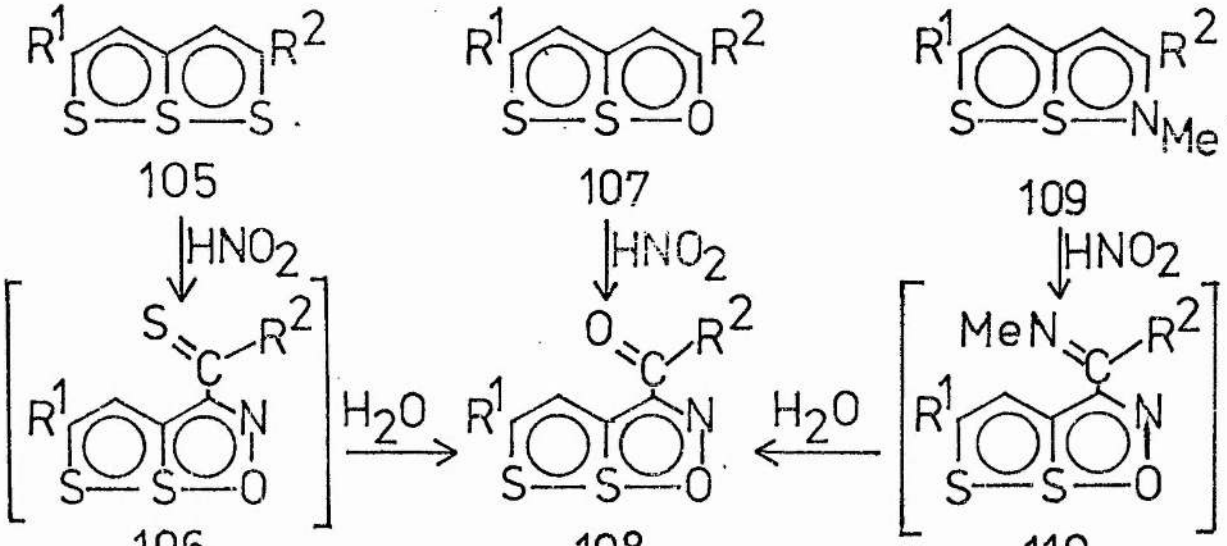
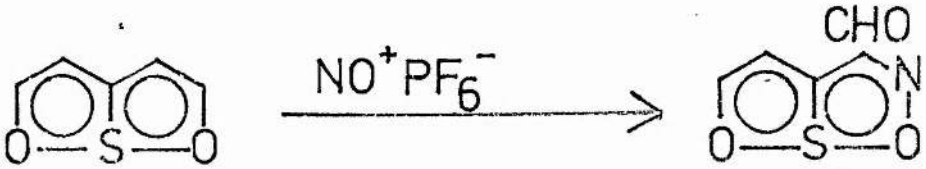


105 107 109

106 108 110

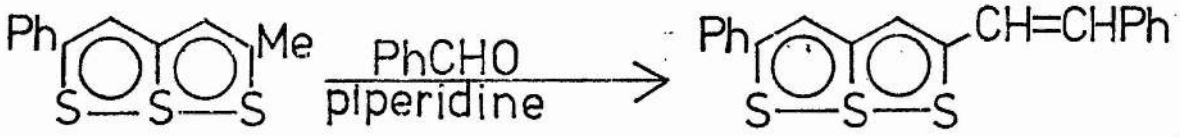


18a 111

product, presumably formed by deformylation of compound (97). Treatment of 3,4-disubstituted trithiapentalenes (99) with tetranitromethane-pyridine gave three compounds, namely, the oxadithiapentalene (100), a nitrosation product (101) and a nitration product (102). Reaction at the unsubstituted 2(5)-position was not observed.

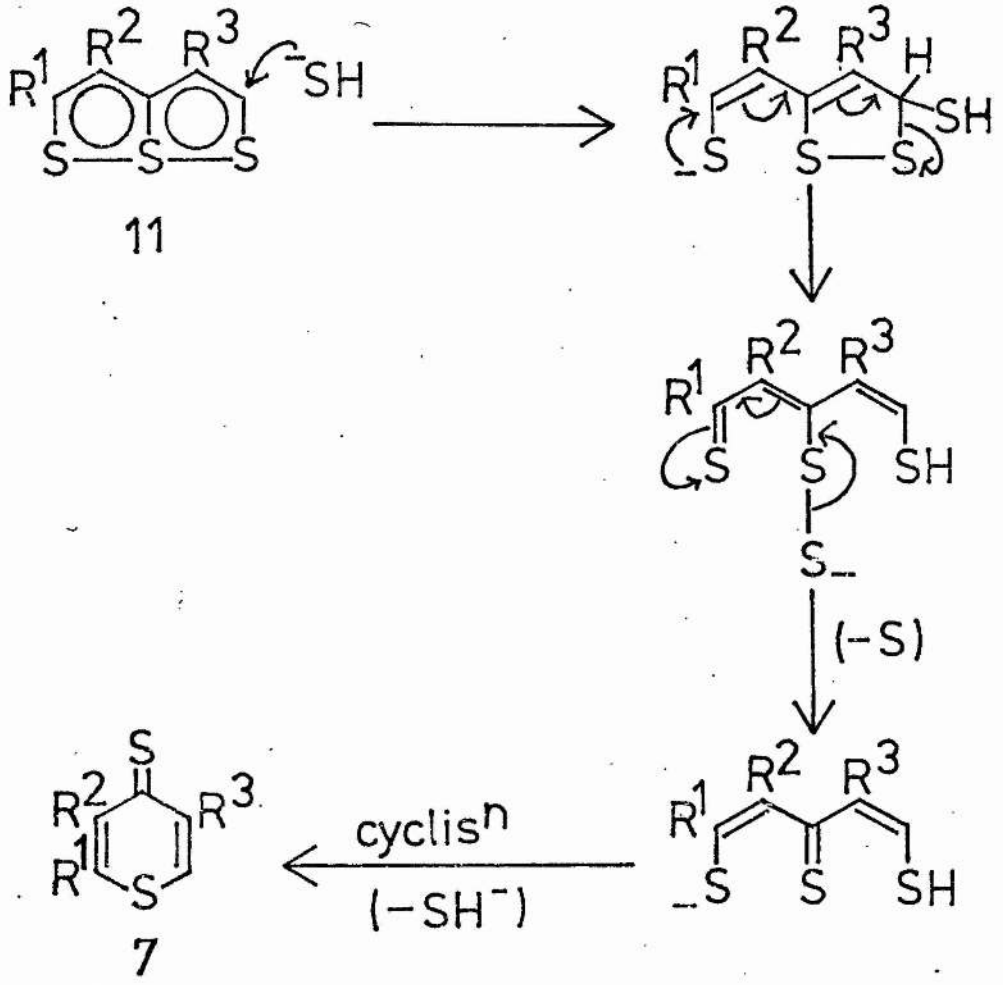
Nitrosation of 2,5-diphenyl-1,6,6a-trithiapentalene with nitrous acid affords compound (95)[44,45], the same product as is obtained from the reaction with nitric acid. Treatment of 2-t-butyl-1,6,6a-trithiapentalene with nitrous acid gives an analogous product (108, R^1=Bu^t, R^2=H)[46]. These two products are thought to arise from hydrolysis of the intermediate thiocarbonyl compound (106). Trithiapentalenes containing a methylthio or dimethylamino group in the 2-position are nitrosated to form compounds (103) or (104) respectively, in which sulphur is retained, because the thiocarbonyl group is stabilised to hydrolysis as the dithioester (103) or thioamide (104)[44,45,46]. Compounds (108) also result from nitrosation of the dithiaazapentalenes (109), presumably via hydrolysis of the intermediate imine (110)[46], and from nitrosation of the oxadithiapentalenes (107)[44,45,46]. The 3,4-disubstituted oxadithiapentalenes (100) give the oxadithiaazapentalenes (101) by nitrosodeformylation, together with small quantities of the corresponding N-oxides (102)[46]. 1,6-Dioxa-6a-thiapentalene (18a) is destroyed by nitrous acid, but treatment with nitrosyl hexafluorophosphate gives the aldehyde (111), the first reported derivative of the 1,6-dioxa-6a-thia-2-azapentalene system[46]. As can be seen from the foregoing examples, nitrosation is accompanied by rearrangement. The reaction of trithiapentalenes and related compounds with arenediazonium salts involves an analogous rearrangement[69], and this, together with a mechanism[46] accounting for the various features of the electrophilic substitution of these systems, will be discussed in detail in Part 2.

A few examples of nucleophilic substitution at the 2(5)-position of trithiapentalenes are known. Methylthio substituents in the



81c 112

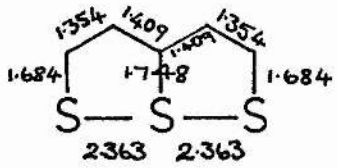
Scheme I



2(5)-position may be replaced by ethoxy groups[28,44] on reaction with sodium ethoxide or by alkylamino groups[44,45] on reaction with amines.

(c) Other reactions

A methyl(ene) group in the 2(5)-position of the trithiapentalene system is relatively acidic. An example of this is the condensation of benzaldehyde with 2-methyl-5-phenyl-1,6,6a-trithiapentalene (81c) in the presence of a weak base such as piperidine to form the styryl-trithiapentalene (112)[70]. Trithiapentalenes containing a free 2(5)-position are converted into 4H-thiopyran-4-thiones (7) by treatment with hydrosulphide or sulphide anion[71]. The proposed mechanism is illustrated in Scheme 1.



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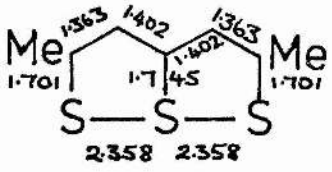
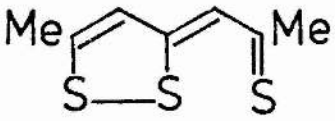
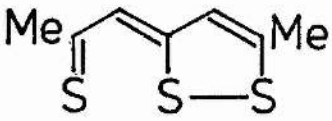


II



IIa



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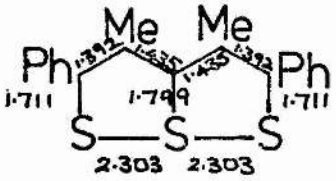
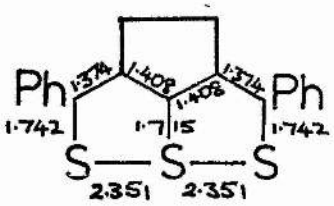


III



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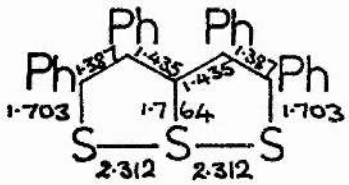


V

Bond lengths in Å

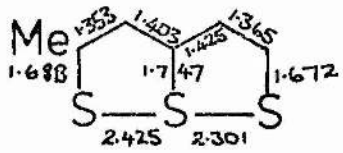
D. Structural Studies of 1,6,6a-trithiapentalenes and related compounds

1,6,6a-Trithiapentalenes and related compounds have been studied extensively by the techniques used in organic structure determination. X-ray crystallography and a variety of spectroscopic techniques have played an important role in these structural studies, and the results have contributed much to an understanding of the unusual structural features of these systems.

1. X-ray crystallography

(a) 1,6,6a-trithiapentalenes

The crystal structure data for 1,6,6a-trithiapentalene (I)[72] shows that the molecule is planar, symmetrical about the central carbon-sulphur bond, and that the three sulphur atoms are collinear. The sulphur-sulphur bond distance (2.363 Å) is longer than that found for a cis-planar disulphide group (2.10 Å)[73], but is considerably shorter than the sum of the van der Waal's radii (3.70 Å)[74]. This indicates the presence of a significant interaction between the central and the lateral sulphur atoms which does not, however, amount to a full single bond. The lateral carbon-sulphur distance (1.684 Å) is intermediate between that of a carbon-sulphur single bond (1.81 Å) and that of a carbon-sulphur double bond (1.61 Å)[74], while the central carbon-sulphur bond (1.748 Å) is slightly shorter than a carbon-sulphur single bond (1.81 Å). The lengths of the carbon(2)-carbon(3) bond (1.354 Å) and the carbon(3)-carbon(3a) bond (1.409 Å) are very similar to the lengths of the carbon(1)-carbon(2) bond (1.358 Å) and the carbon(1)-carbon(8a) bond (1.421 Å)[75] respectively in naphthalene, which possesses an analogous 10π electron system. 2,5-Dimethyl-1,6,6a-trithiapentalene(II) has similar molecular dimensions to the parent compound, and is also symmetrical. Following earlier studies by Bezzi and co-workers[4,5,76], Nyburg[77], in a reinvestigation, found that there was no evidence for a



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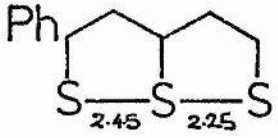
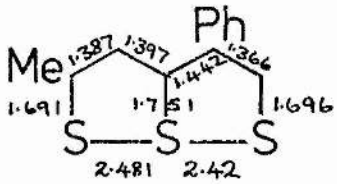


VII



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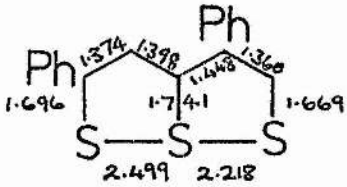

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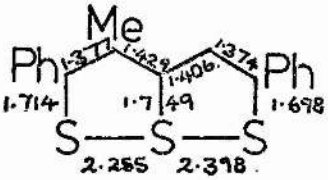

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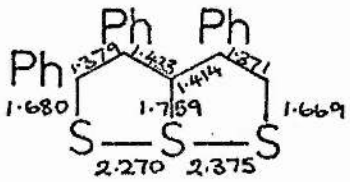
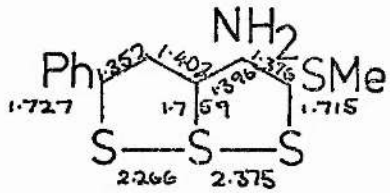


XI



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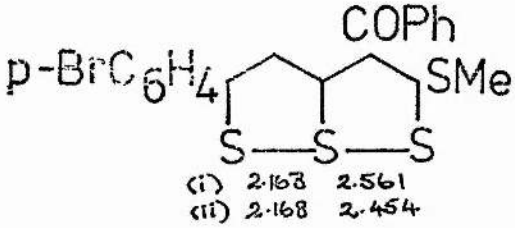

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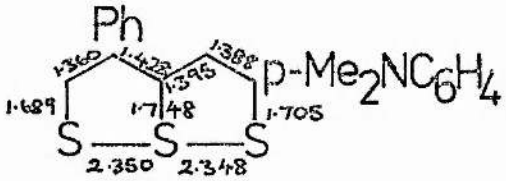

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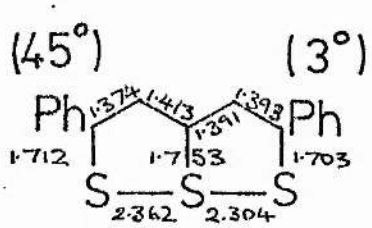

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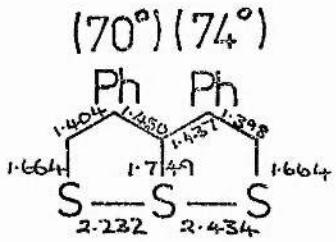
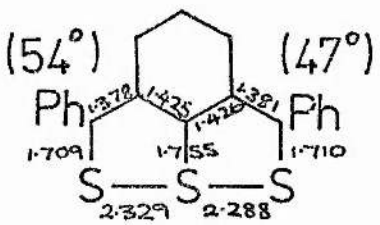


XVI



XVII

Bond lengths in Å

statistically disordered combination of species (IIa) and (IIb), as had been suggested by Johnson et al[78], or that if this disordering existed, the difference in the two molecular geometries was too small to be detectable by X-ray structure analysis. Compounds (III)[79], (IV)[80] and (V)[81] also possess C_{2v} symmetry about the central carbon-sulphur bond.

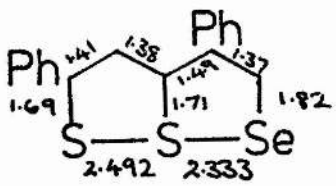
The individual sulphur-sulphur interactions in trithiapentalenes, which have a bond order of less than unity, are extremely sensitive to changes in both intramolecular and intermolecular environment. The unsymmetrically substituted compounds (VI)[82], (VII)[83,84], (VIII)[85], (IX)[86], (X)[87], (XI)[88] and (XII)[89] show unequal sulphur-sulphur distances. The specific effect of phenyl and methyl substitution in these systems has been the subject of CNDO/2 calculations[90], the results of which may be summarised as follows:

(i) a 2-methyl group lengthens the S(1)-S(6a) bond, and a 3-methyl group shortens it.

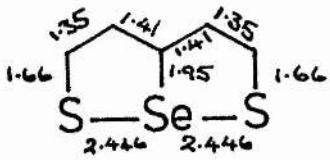
(ii) a 2-phenyl group lengthens the S(1)-S(6a) bond, the effect being negligible at a twist angle of 0^{o} and increasing to a maximum at 90^{o}. A 3-phenyl group shortens the S(1)-S(6a) bond, but the effect is small and independent of the twist angle of the phenyl group.

So far, the observed effects in molecules in which there are no intramolecular strain factors are consistent with the calculations. In the crystal unit of compound (XIII)[78,91], there are two crystallographically independent molecules with quite different dimensions, while the unsymmetrically substituted trithiapentalene (XIV)[92] is found to have equal sulphur-sulphur distances.

The symmetrically substituted compounds (XV)[93], (XVI)[94] and (XVII)[95] have unequal sulphur-sulphur distances. In 3,4-diphenyl-1,6,6a-trithiapentalene (XVI), this deviation from C_{2v} symmetry may be due to steric clashing of the phenyl groups. In the 2,5-diphenyl isomer (XV), the phenyl groups are twisted 45^{o} and 3^{o} about the respective connecting bonds, presumably due to intermolecular



XVIII



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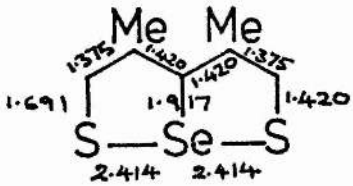

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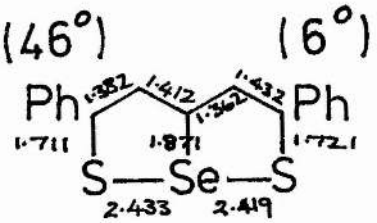
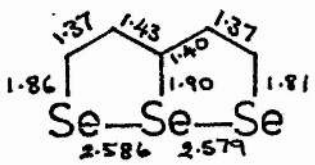
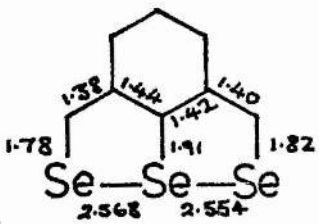


XXI



XXII



XXIII

Table 1

	$Se_I—Se_2$ Å	$Se_I—Se_2$ Å
$K(SeCN)_3 \cdot \frac{1}{2}H_2O$	2.69	2.65
$Rb(SeCN)_3 \cdot \frac{1}{2}H_2O$	2.66	2.66
$Cs(SeCN)_3$	2.65	2.65
$[SeC(NH_2)]_3Cl_2 \cdot H_2O$	2.60	2.72
$[SeC(NH_2)]_3Br_2 \cdot H_2O$	2.62	2.71

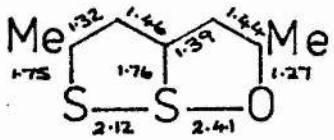
interactions, and it is suggested that an isolated molecule would be symmetrical. Both intermolecular and intramolecular interactions may be operating in compound (XVII).

It is noteworthy that although individual sulphur-sulphur distances may vary by as much as 0.4 Å, the total distance between the lateral sulphur atoms remains fairly constant at about 4.7 Å, unless there is a steric clash of groups in the 3- and 4-positions, when a lower value is observed.

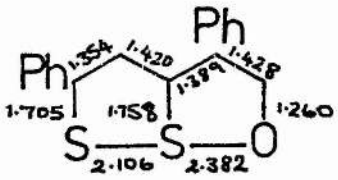
(b) Selenium analogues

Comparison of the dimensions of the dithiaselenapentalene (XVIII)[96] with those of the corresponding trithiapentalene (IX)[86] shows the structural similarity of the two molecules. The sulphur-sulphur bond length (2.492 Å) of the selenium compound is almost identical to that (2.499 Å) in the trithiapentalene. Furthermore, if the difference in the covalent radii of selenium and sulphur is subtracted from the sulphur-selenium distance (2.333 Å) in compound (XVIII), the resulting value (2.21 Å) is just 0.01 Å different from the observed sulphur(6)-sulphur(6a) distance in compound (IX). Structure determinations of three 1,6-dithia-6a-selenapentalenes (XIX)[97], (XX)[98] and (XXI)[99] and of two 1,6,6a-triselenapentalenes (XXII)[100] and (XXIII)[101] have been reported. The selenium-sulphur bonds in compound (XIX) (2.446 Å) are 10.1% longer than the sum of the covalent radii of selenium and sulphur (2.21 Å), the average selenium-selenium bond length in compound (XXII) (2.583 Å) is 10.7% longer than the standard selenium-selenium single bond length (2.34 Å)[74] and the sulphur-sulphur bonds in compound (I) are 12.4% longer than the standard sulphur-sulphur single bond length (2.10 Å)[73]. These data suggest that selenium can replace sulphur in these systems without significantly affecting the nature of the bonding.

Structure investigations of triselenocyanate[102,103] and triselenourea[104] ions have been carried out and the results are given



XXIV



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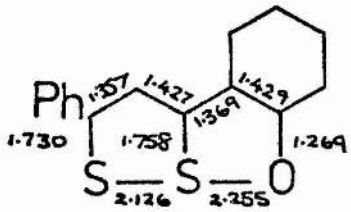

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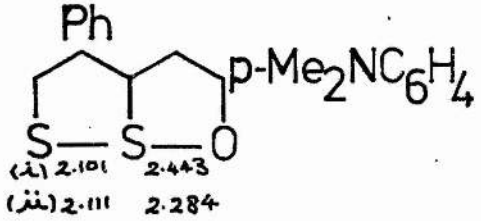
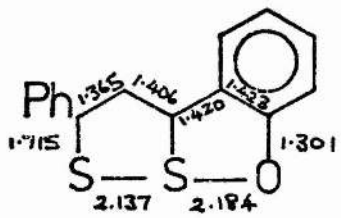


XXVII



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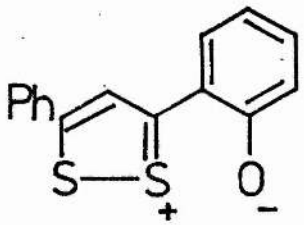

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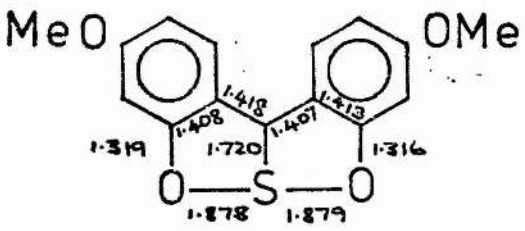
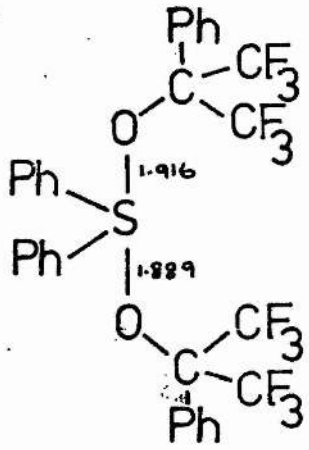


XXIX



XXX

Bond lengths in Å

in table 1. These compounds are comparable with triselena-pentalenes in possessing a linear three-selenium sequence, with a selenium-selenium bond order of less than unity. Trithiocyanates are not known in crystalline form.

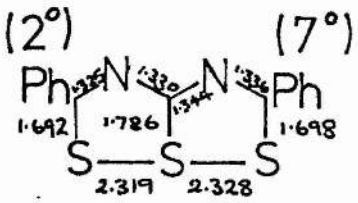
(c) Oxygen analogues

The structures of the 1-oxa-6,6a-dithiapentalenes (XXIV)[105], (XXV)[106], (XXVI)[107] and (XXVII)[108] are almost planar and the S--S--O sequence is almost linear. Replacement of sulphur by oxygen causes a shortening of the sulphur-sulphur bond. In compound (XXV), for example, the sulphur-sulphur bond length (2.106 Å) is close to the sulphur-sulphur bond length of a cis-planar disulphide group (2.10 Å)[73], but, since there is a degree of π-bonding in these systems, this may still be considered as a long bond. The sulphur-oxygen bond length in compound (XXV) (2.382 Å) is considerably longer than the sum of the covalent radii (1.70 Å)[74], but is shorter than the sum of the van der Waal's radii (3.25 Å), so that a weak interaction is seen to exist. This interaction, however, is stronger in compound (XXVIII)[109], as the sulphur-oxygen distance (2.184 Å) and the sulphur-sulphur distance (2.137 Å) demonstrate. It is suggested that this effect is due to a contribution from the dipolar species (XXVIIIa).

In the almost symmetrical planar 1,6-dioxa-6a-thiapentalene (XXIX)[110], the sulphur-oxygen distance (1.88 Å) indicates the presence of a strong interaction. A similar linear O--S--O arrangement with long sulphur-oxygen bonds is present in the sulphurane (XXX)[111].

(d) Nitrogen analogues

The crystal structures of the 1,6,6a-trithia-3,4-diazapentalenes (XXXI)[112] and (XXXII)[113] have been reported. In the 2,5-diphenyl compound (XXXI), the phenyl groups are twisted 2° and 7° respectively



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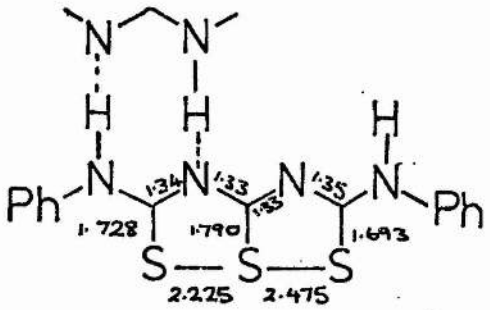

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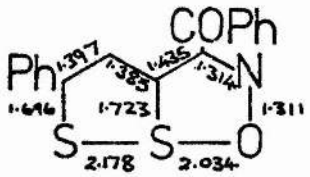

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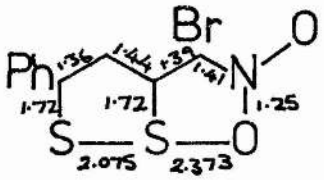

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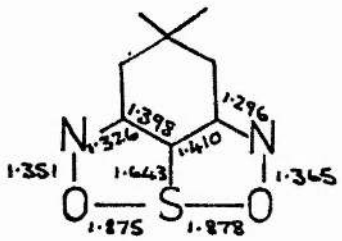

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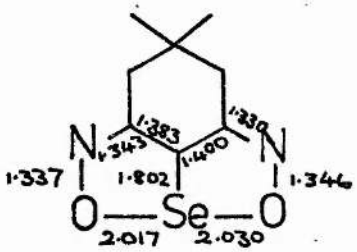

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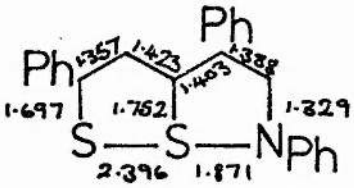

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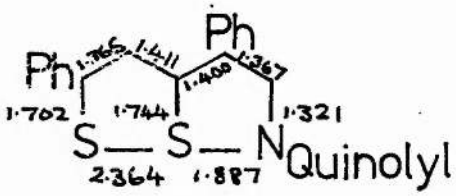
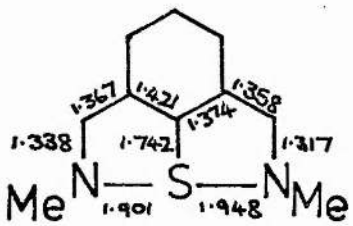


XXXVIII



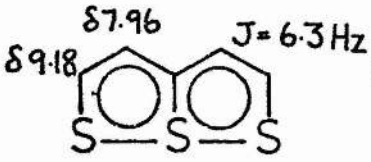
XXXIX

Bond lengths in Å

and the sulphur-sulphur bond lengths (2.319 Å and 2.328 Å) are almost equal and are of the same order as the corresponding distances in trithiapentalenes. The carbon-nitrogen bond lengths (1.325 Å, 1.330 Å, 1.344 Å and 1.336 Å) are close to the carbon-nitrogen bond length in pyridine (1.340 Å)[114]. The 2,5-dianilino compound (XXXII) has very different sulphur-sulphur bond lengths (2.225 Å and 2.475 Å), due, it is suggested, to intermolecular hydrogen bonding.

The 1-oxa-6,6a-dithia-2-azapentalene (XXXIII)[115] has a sulphur-oxygen bond length (2.034 Å) which is considerably shorter than in 1-oxa-6,6a-dithiapentalenes, eg., 2.382 Å in compound (XXV), and a correspondingly longer sulphur-sulphur bond length [2.178 Å, cf. 2.106 Å in (XXV)]. This indicates a relatively strong interaction in this system. In contrast, compound (XXXIV)[116] has sulphur-sulphur and sulphur-oxygen distances (2.075 Å and 2.373 Å respectively) which are comparable to those in compound (XXV) (2.106 Å and 2.382 Å respectively), and thus possesses a weak sulphur-oxygen interaction similar to that in 1-oxa-6,6a-dithiapentalenes. The structures of compounds (XXXV)[117] and (XXXVI)[118] are very similar. Both molecules are almost symmetrical and there is a lengthening of the sulphur-oxygen and selenium-oxygen bonds of about 10% relative to the respective sums of the covalent radii.

Replacement of one sulphur atom in a trithiapentalene by nitrogen to give the 1,6a-dithia-6-azapentalenes (XXVII)[119] and (XXXVIII)[120] shortens the sulphur-sulphur bonds [2.396 Å and 2.364 Å, cf. 2.499 Å in (IX)], although the effect is much less than that caused by replacement by oxygen. The molecules are again planar and the S---S---N sequence is almost collinear. The sulphur-nitrogen distances (1.871 Å and 1.887 Å) are nearer to the sum of the covalent radii (1.74 Å)[74] than to the sum of the van der Waal's radii (3.35 Å)[74]. Structurally, these nitrogen compounds bear more resemblance to the trithiapentalenes than the corresponding oxygen compounds. The 6a-thia-1,6-diazapentalene (XXXIX)[121] is



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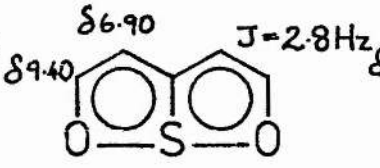
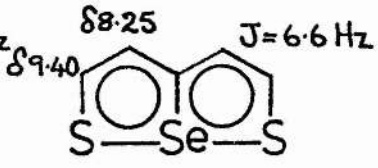


18a



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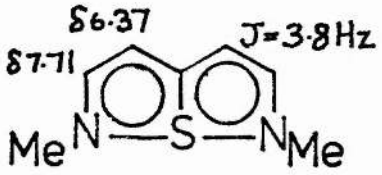

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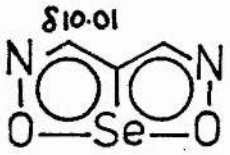

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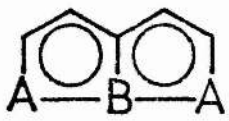

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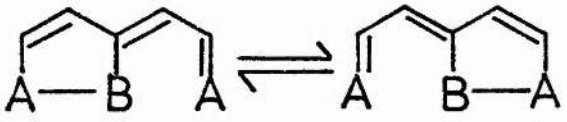
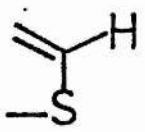


116a 116b



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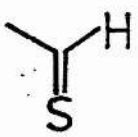

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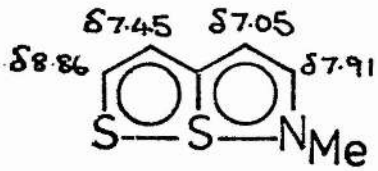

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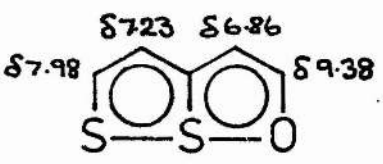

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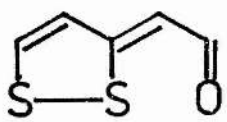


12a

planar and unsymmetrical, due possibly to strain imposed by the trimethylene bridge. The average nitrogen-sulphur bond length (1.924 Å) represents a 10% lengthening relative to the sum of the covalent radii (1.74 Å), an effect common to trithiapentalenes and to a number of related compounds.

2. Vapour Phase Electron Diffraction

A 1,6,6a-trithiapentalene in the gaseous state will be free from constraints which may operate on the system in the solid state due to intermolecular forces. A recent electron diffraction study of the vapour of the parent compound is therefore of interest[122]. Good agreement was obtained between theoretical and experimental radial distribution curves using models with C_{2v} symmetry, while unsymmetrical models (C_s symmetry) gave poor agreement with experiment. Another noteworthy result is that the amplitude of vibration measured for individual sulphur-sulphur bonds is considerably larger than that for the total sulphur-sulphur distance.

3. Nuclear Magnetic Resonance Spectroscopy

The nmr spectra of symmetrically substituted 1,6,6a-trithiapentalenes show in all cases the magnetic equivalence of ring protons or substituents at the pairs of sites C(2), C(5), and C(3), C(4), demonstrating that the molecules possess real or time-averaged C_{2v} symmetry in solution. 2,5-Diphenyl-1,6,6a-trithiapentalene[123] and 3,4-diphenyl-1,6,6a-trithiapentalene[124], for example, show this C_{2v} symmetry in solution, although they have unequal sulphur-sulphur bond lengths in the solid state. This magnetic equivalence is also observed in related systems, as illustrated for the simplest of these, compounds (13)[22], (18a)[21], (113)[35], (114)[56] and (115)[48]. Although the possibility of a rapid interconversion of two valence isomers (116a $\rightleftharpoons$ 116b)

cannot be excluded, the nmr spectra of a number of these systems have not been found to change on cooling to ~60°C[21,52,56,48], and it seems more and more accepted that this is a case of real equivalence corresponding to a symmetrical bonding pattern.

The chemical shift of the thioformyl proton in heterocyclic thioaldehydes does not fall below δ10.2, even when the thioformyl group is highly polarised[22]. The chemical shift of a proton in the 2(5) position of a trithiapentalene is normally in the range δ8.6-9.3 which is consistent with the environment (117a) as opposed to (117b). The ring proton chemical shifts of 1,6,6a-trithiapentalene (13)[22], 6-methyl-1,6a-dithia-6-azapentalene (118)[53], and 1-oxa-6,6a-dithiapentalene (12)[20] are respectively, 2-H[≡5-H in (12)] δ9.18, 8.86 and 7.98; 3-H[≡4-H in (12)] δ7.96, 7.45 and 7.23; 4-H[≡3-H in (12)] δ7.96, 7.05 and 6.86. There is a progressive increase in deshielding of ring protons in the series oxadithiapentalene ⟶ dithiaazapentalene ⟶ trithiapentalene, attributable to a corresponding increase in the size of the ring current, due in turn to a corresponding increase in the degree of π-delocalisation.

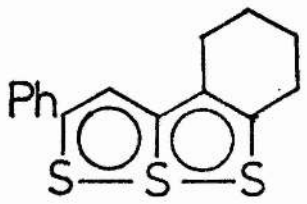
4. Photo-electron spectroscopy

Since the measurements are very rapid compared with molecular vibrations, X-ray photoelectron spectroscopy provides in principle a means of distinguishing between a symmetrical structure and a pair of rapidly interconverting valence tautomers for 1,6,6a-trithiapentalene. The technique has been applied to 2,5-dimethyl-1,6,6a-trithiapentalene by two groups of workers whose interpretation of the results differ. Clark and coworkers[125,126] interpret their spectrum in terms of sulphur core levels split in a 2:1 ratio, and suggest therefore a symmetrical structure. On the other hand, Lindberg et al[127-129] claim a better fit to the overall envelope with three different sulphurs in a 1:1:1 ratio and thus suggest an unsymmetrical structure due to valence tautomers. Both authors admit, however,

that their results are not unambiguous, and the differences in the two investigations may be attributable to differences in lattice environment. Clark's results[125] appear to show the symmetry of 1,6,6a-trithiapentalene and the asymmetry of 3,4-diphenyl-1,6,6a-trithiapentalene and 2-methyl-1,6,6a-trithiapentalene in agreement with crystal structure data. Lindberg[127] has applied the technique to 1-oxa-6,6a-dithiapentalenes and his results show the similarity of the electronic structure of these systems to trithiapentalenes, and indicate a polarised carbonyl bond with a partial negative charge on oxygen. The photoelectron spectra (He 584 Å) of a number of trithiapentalenes have been recorded, but no definite conclusion about the symmetry of the system resulted from these studies[127].

5. Miscellaneous Spectroscopic Techniques

Infrared spectroscopy has been usefully applied to the elucidation of the structure of 1-oxa-6,6a-dithiapentalenes[6]. The prominent feature in the infrared spectra of these systems is the absence of the usual carbonyl frequencies (1620-1720 cm^{-1}) and the presence of one or more strong bands in the range 1500-1610 cm^{-1} [130], which have been identified as C-O absorptions using O^{18} isotopic substitution[131]. These observations are inconsistent with a monocyclic structure (12a) and suggest a sulphur-oxygen interaction. Electronic spectra of trithiapentalenes are characterised by strong absorption bands near 500 nm in the visible and near 260 nm in the ultraviolet. Electronic spectra of related systems containing oxygen[37], selenium[22] and nitrogen[39,51] have been studied and have often been used as proof of the similarity of these compounds. The electronic polarisation spectrum of 2,5-dimethyl-1,6,6a-trithiapentalene has been measured by the stretched film technique[132], and has been found to give best agreement with calculations based on



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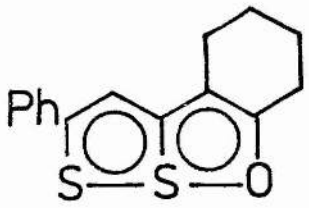

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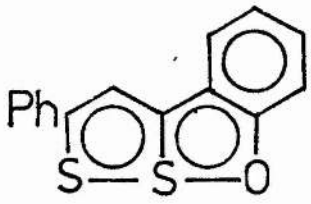

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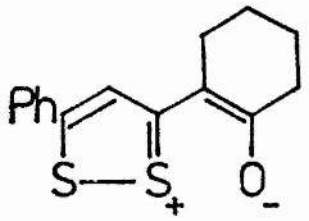

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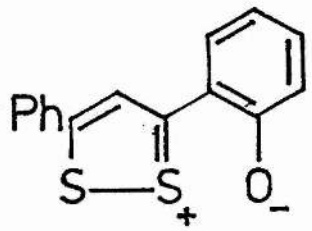

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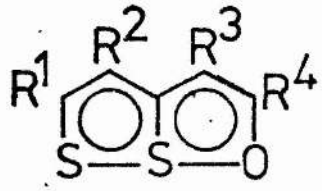

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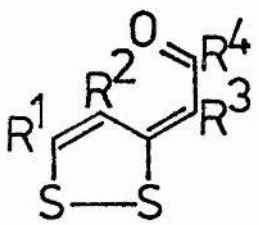
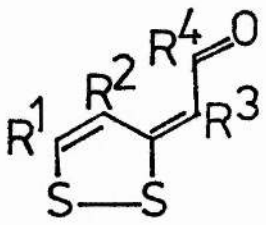
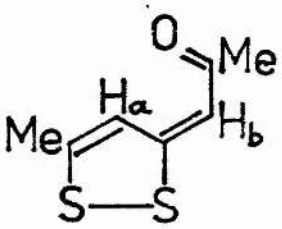


122a

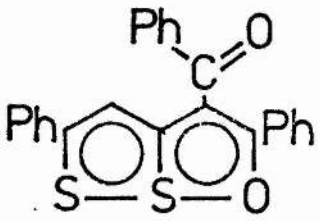


122b

123



123a



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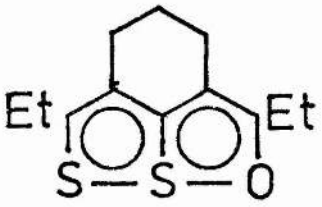


125

an unsymmetrical ground state. The ESR data for radical anions of several symmetrical trithiapentalenes[133,134] show that these retain the C_{2v} symmetry of the precursors even when the samples are cooled to $-60^{o}C$.

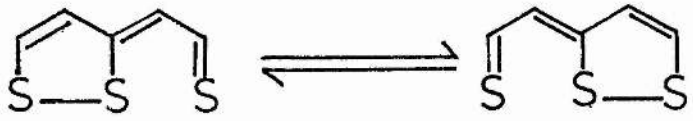
6. Dipole Moments

Dipole moments, which give an indication of the degree of charge distribution in a molecule, have been measured for a number of trithiapentalenes and oxadithiapentalenes[17,34,135,136]. The dipole moment of the oxadithiapentalene (120) (4.18 D) is larger than that of the corresponding trithiapentalene (119) (4.01 D), due to a contribution from the ionic form (120a). This contribution is even larger in the benzo-compound (121) as indicated by a dipole moment of 4.40 D. This value, however, is much lower than the value (13 D) calculated for the completely ionic structure (121a), in support of a largely covalent bicyclic formulation for these systems.

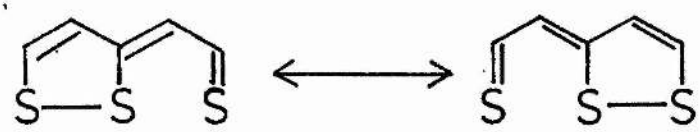
7. Photochemical Studies

Pederson and Lohse[137,138] have demonstrated that a 1-oxa-6,6a-dithiapentalene (122) undergoes a photochemically-induced isomerisation to a product for which they propose the structure (122a). The trans isomer reverts to the cis isomer by a dark process which obeys first order kinetics and which, due to a viscosity effect, is slower if the species is trapped in a matrix rather than in solution. Gleiter and coworkers[139] have also studied these reactions, and discuss the structure of the products in terms of an equilibrium (122a ⇌ 122b) which, for steric reasons, lies to the left. They also report spectroscopic evidence for the trans structures. The nmr spectrum of species (123a), for example, shows a downfield shift of the dithiole ring proton (Ha) compared to the spectrum of the cis isomer (123), due to the anisotropy of the carbonyl group, and there is a "normal"

carbonyl absorption (1645 cm^{-1}) in the infrared spectrum of compound (123a). Compound (124)[137,138], which is invariant to cis-trans isomerism, and compound (125)[139], which has restrictions to rotation imposed by the trimethylene bridge, are photostable. Gleiter et al[140] have shown that 2,5-dimethyl-1,6,6a-trithiapentalene and a series of 1,6a-dithia-6-azapentalenes are transformed photochemically into species whose kinetic and spectroscopic properties are very similar to those observed for compounds (122a). Further investigations are required, however, before definite structural assignments can be made to these species.



126a 126b



126a 126b

126c 126d

E. Theories of Bonding in 1,6,6a-trithiapentalenes

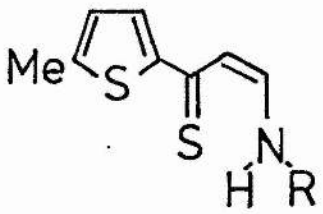
A theoretical description of the bonding in 1,6,6a-trithiapentalenes must explain the planarity of the system, the collinearity or near collinearity of the three sulphur atoms, the sulphur-sulphur distances which indicate a bond order of less than unity, and the apparent C_{2v} symmetry of the parent compound. Although the possibility that future refinements of experimental technique might prove the existence of a rapid valence isomerisation (126a ⇌ 126b) cannot be excluded, this theory is at present not supported by unambiguous experimental evidence. The first hypothesis put forward was the concept of "one-bond, no-bond" resonance (126a ⟷ 126b)[4,141], later used in Huckel MO calculations[60], in which it was assumed that d-orbitals of the central sulphur atom take no part in the bonding. Guillouzo and Lozac'h[15] discuss the feasibility of an ylid structure (126c), but this, by mesomeric displacement of the negative charge, would lead to a charge distribution inconsistent with the properties of the system. To overcome this difficulty, the structure (126d) may be postulated, which requires valence shell expansion at the central sulphur atom. Maeda[142-144] has suggested a structure in which the central sulphur atom uses two pd hybrid orbitals to form σ-bonds with p-orbitals of each of the lateral sulphur atoms, and one of the remaining p-orbitals forms a σ-bond to the central carbon atom. The σ-framework is completed using sp^2 hybridised carbon atoms. A 10π electron system (one from each carbon and the central sulphur, and two from each lateral sulphur) is superimposed. In order that the SCF MO calculation might show a strong positive overlap between the pd hybrids and the adjacent sulphur p-orbitals, Maeda[144] had to postulate a contraction of the 3d-orbitals on the central sulphur atom, caused by a charge distribution around the molecule. Johnstone and Ward[145] used a similar model, involving three p^2d hybrid orbitals at the central sulphur atom for σ-bonding, in SCF MO calculations, the results of which were consistent with ultraviolet spectral data.

Gleiter and Hoffmann[146] have made an important contribution to theories of bonding in these systems. They propose that the three sulphur atoms form an electron-rich 3-centre system in which the bonding is analogous to that in trihalide ions[147,148] and other hypervalent[149] species. In this bonding scheme, three molecular orbitals are formed in a linear three-centre arrangement of atoms: one occupied bonding orbital involving all three atoms, one occupied non-bonding orbital with the electron density localised on the lateral atoms, and one empty antibonding orbital. The three centres are thus held together by only one bonding electron pair. The similarity of the trithiapentalene system to the triiodide ion, for example, is reflected in the fact that the iodine-iodine distance in this ion (2.90-2.93 Å)[150-152] is 0.23-0.26 Å longer than that in molecular iodine. The similarity of triselenapentalenes to triselenocyanates and of dioxathiapentalenes to sulphuranes in this respect has already been indicated [see D, 1, (b) and (c)]. Gleiter and Hoffmann[146], then, propose that this three-centre bond forms part of the σ-structure of the trithiapentalene and there is an additional stabilisation due to the superimposed π-system. A calculation of the variation of potential energy with the displacement of the central sulphur atom towards the lateral sulphur atom shows a clear preference for an unsymmetrical structure when 3d orbitals on the central sulphur atom are not utilised, and a nearly symmetrical structure with a very flat minimum of about 0.2 Å when d-orbitals are included. These results are consistent with the observations that the sum of the sulphur-sulphur distances in trithiapentalenes remains approximately constant, although individual sulphur-sulphur distances can vary over a range of 0.4 Å, and that the amplitude of vibration measured for individual sulphur-sulphur bonds in a vapour-phase electron diffraction study of the parent compound is considerably larger than that for the total sulphur-sulphur distance.

PART TWO

DISCUSSION

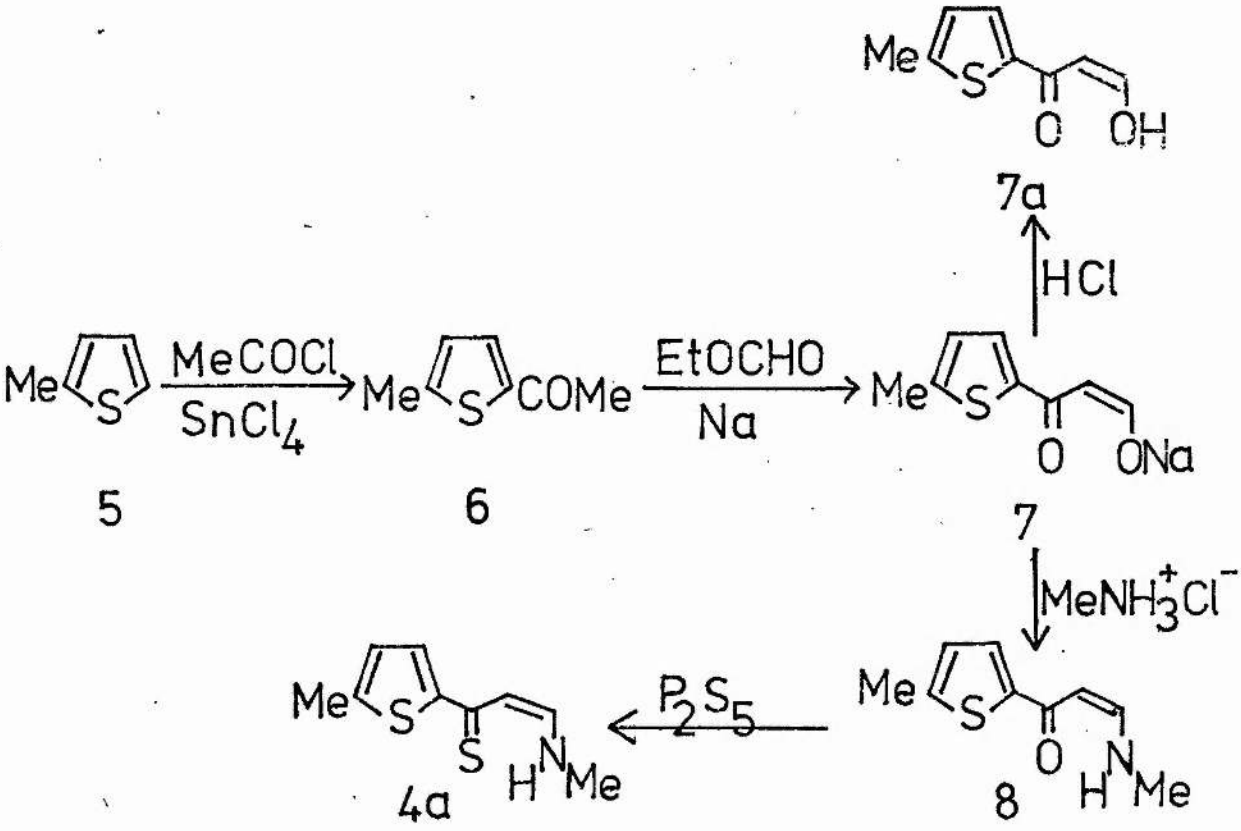
1 2 3



4

(a) R = Me
(b) R = Et
(c) R = NMe_2

Scheme I



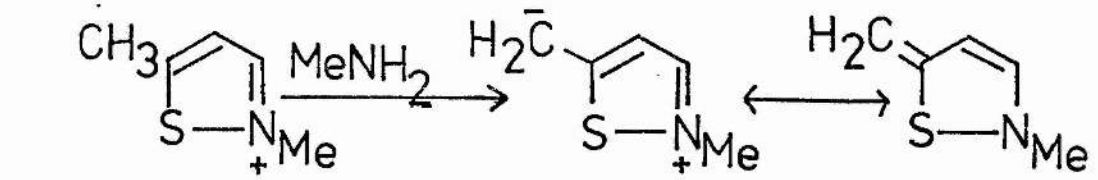
A. An Attempted Synthesis of 1,6-Dimethyl-6a-thia-1,6-diazapentalene from 2,5-Dimethylisothiazolium Perchlorate

1,6-Dimethyl-6a-thia-1,6-diazapentalene (3) has been synthesised from 6-methyl-1,6a-dithia-6-azapentalene [see Part 1, B, (c), (iii)]. An alternative synthesis was visualised, analogous to that of 1,6a-dithia-6-azapentalenes from 3-methyl(ene)-1,2-dithiolium salts [see Part 1, B, (c), (iii)]. It was envisaged that the reaction of 2,5-dimethylisothiazolium perchlorate (1) with dimethylthioformamide would give the Vilsmeier salt (2) which would subsequently react with methylamine to give the thiadiazapentalene (3). In the event, reaction of the isothiazolium salt with dimethyl-$\overset{\text{thioformamide}}{\wedge}$ produced an oil[153] which reacted with methylamine to give 5-methyl-2-(3-methylamino-1-thionopropenyl)thiophen (4a) as the only product. It was later demonstrated that this thione, together with elemental sulphur, was formed by the reaction of methylamine with 2,5-dimethylisothiazolium perchlorate, and that the Vilsmeier salt (2) had not in fact formed, at least in significant quantity.

The structure of the thione (4a), which was deduced from its nmr and mass spectra and analysis, has now been formally established by the synthesis illustrated in Scheme I. Friedel-Crafts acetylation of 2-methylthiophen (5) with acetyl chloride and stannic chloride gave 2-acetyl-5-methylthiophen (6). The ketone (6) was formylated using sodium and ethyl formate to give the sodium salt of 2-(3-hydroxy-1-oxopropenyl)-5-methylthiophen (7), which reacted with methylammonium chloride to form 5-methyl-2-(3-methylamino-1-oxo-propenyl)thiophen (8). Thionation of compound (8) with phosphorus pentasulphide afforded the thione (4a), identical by analysis, nmr, mass spectrum and melting point with the product obtained from the reaction of the isothiazolium salt with methylamine.

Two alternative mechanisms for the rearrangement are illustrated in Schemes IIa and IIb. Evidently two molecules of the isothiazolium

Schemes IIa and IIb



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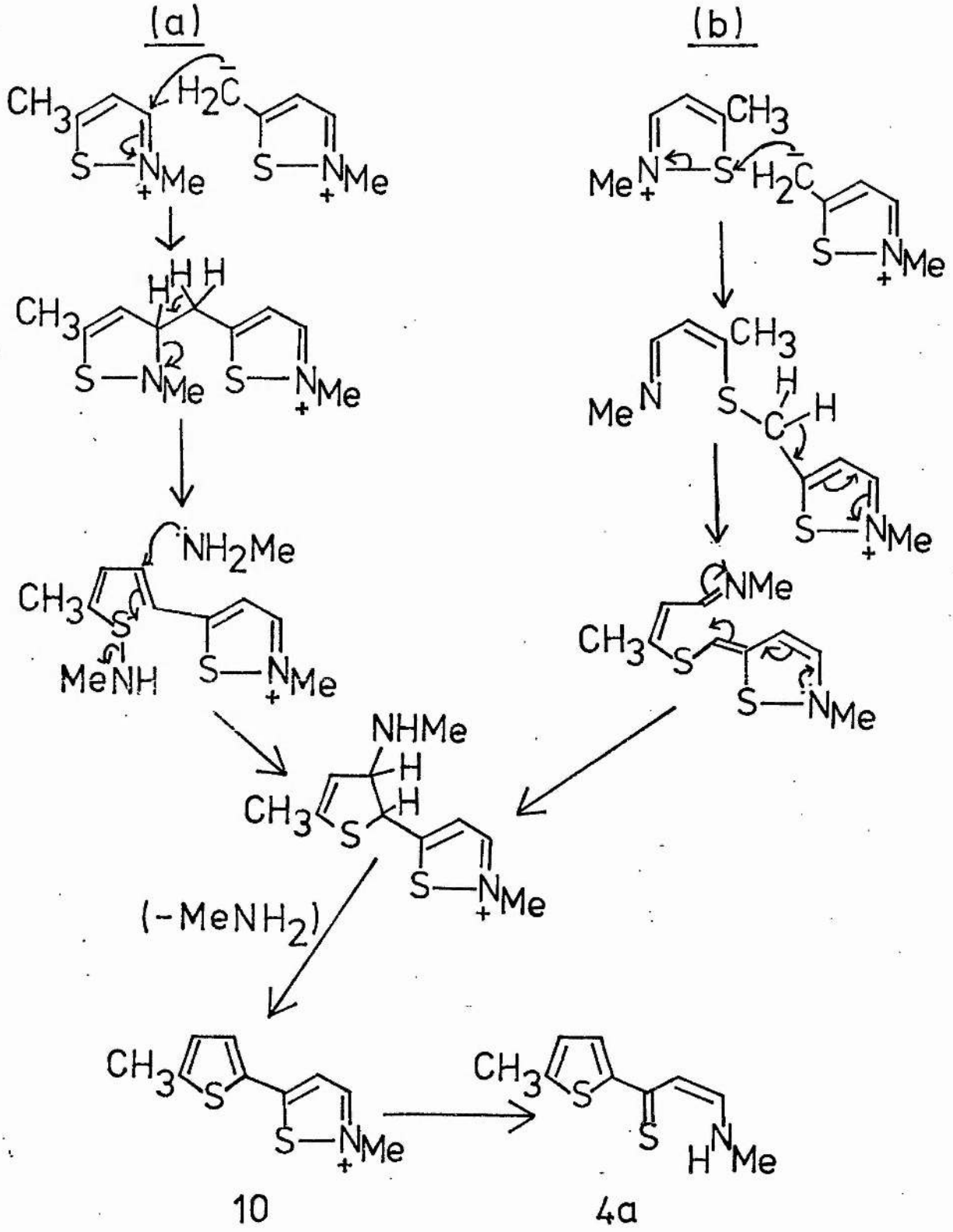
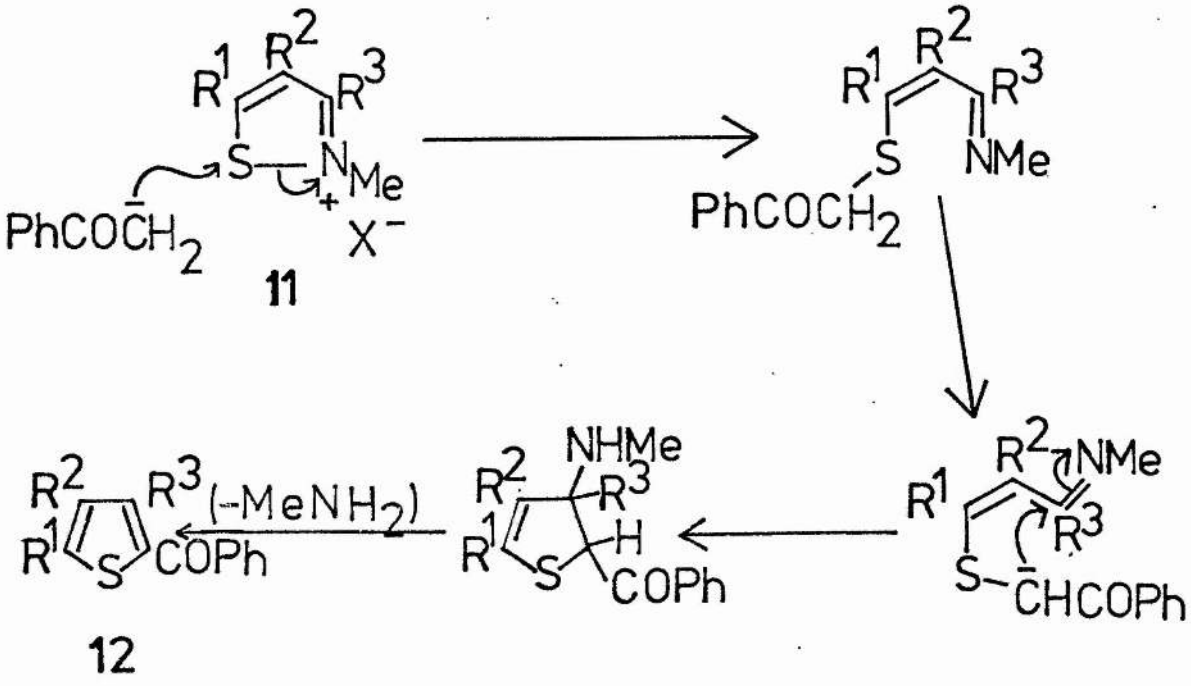
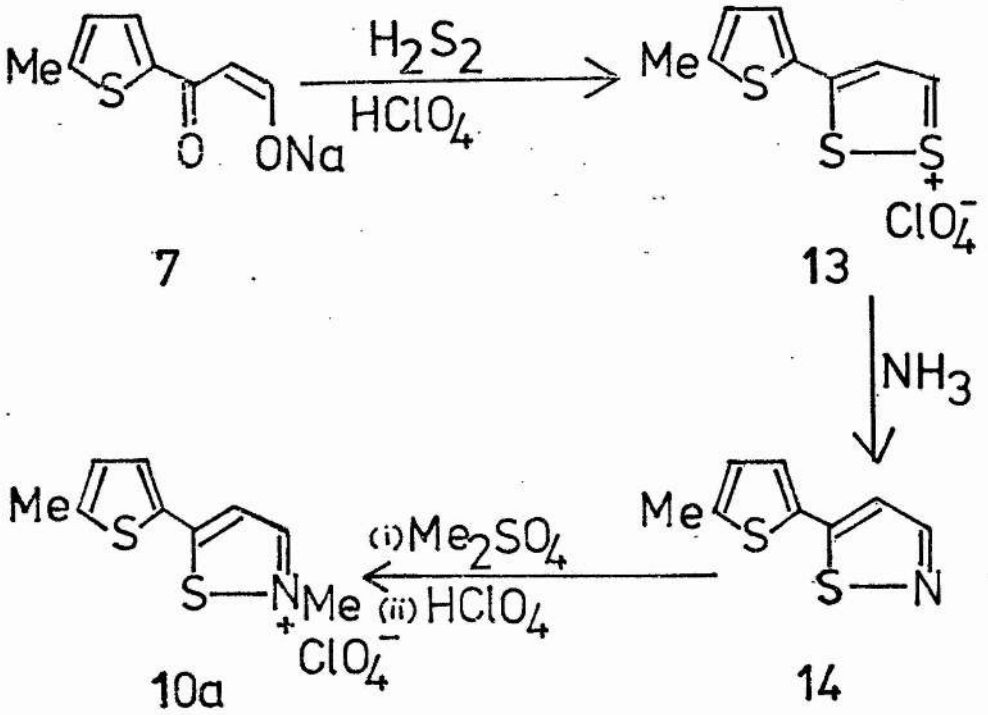


10

4a

Scheme III

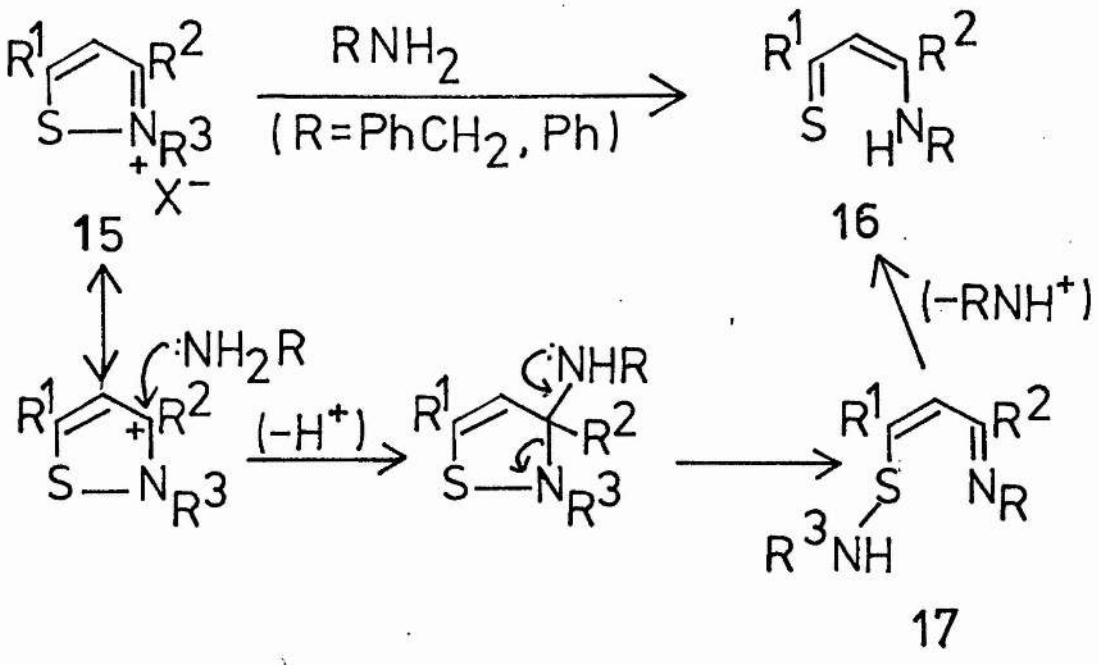

R1 R2 R3
S N Me
PhCOCH2
X−
11
NMe
NHMe
R3
H
COPh
CHCOPh
(-MeNH2)
12

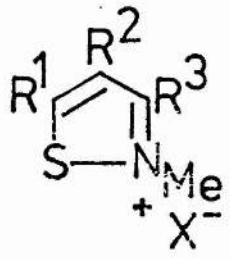

Me
S
O
ONa
7
H2S2
HClO4
S—S+
ClO4−
13
NH3
N
14
(i)Me2SO4
(ii) HClO4
10a

salt are incorporated into the product. The first step is the removal by methylamine of a proton from the acidic 5-methyl group of the isothiazolium cation to produce the resonance-stabilised species (9). It is suggested that this condenses with another molecule of the salt by nucleophilic attack either at the 3-position (Scheme IIa) or at sulphur (Scheme IIb), both processes leading to the 2-methyl-5-(5-methyl-2-thienyl)isothiazolium cation (10). A mechanistically related reaction has been reported by McKinnon and Hassan[154]. Treatment of the isothiazolium salt (11) with sodium benzoylacetate leads to a 2-benzoylthiophen (12), and the authors propose the mechanism illustrated in Scheme III, in which reaction is initiated by nucleophilic attack by a phenacyl ion (actual or potential) at sulphur. Salts containing a methylthio group at the 3- or 5-position lead to 2-benzoylthiophens, whereas 3- or 5-acylmethyleneisothiazoles might have been expected by analogy with related systems[27], if nucleophilic attack had taken place at carbon. This evidence suggests that Scheme IIb is the more likely pathway for the reaction of 2,5-dimethylisothiazolium perchlorate with methylamine.

In order to study the question of the conversion of the cation (10) into the thione (4a) more fully, a synthesis of 2-methyl-5-(5-methyl-2-thienyl)isothiazolium perchlorate (10a) was devised. Treatment of the sodium salt of 2-(3-hydroxy-1-oxopropenyl)-5-methylthiophen (7) with hydrogen disulphide and perchloric acid formed 3-(5-methyl-2-thienyl)-1,2-dithiolium perchlorate (13), which reacted with ammonia to give 5-(5-methyl-2-thienyl)isothiazole (14). Methylation with dimethyl sulphate followed by the addition of perchloric acid gave the perchlorate (10a).

Sykes and Ullah[155] investigated the reaction of isothiazolium salts with a variety of nucleophiles. They demonstrated that 5-mono and 3,5-disubstituted isothiazolium salts (15) react with benzylamine and aniline to form the ring-opened benzylamino- or





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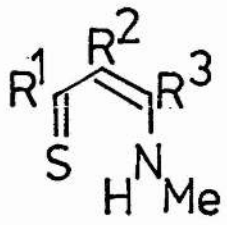


18

(a) R^I = Ph, R^2 = H, R^3 = H, X = ClO_4
(b) R^I = Ph, R^2 = H, R^3 = Ph, X = ClO_4
(c) R^I = Me, R^2 = H, R^3 = H, X = ClO_4
(d) R^I = H, R^2 = H, R^3 = Me, X = ClO_4

anilino-thiones (16). It is suggested by the authors that reaction proceeds by nucleophilic attack at the 3-position of the isothiazolium cation, followed by ring-opening. The amino-thione (16) results from loss of RNH^+ from the intermediate (17). In the same way the thienylisothiazolium salt (10a) reacted with methylamine to form the thione (4a), although in only 23% yield. Sykes and Ullah[155] also showed that the 2-methylisothiazolium salts (11a) and (11b) were converted into the methylamino-thiones (18a) and (18b) respectively, by treatment with benzenethiol. The facts that diphenyl disulphide was also formed in the reaction, and that no benzenethiolate residue was incorporated into the product suggest that the reaction is a reduction rather than a simple nucleophilic attack. In our laboratories it was shown that 2,5-dimethyl, 2,3-dimethyl and subsequently the thienylisothiazolium perchlorate (11c), (11d) and (10a) respectively were reduced in high yield to the corresponding amino-thiones (18c), (18d) and (4a) respectively by sodium hydrogen sulphide. McKinnon and Hassan[154] have reported similar reductions of isothiazolium salts with sodium hydrogen sulphide. It is possible that hydrosulphide ion, resulting from breakdown of the isothiazolium salt, is the reducing agent in the rearrangement reaction, and this is consistent with the fact that elemental sulphur was formed in the reaction.

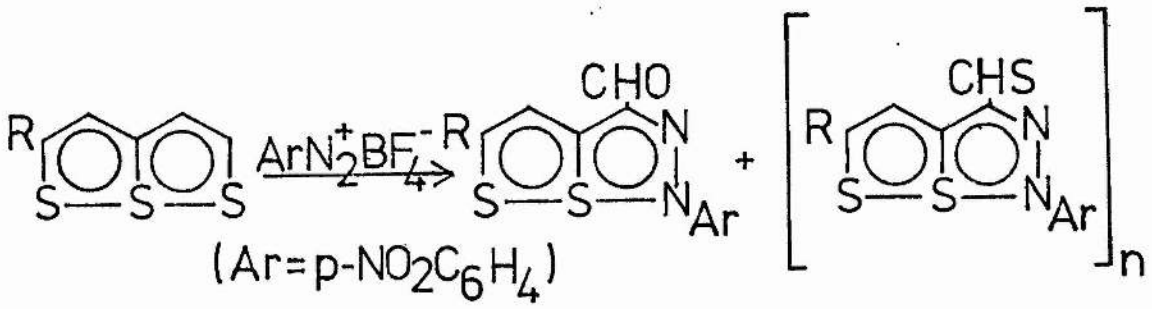
Reaction of 2,5-dimethylisothiazolium perchlorate (1) with ethylamine gave 2-(3-ethylamino-1-thionopropenyl)-5-methylthiophen (4b). The most likely explanation for this is the formation of the thione (4a) by the mechanism proposed and subsequent reaction of this with the excess of ethylamine present. It was demonstrated in a separate experiment that ethylamine readily displaced methylamine from the thione (4a) to form the thione (4b). In the same way, 1,1-dimethylhydrazine reacted with 2,5-dimethylisothiazolium perchlorate (1) to give predominantly 2-(3-N,N-dimethylhydrazino-1-thionopropenyl)-5-methylthiophen (4c) although a small amount of

the thione (4a) was also isolated, presumably because a limited excess of the amine was used, insufficient to effect complete conversion to the thione (4c).

B. The Reaction of 1,6,6a-Trithiapentalenes and Related Compounds with Arenediazonium Salts

(a) Although there has been considerable interest in recent years centred on the synthesis and structure of 1,6,6a-trithiapentalenes and related systems, comparatively little attention has been paid to the reactivity of these systems. A number of electrophilic substitution reactions of 1,6,6a-trithiapentalenes and related systems have been reported [Part 1, C, (b)], but a detailed study has not yet been carried out. The few investigations so far reported have been restricted mainly to the reactions of 1,6,6a-trithiapentalenes, often containing aryl substituents in the 2- and 5-positions, and only a few isolated examples of the reactions of oxygen and nitrogen analogues have been reported. It has been observed that electrophilic attack may proceed at the 3(4)-position to give the normal substitution product, eg., bromination[44,45,61] and formylation[62-64,68] or it may be accompanied by a rearrangement, eg., in nitrosation reactions.

As part of a detailed investigation, a systematic study of the reaction of 1,6,6a-trithiapentalenes, 1-oxa-6,6a-dithiapentalenes and 1,6a-dithia-6-azapentalenes with arenediazonium fluoroborates was carried out. Syntheses of unsubstituted and simply-substituted derivatives of these systems have been developed in our laboratories in recent years, thus making the compounds available in quantities sufficient for studies of their reactivity. The reactions of compounds containing a t-butyl group in the 2(5)-position were studied initially, because the t-butyl group blocks one position sterically, and at the same time activates the system as a whole towards electrophilic attack. The investigation subsequently included the unsubstituted trithiapentalene, oxadithiapentalene and dithiaazapentalene, and the compounds containing a phenyl substituent in the 2(5)-position. 1,6,6a-Trithiapentalenes and related systems were found to undergo diazo-coupling reactions



19 20 21

(a) R = Bu^t

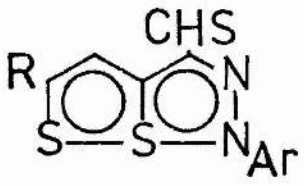
(b) R = H

(c) R = Ph

(a) R = Bu^t, Ar = p-$NO_2C_6H_4$

(b) R = H , Ar = p-$NO_2C_6H_4$

(c) R = Ph , Ar = p-$NO_2C_6H_4$



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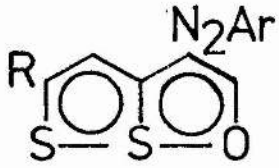

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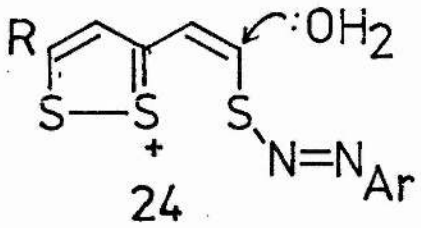
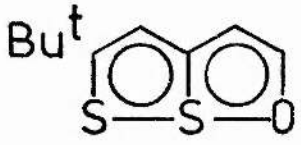


24

(a) R = Bu^t, Ar = p-$NO_2C_6H_4$

(b) R = H , Ar = p-$NO_2C_6H_4$

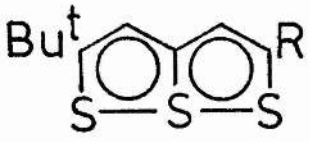
(c) R = Ph , Ar = p-$NO_2C_6H_4$



33a

which involve a rearrangement analogous to that observed in nitrosation reactions. From the investigation, a clearer picture of the various features of the electrophilic substitution of these systems emerged, and a mechanism accounting for these features was proposed.

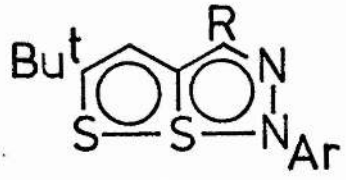
At the start of the investigation, the relatively reactive electrophile p-nitrobenzenediazonium fluoroborate was used. Treatment of 2-t-butyl-1,6,6a-trithiapentalene (19a) with p-nitrobenzenediazonium fluoroborate gave two products, the thioaldehyde polymer (21a) and 4-formyl-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (20a) in yields of 1.5 and 8% respectively. TLC indicated that there were a number of other products formed in trace amounts, insufficient for isolation. A large amount of intractable polymeric material was also formed. This reaction may be rationalised in terms of electrophilic attack at the 4-position by the diazonium cation, accompanied by a rearrangement involving rotation about the C(3a)-C(4) bond to form the thioaldehyde (22a), part of which polymerises in the well-known manner of thioaldehydes and part of which hydrolyses to the aldehyde (20a). Evidence for the involvement of the thioaldehyde (22a) as a transient intermediate is the fact that the addition of water to the reaction mixture increased the yield of aldehyde (20a) to 22%. The yield of polymer (21a) was also observed to increase (to 16%). A possible explanation for this unexpected result is the involvement of water together with liberated fluoroboric acid in catalysis of the polymerisation. Another possible route to the aldehyde (20a) which cannot be discounted would involve attack by the diazonium salt at sulphur to give the intermediate (24a). This yields on hydrolysis the oxadithiapentalene (33a) which would subsequently react with the excess of the diazonium salt to give the aldehyde (20a). Compound (20a) shows strong infrared absorption at



25

(a) R = SMe

(b) R = NMe_2



26

(a) R = CS_2Me, Ar = p-$NO_2C_6H_4$

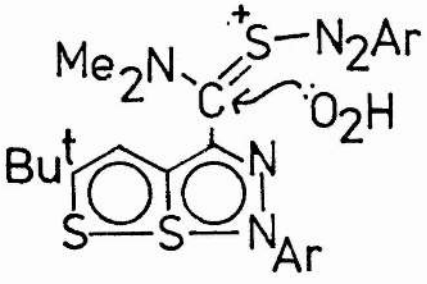
(b) R = $CSNMe_2$, Ar = p-$NO_2C_6H_4$

(c) R = $CSNMe_2$, Ar = Ph

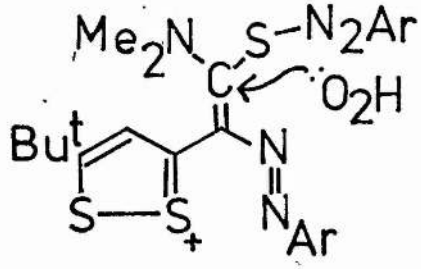
(d) R = COSMe, Ar = p-$NO_2C_6H_4$

(e) R = $CONMe_2$, Ar = p-$NO_2C_6H_4$

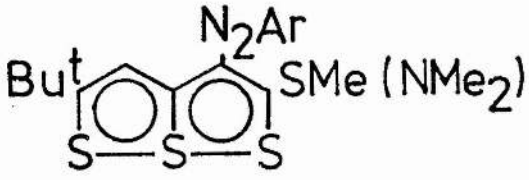
(f) R = $CONMe_2$, Ar = Ph



27a



27b

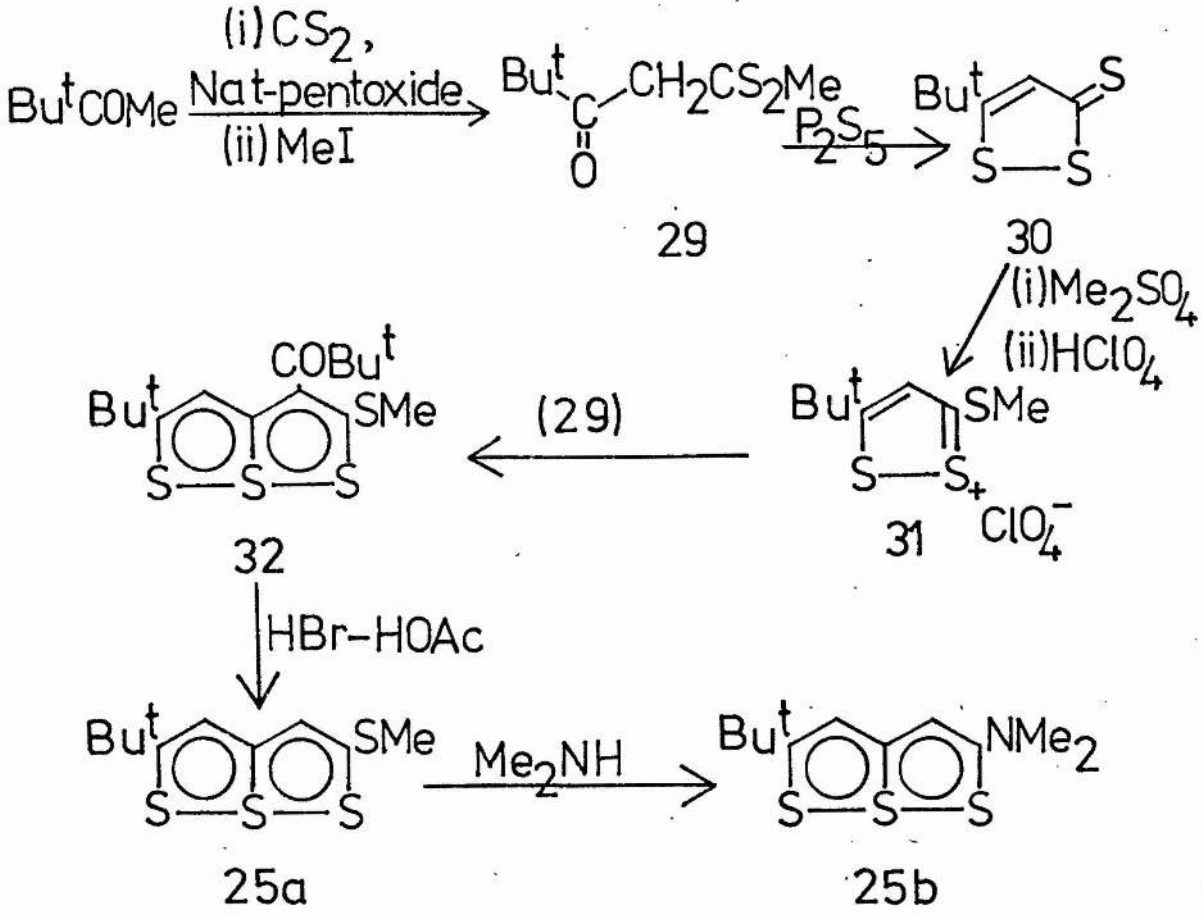


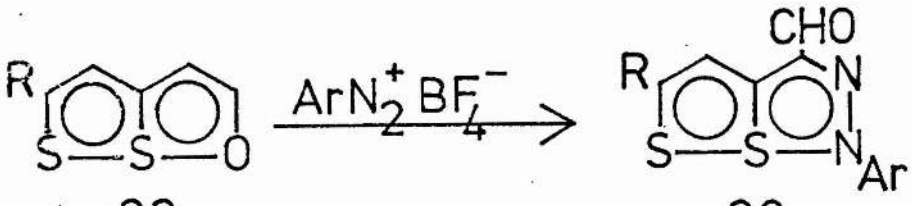
28

1680 cm^{-1}, which is inconsistent with structure (23a) and confirms the 1,6a-dithia-5,6-diazapentalene structure (20a). Treatment of 1,6,6a-trithiapentalene (19b) with p-nitrobenzenediazonium fluoroborate in aqueous acetonitrile likewise afforded the thioaldehyde polymer (21b) (0.5%) and the aldehyde (20b) (8%). However, under the same conditions 2-phenyl-1,6,6a-trithiapentalene (19c) did not give the polymer, although the aldehyde (20c) (7%) was isolated.

In the foregoing examples, it is suggested that reaction proceeds initially to give the unstable species (22). It was of interest to investigate the reaction of diazonium salts with trithiapentalenes which might lead to more stable species. 2-Methylthio-5-t-butyl-1,6,6a-trithiapentalene (25a) reacted readily with p-nitrobenzenediazonium fluoroborate at the 3-position to give methyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6 -diazapentalene-4-dithiocarboxylate (26a). In this case the 2-methylthio group activates the 3-position to electrophilic attack, and the dithioester group which results after rearrangement is not susceptible to polymerisation or hydrolysis, unlike the thioformyl group in the previous cases. In a similar way, 2-dimethylamino-5-t-butyl-1,6,6a-trithiapentalene (25b) reacted with p-nitrobenzenediazonium fluoroborate to afford N,N-dimethyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarboxamide (26b) as the major product, together with a small amount of the corresponding amide (26e). The amide (26e) probably results from hydrolysis of an intermediate, which may be formulated as (27a) or (27b), formed by attack by the diazonium cation at sulphur in the thioamide (26b). Evidence for this is that treatment of the thioamide (26b) with p-nitrobenzenediazonium fluoroborate led to a partial conversion to the amide (26e), whereas the thioamide was recovered quantitatively after treatment with fluoroboric acid. Compound (25b) was the only trithiapentalene studied which was sufficiently reactive to react with the weaker electrophile benzenediazonium fluoroborate. It

Scheme IV





33

(a) R = Bu^t
(b) R = H
(c) R = Ph

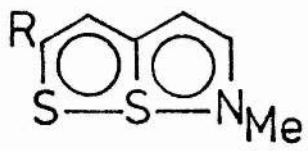
20

(a) R = Bu^t, Ar = p-$NO_2C_6H_4$
(b) R = H , Ar = p-$NO_2C_6H_4$
(c) R = Ph , Ar = p-$NO_2C_6H_4$
(d) R = Bu^t, Ar = Ph
(e) R = H , Ar = Ph
(f) R = Ph , Ar = Ph

gave the thioamide (26c) in high yield. Selective desulphurisation of compounds (26a)-(26c) by mercury(II)acetate gave the corresponding oxygen compounds (26d)-(26f), the structures of which were assigned conclusively on the basis of their infrared spectra, which showed strong carbonyl absorptions (1650, 1642, and 1640 cm^{-1} respectively). The dithiadiazapentalene structure of compounds (26a)-(26c), as opposed to the isomeric structure (28) in which the trithiapentalene system remains intact, is confirmed by the similarity of the uv spectra of the compounds to the spectra of the corresponding oxygen compounds.

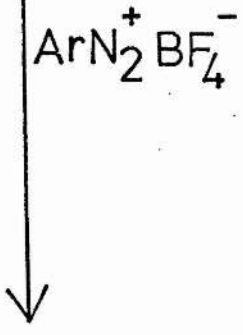
The trithiapentalenes (25a) and (25b) were new compounds and their synthesis is illustrated in Scheme IV. The dithioester (29) was prepared by the method of Thuillier and Vialle[156,157], which involves the condensation of pinacolone with carbon disulphide in the presence of sodium t-pentoxide, followed by methylation with methyl iodide. Treatment of the dithioester (29) with phosphorus pentasulphide gave the thione (30), which was S-methylated by dimethyl sulphate followed by treatment with perchloric acid to yield 3-methylthio-5-t-butyl-1,2-dithiolium perchlorate (31). Condensation of the salt (31) with the dithioester (29) according to a modification of the procedure of Beer[28] gave 2-methylthio-3-pivaloyl-5-t-butyl-1,6,6a-trithiapentalene (32). Protodeacylation of compound (32) gave compound (25a) which, with ethanolic dimethylamine, afforded compound (25b).

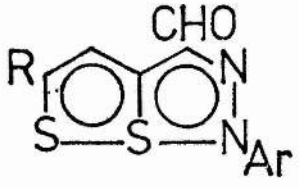
The 1-oxa-6,6a-dithiapentalenes (33a)-(33c) reacted smoothly with p-nitrobenzenediazonium fluoroborate to give respectively compounds (20a)-(20c), also obtained from the trithiapentalenes (19a)-(19c). These reactions occur by electrophilic attack at the 3-position of the oxadithiapentalenes with subsequent rearrangement into the dithiadiazapentalenes (20a)-(20c). There was no evidence for attack at the 4-position. The higher reactivity of oxadithiapentalenes towards electrophiles compared with trithiapentalenes is

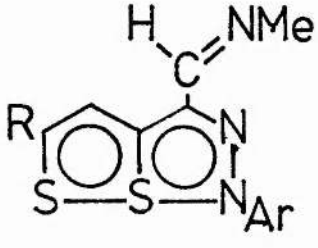


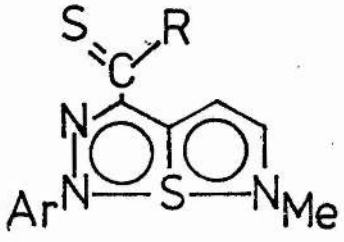
(a) R = Bu^t
(b) R = H
(c) R = Ph

34









20 35 36

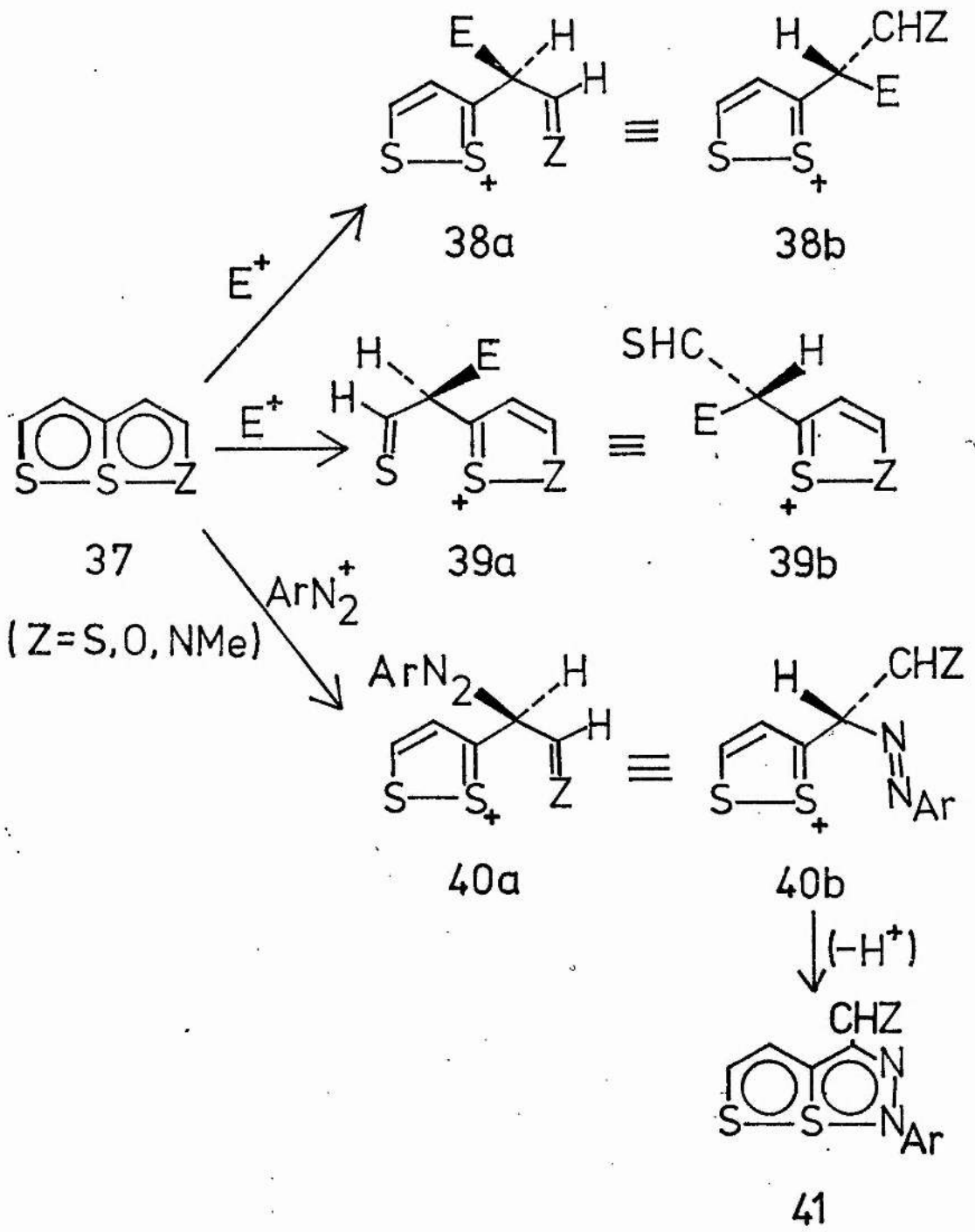
(a) R = Bu^t, Ar = p-$NO_2C_6H_4$
(b) R = H , Ar = p-$NO_2C_6H_4$
(c) R = Ph , Ar = p-$NO_2C_6H_4$
(d) R = Bu^t, Ar = Ph
(e) R = H , Ar = Ph
(f) R = Ph , Ar = Ph

reflected in the fact that compounds (33a)-(33c) reacted with benzenediazonium fluoroborate to give the aldehydes (20d)-(20f) in high yield, whereas the corresponding trithiapentalenes were unreactive towards this reagent.

Treatment of the 1,6a-dithia-6-azapentalenes (34a)-(34c) with p-nitrobenzenediazonium fluoroborate also led to the aldehydes (20a)-(20c) in respective yields of 83, 10 and 4%. It is suggested that the reaction proceeds via electrophilic attack by the diazonium cation at the 4-position followed by a rearrangement into the imine (35), which hydrolyses rapidly to the aldehyde. The low yields from compounds (34b) and (34c) are possibly due to attack in part at the 3-position. This would lead to the thioaldehyde (36b) and the thioketone (36c), unstable species which would tend to polymerise. Compound (34a), however, contains the bulky t-butyl group in the 2-position, which blocks the 3-position to electrophilic attack, and a high yield of the aldehyde (20a) results. Benzenediazonium fluoroborate reacted with the dithiaazapentalenes (34a) and (34c) to form the aldehydes (20d) and (20f) in yields of 89 and 34% respectively, but did not give a product with compound (34b) which is less reactive because of the absence of activating alkyl or aryl substituents in the ring.

A mechanism may now be proposed to account for the various features of the electrophilic substitution of 1,6,6a-trithiapentalenes and related systems, and in particular for the results of the diazo-coupling reactions.

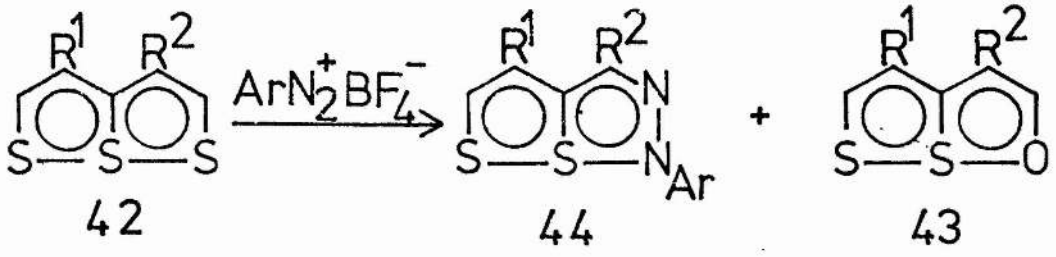
The initial step is the attack by an electrophile (E^+) at the 3- or 4-position of the heterocycle (37), accompanied by a breaking of the S-Z (Z = S, O, NMe) or S-S bond to give a stable 6π-electron monocyclic intermediate (38a) or (39a), which will be a derivative of the 1,2-dithiolium (Z=S), 1,2-oxathiolium (Z=O), or isothiazolium (Z=NMe) system, depending on the position of attack. Since there is free rotation about the C(3)-C(3a) or C(3a)-C(4) bond, the group E


E
H
H
Z
S
S
+
38a
≡
H
CHZ
E
38b
E+
H
E
H
S
39a
SHC
H
E
39b
37
(Z=S,O,NMe)
ArN2+
ArN2
40a
40b
(-H+)
CHZ
N
N
Ar
41

can come into the proximity of the central sulphur atom in the conformations (38b) and (39b). In brominations and formylations, the group E (Br and $CH{=}\overset{+}{N}Me_2$) cannot interact with the central sulphur atom to complete a stable three-centre heteroatom sequence, and loss of a proton from the intermediate gives the normal substitution product. In the diazo-coupling reactions, however, such an interaction is possible and there are two pathways open. The intermediate (40) may lose a proton either to regenerate the S-S-Z interaction via conformation (40a), or to form the dithiadiazapentalene (41) via conformation (40b). In all the reactions studied, however, the latter pathway is taken. This suggests that there is a strong S--S--N interaction in the 1,6a-dithia-5,6-diazapentalene system, which serves as the driving force for these rearrangements. Oxadithiapentalenes undergo electrophilic attack exclusively at the 3-position, probably because of the greater stability of the resulting 1,2-dithiolium intermediate compared with the intermediate, derived from the unknown 1,2-oxathiolium system, which would result from electrophilic attack at the 4-position. Although only products arising from electrophilic attack at the 4-position of dithiaazapentalenes have so far been isolated, attack in part at the 3-position has been suggested as the explanation for the low yields obtained from the reactions of compounds (34b) and (34c) with diazonium salts. The intermediates involved would be derivatives of the well-known isothiazolium system and would be expected to be stable.

Nitrosation reactions which lead to 1-oxa-6,6a-dithia-2-azapentalenes can be accounted for in a similar mechanism with $E{=}NO^{+}$.

(b) In all the cases of electrophilic substitution of 1,6,6a-trithiapentalenes and related systems so far reported, attack takes place exclusively at the 3(4)-position. The next step in the

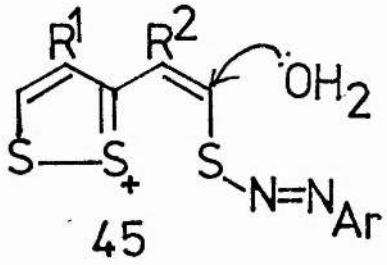


42 44 43

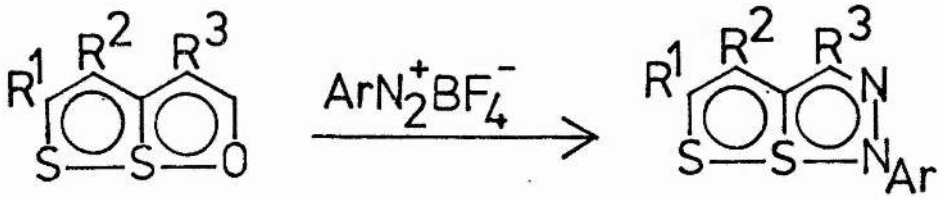
	R^1	R^2
(a)	Me	Me
(b)	$CH_2CH_2CH_2$	

	R^1	R^2	Ar
(k)	Me	Me	p-$NO_2C_6H_4$
(l)	$CH_2CH_2CH_2$		p-$NO_2C_6H_4$

	R^1	R^2
(a)	Me	Me
(b)	$CH_2CH_2CH_2$	



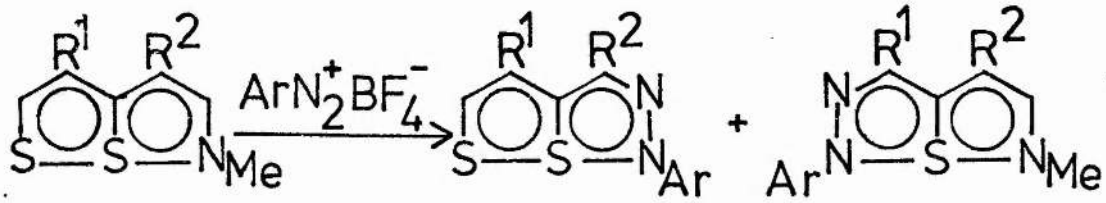
45



43 44

	R^1	R^2	R^3
(a)	H	Me	Me
(b)	H	$CH_2CH_2CH_2$	
(c)	Ph	H	Me

	R^1	R^2	R^3	Ar
(k)	H	Me	Me	p-$NO_2C_6H_4$
(l)	H	$CH_2CH_2CH_2$		p-$NO_2C_6H_4$
(m)	Ph	H	Me	p-$NO_2C_6H_4$



46 44 48

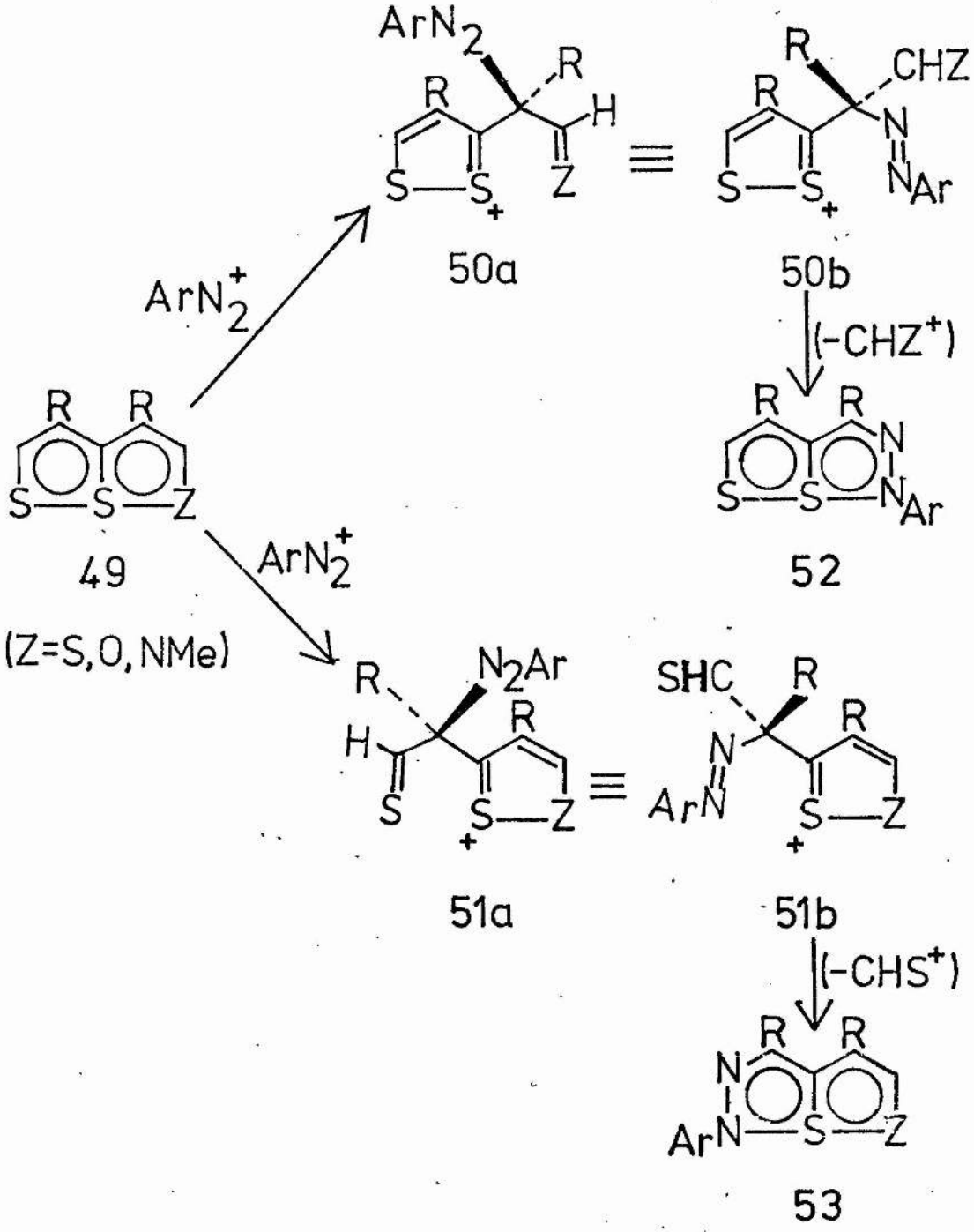
	R^1	R^2
(a)	Me	Me
(b)	$CH_2CH_2CH_2$	

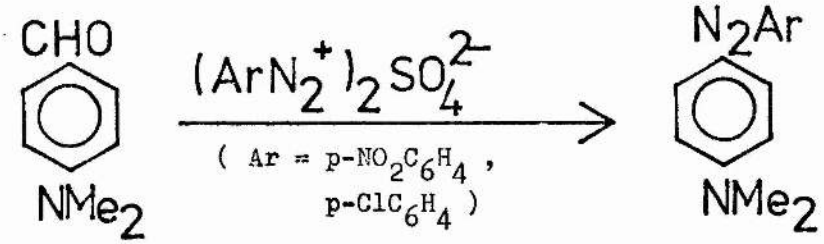
	R^1	R^2	Ar
(k)	Me	Me	p-$NO_2C_6H_4$
(l)	$CH_2CH_2CH_2$		p-$NO_2C_6H_4$

	R^1	R^2	Ar
(e)	Me	Me	p-$NO_2C_6H_4$
(f)	$CH_2CH_2CH_2$		p-$NO_2C_6H_4$

investigation was to examine the reaction of p-nitrobenzenediazonium fluoroborate with 1,6,6a-trithiapentalenes and related systems containing alkyl substituents at the 3- and 4-positions. A number of possibilities were envisaged. For example, these alkyl substituents might block the 3- and 4-positions to electrophilic attack and at the same time direct substitution to the 2-position, or reaction might not in fact take place. In the event, however, electrophilic attack at the 3(4)-position still took place, and was accompanied by the elimination of a CHS, CHO or CHNMe group. 3,4-Dimethyl- and 3,4-trimethylene-1,6,6a-trithiapentalenes (42a) and (42b) gave the corresponding 6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalenes (44k) and (44 l), although in low yield, together with small amounts of the oxadithiapentalenes (43a) and (43b). These latter products probably arise from hydrolysis of the intermediates (45), which are formed by electrophilic attack at sulphur by the diazonium cation. The 1-oxa-6,6a-dithiapentalenes (43a)-(43c) reacted smoothly to give the dithiadiazapentalenes (44k)-(44m) respectively. The 1,6a-dithia-6-azapentalenes (46a) and (46b) gave not only the dithiadiazapentalenes (44k) and (44 l), the same products as were obtained from the corresponding trithiapentalenes and oxadithiapentalenes, but also 3,4,6-trimethyl-1-p-nitrophenyl- and 6-methyl-3,4-trimethylene-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (48e) and (48f) respectively. The products (48e) and (48f) arise from electrophilic attack by the diazonium cation at the 3-position followed by elimination of the thioformyl group.

These reactions may be explained by a mechanism, similar to that already proposed [see B, (a)] for diazo-coupling reactions of trithiapentalenes and related systems in which a proton is lost to give the product, but differing in that a group CHZ (Z=S, O, NMe) is eliminated. Electrophilic attack by a diazonium cation at the 3- or 4-position of compound (49) gives the stable 6π monocyclic intermediate (50) or (51), and formal elimination of CHZ^+ (Z=S,O,NMe) from the conformations (50b) or (51b) gives the corresponding

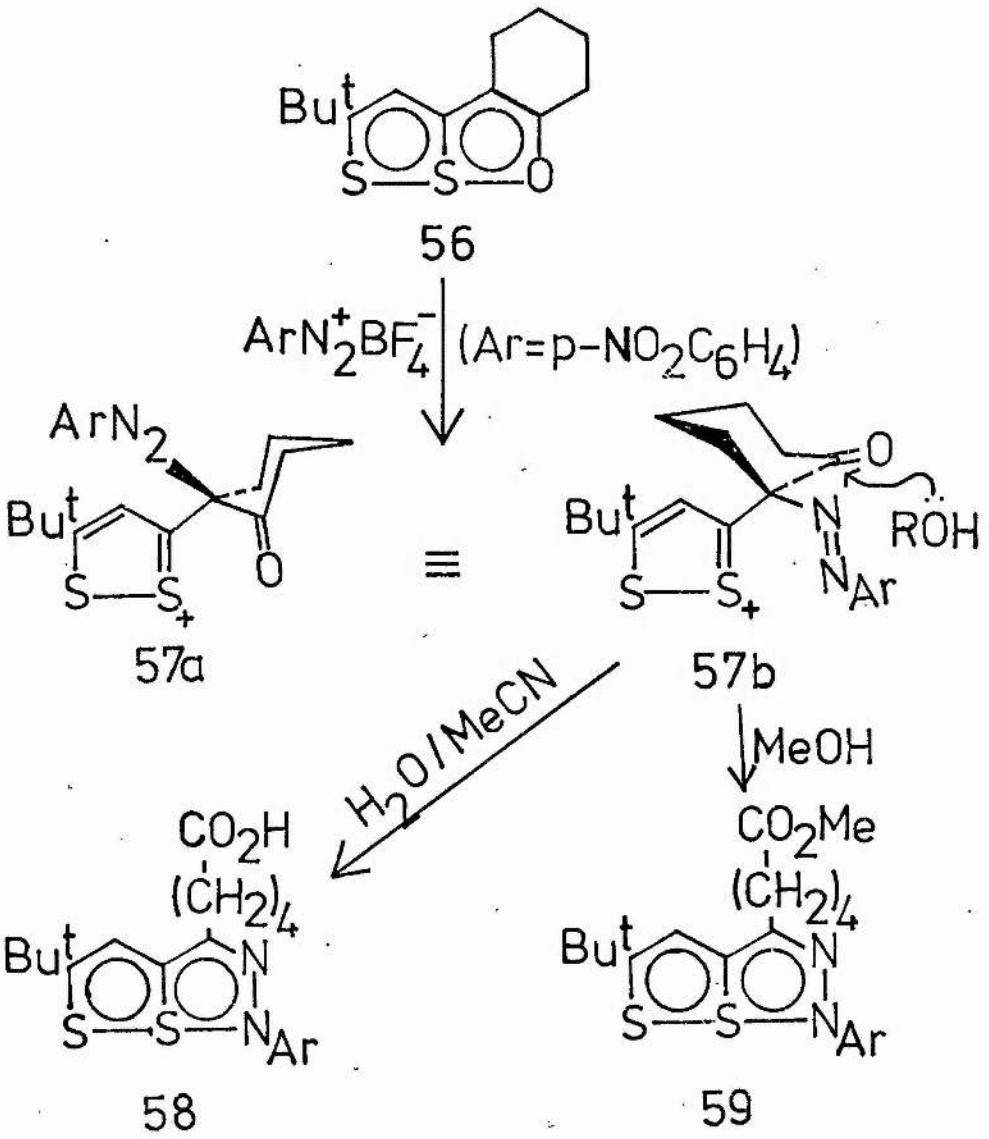

ArN2
R
R
H
S—S+
Z
≡
R
CHZ
N
NAr
50a
50b
(-CHZ+)
ArN2+
R R
S—S—Z
49
(Z=S, O, NMe)
R R
N
N
S—S—NAr
52
ArN2+
N2Ar
R
H
S
S—Z
+
≡
SHC
R
N
ArN
51a
51b
(-CHS+)
N
ArN—S—Z
53

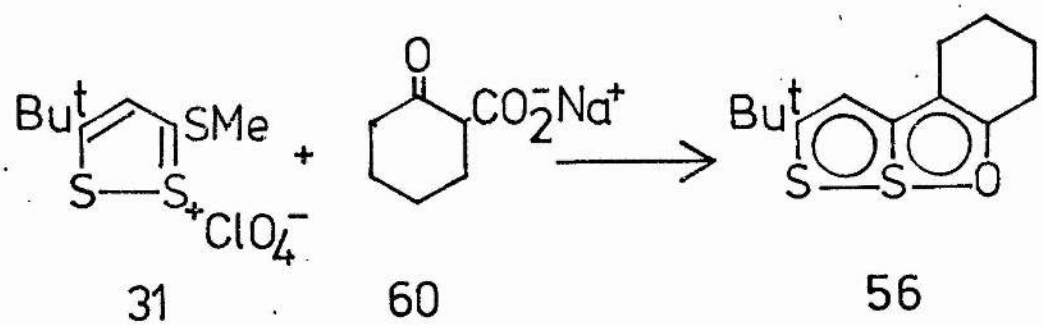

CHO
NMe2
(ArN2+)2SO4 2-
(Ar = p-NO2C6H4 ,
p-ClC6H4)
N2Ar
NMe2

54 55

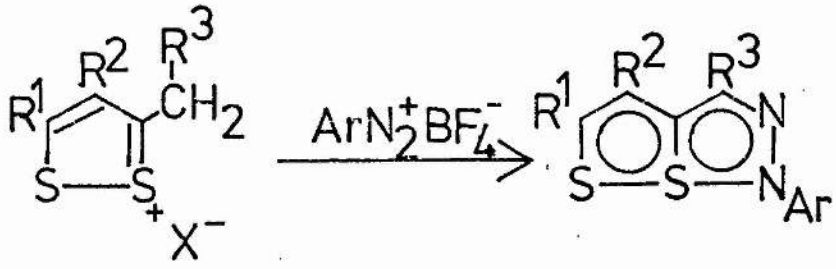
product (52) or (53). In the case of the symmetrical trithiapentalenes (49, Z=S), the products (52) and (53) are identical. The fact that the dithiaazapentalenes (49, Z=NMe) give two products, the dithiadiazapentalenes (52) and the thiatriazapentalenes (53, Z=NMe), indicates that both pathways are followed. The oxadithiapentalenes (49, Z=O) give a single product (52), probably due again to the greater stability of the 1,2-dithiolium intermediate (50) compared with the 1,2-oxathiolium intermediate (51, Z=O) which would be generated by electrophilic attack at the 4-position.

A large number of diazo-coupling reactions are known in which groups other than the proton are eliminated.[158,159] A sulphonic group, SO_3^-, is eliminated as sulphur trioxide[160], and a carboxy group, CO_2^- or CO_2H as carbon dioxide[161], while a whole series of examples of the replacement of the halogen atoms in phenols by diazonium cations is recorded in the literature[162]. Ziegler[159] has described a number of reactions in which groups such as RCHOH, $RCHNR_2$ and RCO are eliminated. A precedent for the elimination of a formyl group by a diazonium cation, as observed in the reactions of the oxadithiapentalenes (43) with p-nitrobenzenediazonium fluoroborate, is seen in the reactions of p-dimethylaminobenzaldehyde (54) with p-nitro and p-chlorobenzenediazonium sulphates, which give the azo compounds (55)[163]. In these reactions, the dimethylamino group directs electrophilic attack to the para-position, and elimination of the formyl group follows. A number of electrophilic deformylation reactions have been reported[164], but the fate of the eliminated formyl group is often unspecified. The displaced formyl group has, however, been shown to give rise to formic acid in protodeformylation reactions[165]. It has been suggested that traces of carbon dioxide[166] or carbon monoxide[167], which have been detected as products of deformylation reactions, result from oxidation or decarbonylation of the initially-formed formic acid.


56
ArN2+BF4− (Ar=p-NO2C6H4)
ArN2
57a
≡
57b
ROH
H2O/MeCN
MeOH
CO2H
(CH2)4
58
CO2Me
(CH2)4
59


SMe
ClO4−
31
CO2−Na+
60
56

In order to study the fate of the group eliminated from 1-oxa-6,6a-dithiapentalenes containing an alkyl substituent at the 3-position on reaction with arenediazonium salts, the reaction of 2,3-tetramethylene-5-t-butyl-1-oxa-6,6a-dithiapentalene (56) with p-nitrobenzenediazonium fluoroborate was investigated. It was found that the reaction was dependent on the solvent in which the reaction was carried out. In acetonitrile, 5-(6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalen-4-yl)-n-pentanoic acid (58) resulted, whereas in methanol, the corresponding methyl ester (59) was formed. It is suggested that the reaction proceeds by electrophilic attack at the 3-position to give the intermediate (57). This intermediate then, in the same way as intermediate (50), tends to form the dithiadiazapentalene system by breaking a carbon-carbon bond. The carbonyl group is thus detached from the ring system but, in this case, is retained in the molecule at the end of the tetramethylene chain. The breaking of the carbon-carbon bond is preceded by nucleophilic attack at the carbonyl group of intermediate (57) by either water (present in acetonitrile) or by methanol. The acid (58) is therefore formed when the reaction is carried out in acetonitrile, and the ester (59) results when methanol is the reaction solvent. It is now reasonable to suggest that the formyl group eliminated from the oxadithiapentalenes (43a)-(43c) in their reactions with p-nitrobenzenediazonium fluoroborate, carried out in acetonitrile, gives rise to formic acid. The oxadithiapentalene (56), a new compound, was prepared by the reaction of 3-methylthio-5-t-butyl-1,2-dithiolium perchlorate (31) with the sodium salt of cyclohexanone-2-carboxylic acid (60).



61

	R^I	R^2	R^3	X
(a)	Bu^t	H	H	ClO_4
(b)	H	H	H	ClO_4
(c)	H	Me	Me	ClO_4
(d)	H	$CH_2CH_2CH_2$		ClO_4
(e)	Ph	H	H	ClO_4
(f)	H	Ph	H	ClO_4
(g)	Ph	H	Me	ClO_4
(h)	H	Ph	Ph	Br

44

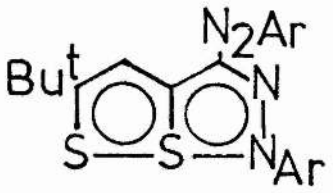
	R^I	R^2	R^3	Ar
(a)	Bu^t	H	H	Ph
(b)	H	H	H	Ph
(c)	H	Me	Me	Ph
(d)	H	$CH_2CH_2CH_2$		Ph
(e)	Ph	H	H	Ph
(f)	H	Ph	H	Ph
(g)	Ph	H	Me	Ph
(h)	H	Ph	Ph	Ph
(i)	Bu^t	H	H	p-$NO_2C_6H_4$
(j)	H	H	H	p-$NO_2C_6H_4$
(k)	H	Me	Me	p-$NO_2C_6H_4$
(l)	H	$CH_2CH_2CH_2$		p-$NO_2C_6H_4$
(m)	Ph	H	Me	p-$NO_2C_6H_4$
(n)	Bu^t	H	H	p-$MeOC_6H_4$
(o)	H	H	H	p-$MeOC_6H_4$
(p)	H	Me	Me	p-$MeOC_6H_4$
(q)	H	$CH_2CH_2CH_2$		p-$MeOC_6H_4$
(r)	Bu^t	H	H	p-$MeCOC_6H_4$
(s)	H	H	H	p-$MeCOC_6H_4$
(t)	H	Me	Me	p-$MeCOC_6H_4$
(u)	H	$CH_2CH_2CH_2$		p-$MeCOC_6H_4$
(v)	Bu^t	H	H	p-MeC_6H_4
(w)	Bu^t	H	H	p-BrC_6H_4
(x)	H	H	H	p-BrC_6H_4

C. Synthesis and Structure of 1,6a-Dithia-5,6-diazapentalenes and 1,6a-Diselena-5,6-diazapentalenes

(a) Synthesis

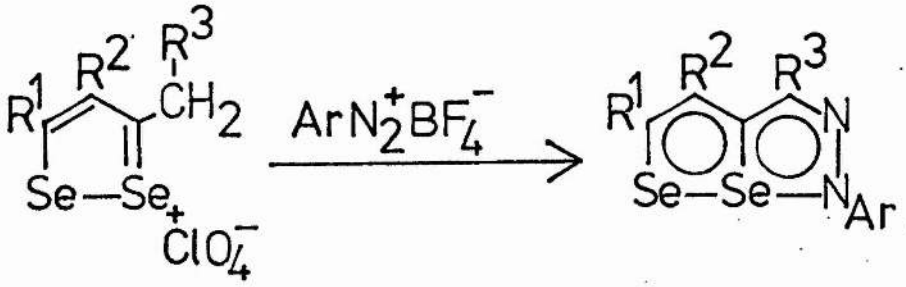
The reactions of 1,6,6a-trithiapentalenes and related systems with arenediazonium salts have led to the isolation of a number of 1,6a-dithia-5,6-diazapentalenes, a novel class of hypervalent heterocyclic compounds of the 1,6,6a-trithiapentalene type. It was decided that a general synthesis of 1,6a-dithia-5,6-diazapentalenes should be developed, in order that a detailed investigation of the structure and reactivity of the system might be carried out.

The most versatile syntheses of trithiapentalenes and related systems yet developed, utilise the reactivity of a 3-methyl(ene) group of a 1,2-dithiolium salt towards electrophiles [see Part 1, B, (a), (iv) and c, (ii)]. An analogous synthesis of 1,6a-dithia-5,6-diazapentalenes has now been devised which involves the reaction of the 3-methyl(ene)-1,2-dithiolium salts (61a)-(61h) with arenediazonium fluoroborates in an ethanol-water mixture. Because several 3-methyl(ene)-1,2-dithiolium salts are available, and because a very large number of arenediazonium salts may be prepared from the appropriate aromatic amines, this synthesis is fairly general and compounds (44a)-(44x) have been prepared from the appropriate starting materials. 6-Alkyl-1,6a-dithia-5,6-diazapentalenes, however, may not be synthesised in this way, since stable aliphatic diazonium salts are not known. Treatment of 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (61a) with an arenediazonium fluoroborate gave, as well as the dithiadiazapentalene, a second product (62). This arises from reaction of the initially-formed dithiadiazapentalene with the excess of the diazonium salt by electrophilic attack at the 4-position. A series of these diazo-coupling reactions are described in a later section [D, (a), (i)]. Dithiadiazapentalenes (44c), (44d), (44g), (44h), (44k), (44 l),



62

(a) Ar = Ph
(b) Ar = p-$NO_2C_6H_4$
(c) Ar = p-$MeOC_6H_4$
(d) Ar = p-$MeCOC_6H_4$
(e) Ar = p-MeC_6H_4
(f) Ar = p-BrC_6H_4



63

	R^I	R^2	R^3
(a)	Me	H	H
(b)	H	Me	Me

64

	R^I	R^2	R^3	Ar
(a)	Me	H	H	Ph
(b)	H	Me	Me	Ph
(c)	Me	H	H	p-$NO_2C_6H_4$
(d)	H	Me	Me	p-$NO_2C_6H_4$
(e)	Me	H	H	p-$MeOC_6H_4$

(44m), (44p), (44q), (44t) and (44u), in which the 4-position is blocked by alkyl substituents to electrophilic attack, were obtained in very high yield, whereas compounds (44a), (44b), (44e), (44f), (44i), (44j), (44n), (44o), (44r) (44s), (44v), (44w) and (44x), in which the 4-position is open to electrophilic attack, were obtained in much lower yield. Compounds (62), however, were isolated only from the reactions of the dithiolium salt (61a) with arenediazonium fluoroborates.

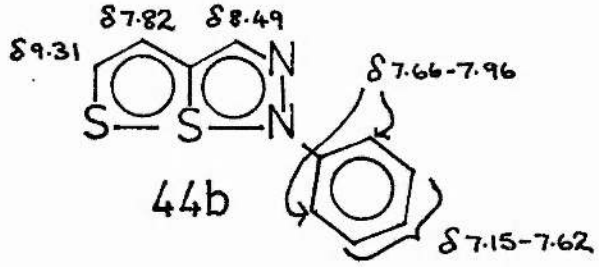
An analogous synthesis of derivatives of the 1,6a-diselena-5,6-diazapentalene system (64), another new heterocyclic system of the 1,6,6a-trithiapentalene type, has been devised. Compounds (64a)-(64e) were prepared by the reaction of the 3-methyl(ene)-1,2-diselenolium salts (63) with arenediazonium fluoroborates.

6-Phenyl-, 6-p-methoxyphenyl-, 6-p-bromophenyl- and 6-p-tolyl-1,6a-dithia-5,6-diazapentalenes are orange to red crystalline solids which are soluble in organic solvents, while the 6-p-nitrophenyl and 6-p-acetylphenyl compounds are deeper red and less soluble. These compounds are stable at their melting points which range from 95-96° (44b) up to 267-268° (44i). 1,6a-Diselena-5,6-diazapentalenes are deep purple crystalline solids which show similar solubility and melting point characteristics.

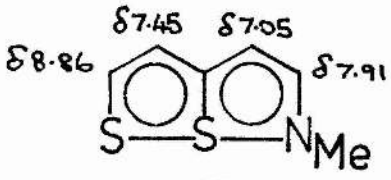
X-ray crystallography and a variety of spectroscopic techniques, especially ^{1}H nmr, have played an important role in investigations into the structure of 1,6,6a-trithiapentalenes and related systems. 1,6a-Dithia-5,6-diazapentalenes were therefore studied by the techniques of nmr, uv, and mass spectroscopy and by X-ray crystallography with a view to determining whether these systems should be formulated as bicyclic species of the 1,6,6a-trithiapentalene type.

(b) Nmr spectra

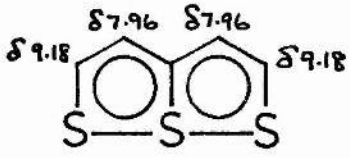
Nmr data for the dithiadiazapentalenes (44a)-(44x) are contained in Table A2, and for the diselenadiazapentalenes (64a)-(64e) in Table



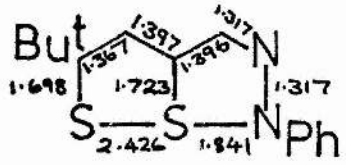
44b



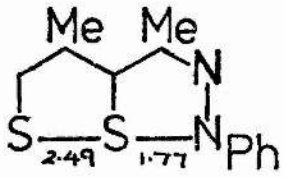
65



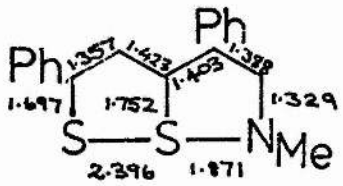
66



44a



44c



67

Bond lengths in Å

A3. The 2-, 3- and 4-proton signals of 6-phenyl-1,6a-dithia-5,6-diazapentalene (44b) (δ9.31, 7.82, and 8.49 respectively) occur at lower field than those of 6-methyl-1,6a-dithia-6-azapentalene (65)[53] (δ8.86, 7.45 and 7.05 respectively). The difference in chemical shifts is largest for the 4-proton (1.44 ppm) as this experiences the largest deshielding effect from the adjacent 5-nitrogen atom. The difference is smaller for the 2- and 3-protons (0.45 and 0.37 ppm respectively) although still appreciable, and the deshielding may be due in part to the additional nitrogen atom, and in part to an increased ring current in compound (44b) compared with compound (65). The deshielding may also be partly due to the fact that compound (44b) contains an N-phenyl group, whereas compound (65) contains an N-methyl group, although this effect would not be expected to be large. The similarity of the chemical shifts of the 2- and 3-protons in compound (44b) (δ9.31 and 7.82) to those in 1,6,6a-trithiapentalene (66)[22] (δ 9.18 and 7.96) suggests that the two molecules possess similar ring currents. The protons in the phenyl ring in compound (44b) which are meta and para to the 6-nitrogen atom give rise to a multiplet (δ7.15-7.62) while the two ortho protons form a multiplet (δ7.66-7.96) which is at lower field because of the deshielding effect of the adjacent nitrogen atom. When the phenyl ring contains a substituent in the para position, the ortho and meta protons give rise to an AA'BB' system as in para-disubstituted benzene derivatives. A nitro group in this para-position causes a downfield shift not only of the adjacent benzene ring protons, but also of the dithiadiazapentalene ring protons, although this latter shift is only of 0.06-0.13 ppm. A para-methoxy group causes an upfield shift of these protons of comparable size. A comparison of the nmr data for the diselena-diazapentalene (64b) and the corresponding dithiadiazapentalene (44c) reveals that the replacement of the two sulphur atoms by selenium in this system causes a marked downfield shift of the

2-proton (1.17 ppm), an effect which has been observed in the case of a number of selenium analogues of trithiapentalene[168].

(c) Electronic spectra

The electronic spectrum of a dithiadiazapentalene shows two strong absorption bands in the ranges 202-209 nm and 225-258 nm. There is also a band of medium intensity in the visible region in the range 483-521 nm, which is responsible for the orange colour of the solutions. This band occurs at longer wavelength in the spectra of compounds containing substituents in the 3- and 4-positions compared with the spectra of compounds containing no substituents, an effect which has also been encountered in the spectra of trithiapentalenes[124] and a number of related systems[161]. The electronic spectra of diselenadiazapentalenes similarly show two intense bands (202-216 nm) and (244-251 nm) and a medium intensity band in the visible region (529-561 nm) responsible for the red colour of solutions of these compounds.

(d) X-ray crystallography

All the reactions of 1,6,6a-trithiapentalenes, 1-oxa-6,6a-dithiapentalenes and 1,6a-dithia-6-azapentalenes with arenediazonium salts lead to derivatives of the 1,6a-dithia-5,6-diazapentalene system (see Part B). Because rearrangement to the dithiadiazapentalene is invariably preferred to formation of the normal substitution product, in which the trithiapentalene, oxadithiapentalene, or dithiaazapentalene system is retained, it has been suggested that a sulphur-nitrogen bond must be present in the dithiadiazapentalene system. Conclusive evidence for this bond has now been provided by X-ray crystal structure determinations of compounds (44a) and (44c)[170]. The sulphur-nitrogen bond length in compound (44a) (1.841 Å) is longer than the sum of the covalent radii (1.74 Å)[74], but considerably shorter than the sum of the van der Waal's radii

(3.35 Å)[74]. This indicates a significant S--N interaction which does not, however, amount to a full single bond. The sulphur-nitrogen distance in compound (44c) (1.77 Å) is only slightly longer than the sum of the covalent radii (1.74 Å) and indicates a stronger interaction. The sulphur-sulphur bond lengths in compounds (44a) and (44c) (2.426 Å and 2.49 Å respectively)are similar to those in certain trithiapentalenes. The sulphur-sulphur and sulphur-nitrogen distances (2.396 Å and 1.871 Å respectively) in the 1,6a-dithia-6-azapentalene (67)[119] indicate that a stronger S---S and a weaker S--N interaction are present in compound (67) than in the dithiadiazapentalenes (44a) and (44c).

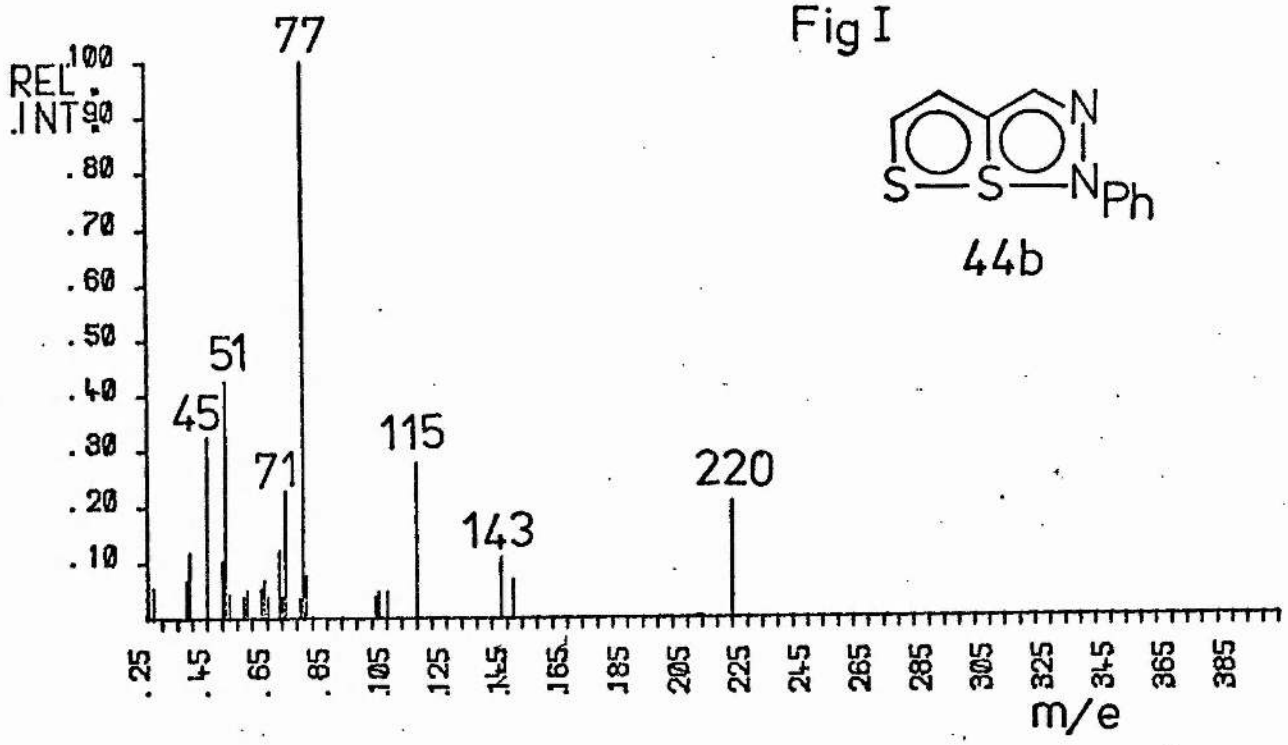
It has already been noted [see Part 1, D, 1, (a)] that, while the individual sulphur-sulphur distances in trithiapentalenes may vary by as much as 0.4 Å, the total sulphur-sulphur distance remains fairly constant. A similar effect is observed with compounds (44a), (44b) and (67) as indicated by the sum of the sulphur-sulphur and sulphur-nitrogen distances (4.267 Å, 4.26 Å and 4.267 Å respectively). The carbon-sulphur and carbon-carbon bond lengths in compound (44a) are similar to those in trithiapentalenes, while the carbon-nitrogen distance (1.317 Å) and nitrogen-nitrogen distance (1.317 Å) indicate bond orders of between one and two[74].

It is clear from these results that, structurally, the 1,6a-dithia-5,6-diazapentalene system is closely related to the 1,6,6a-trithiapentalene system. The bonding in dithiadiazapentalenes may therefore be described by an approach analogous to that proposed by Gleiter and Hoffmann[146] for trithiapentalenes [see Part 1, E]. S-1, S-6a and N-6 are linked by a three-centre four-electron bond which forms part of the σ-framework of the system, and a 10π-electron system is superimposed.

(e) Mass Spectra

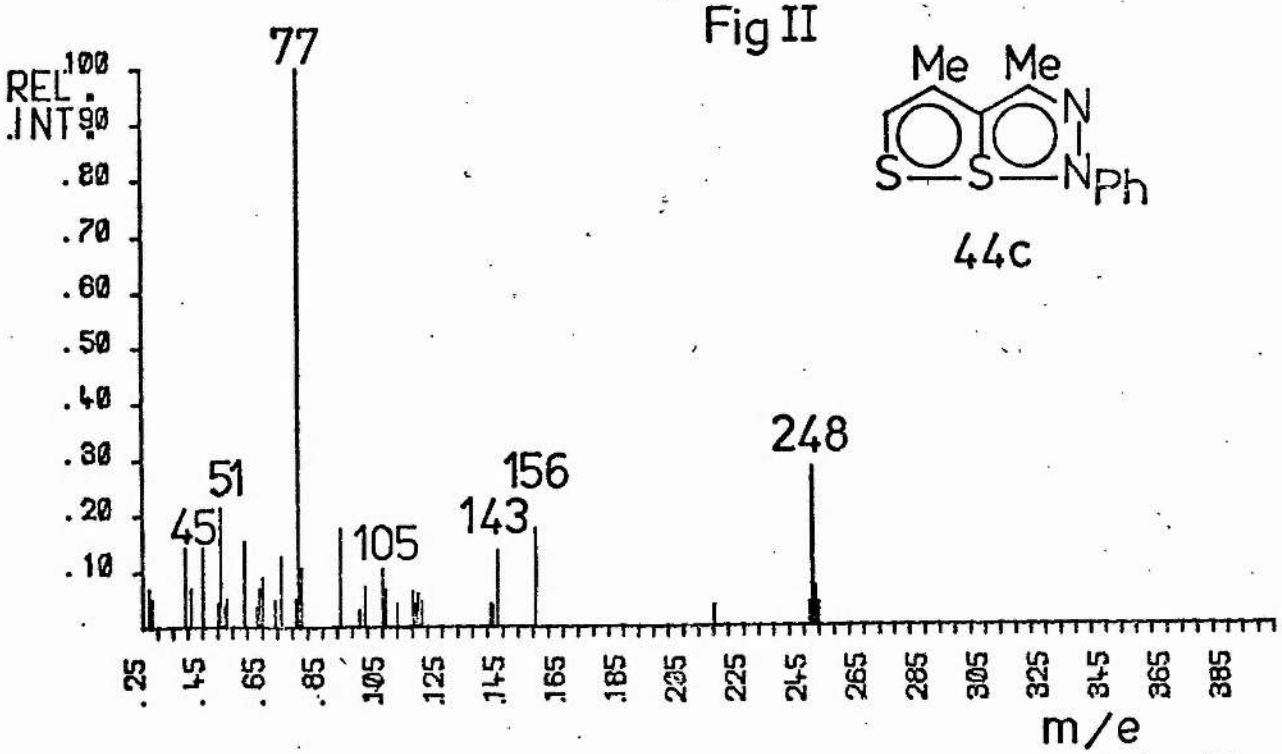
The mass spectra of all the 1,6a-dithia-5,6-diazapentalenes

Fig I



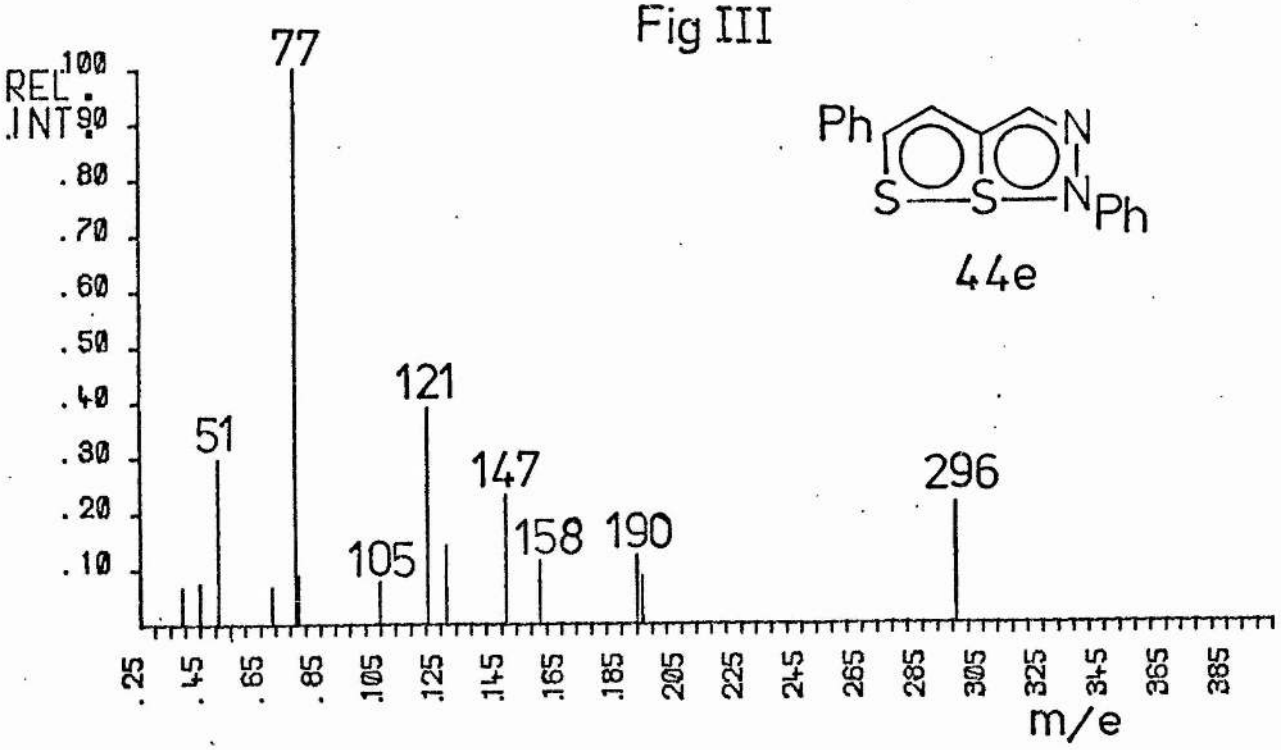
44b

Fig II



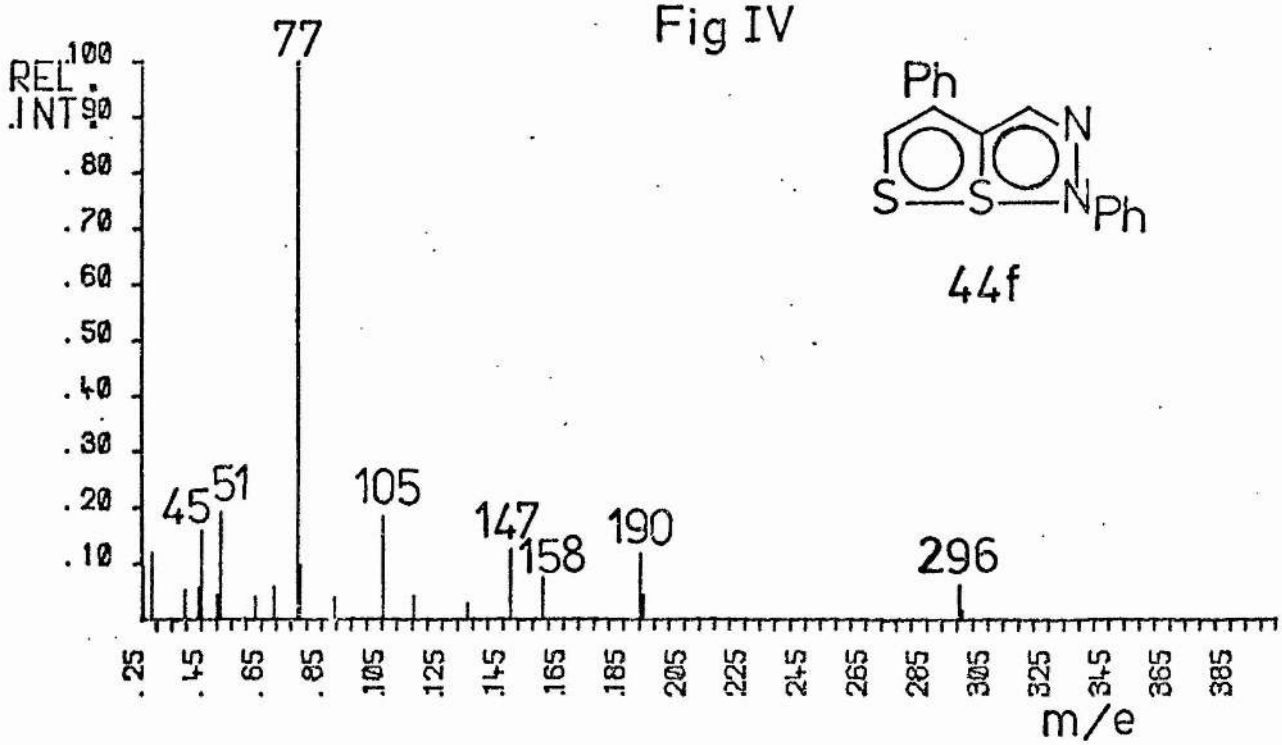
44c

Fig III



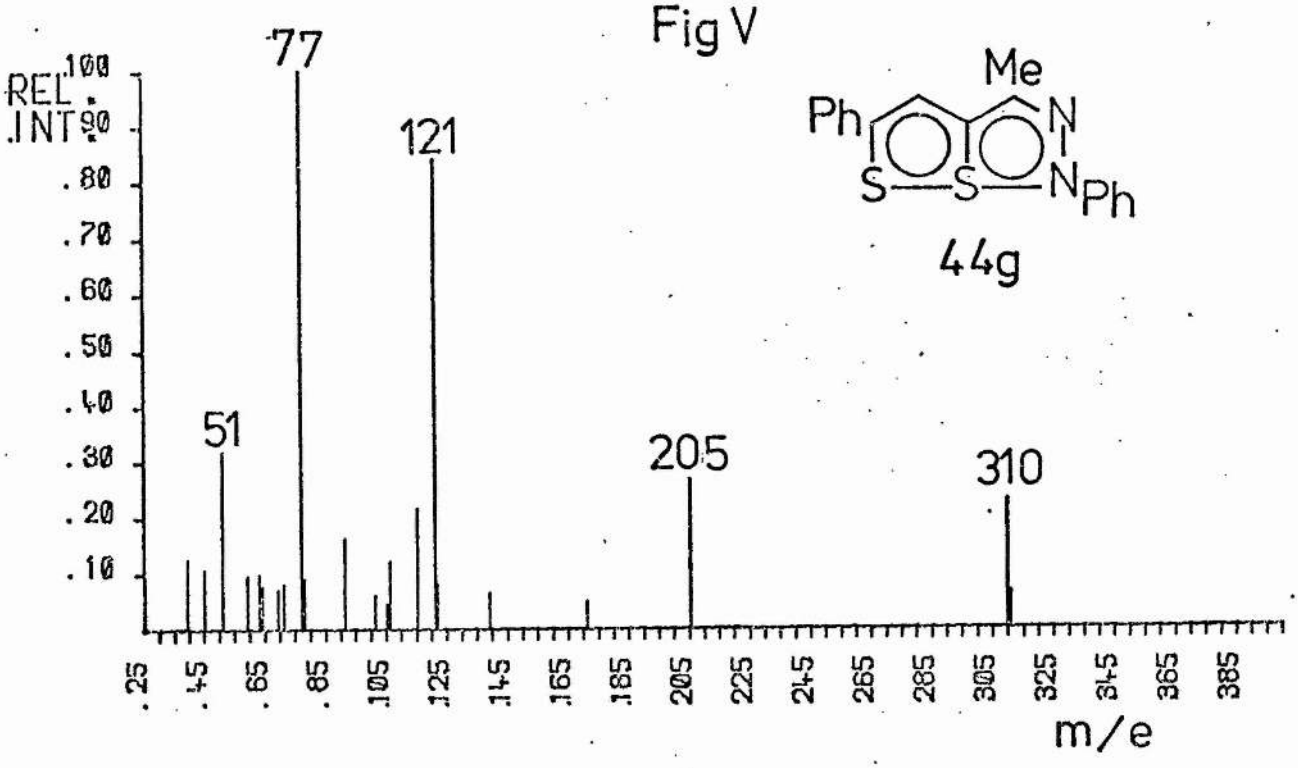
44e

Fig IV



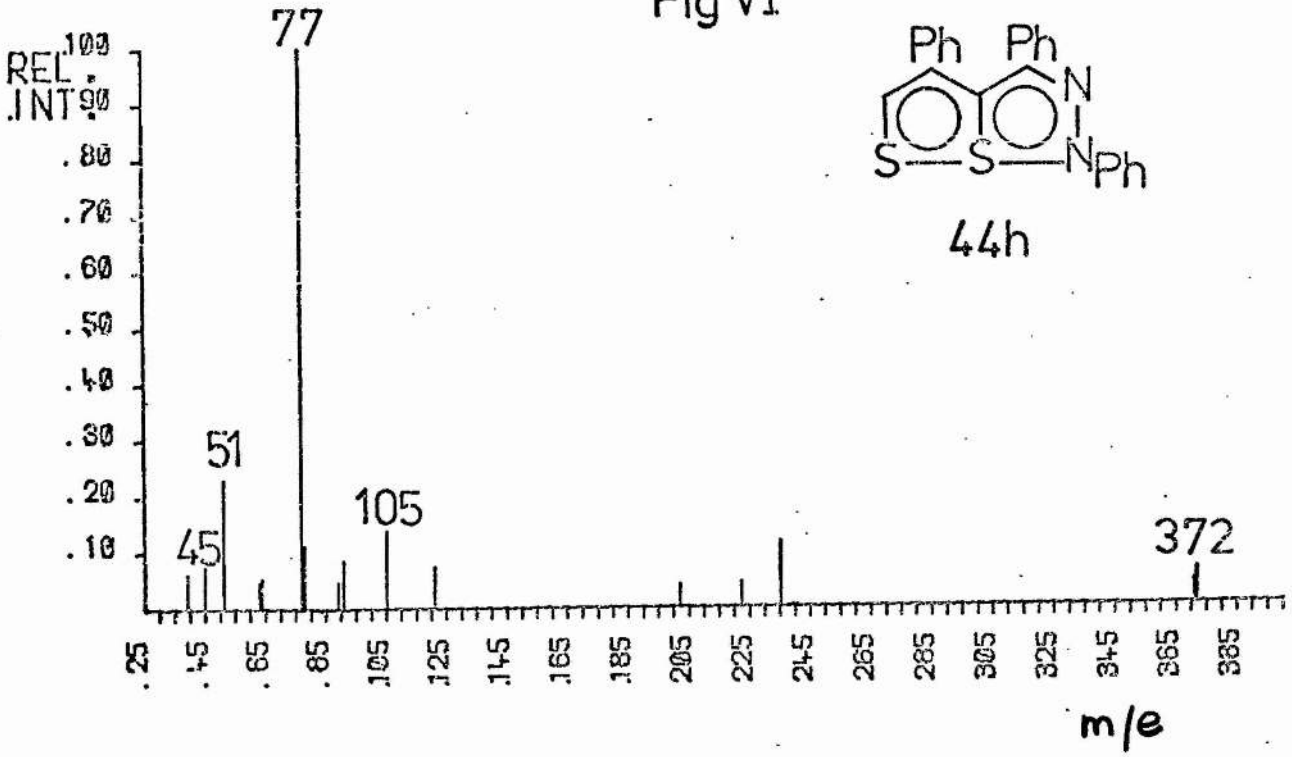
44f

Fig V



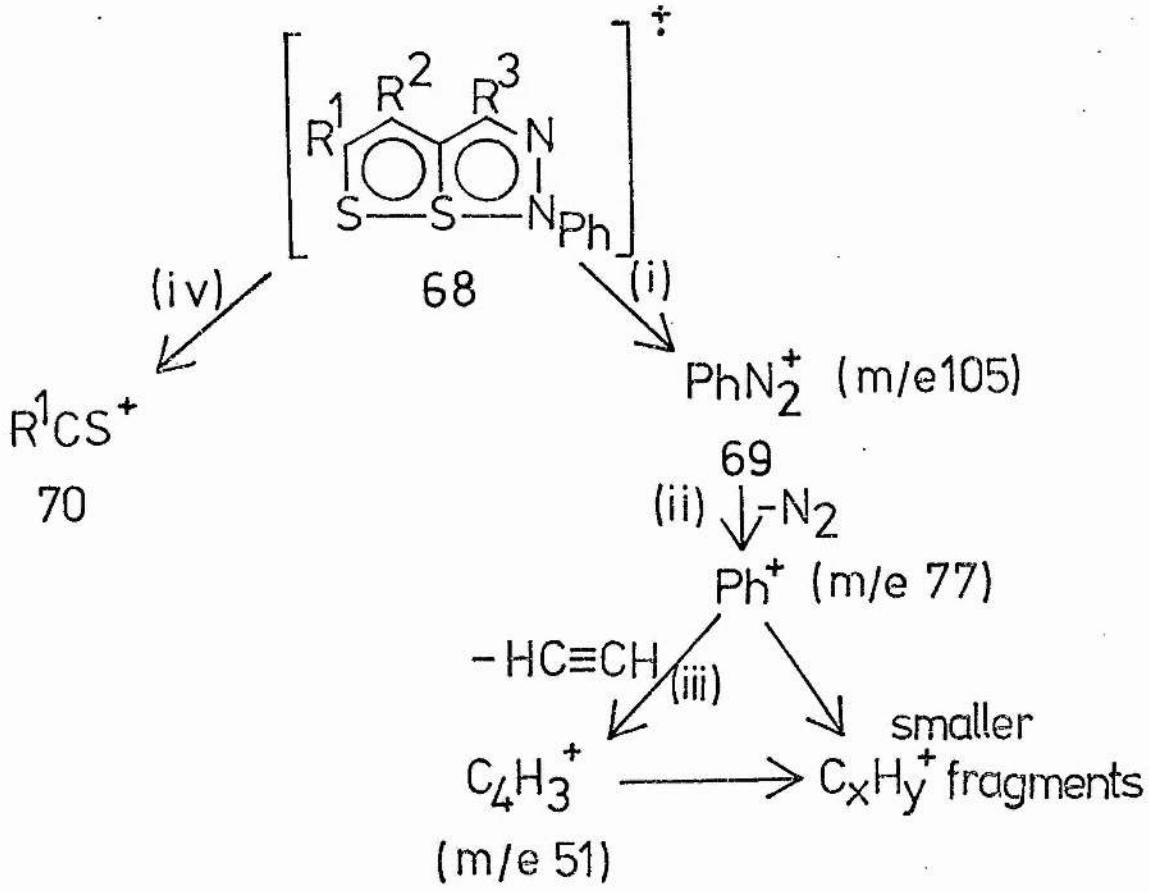
44g

Fig VI

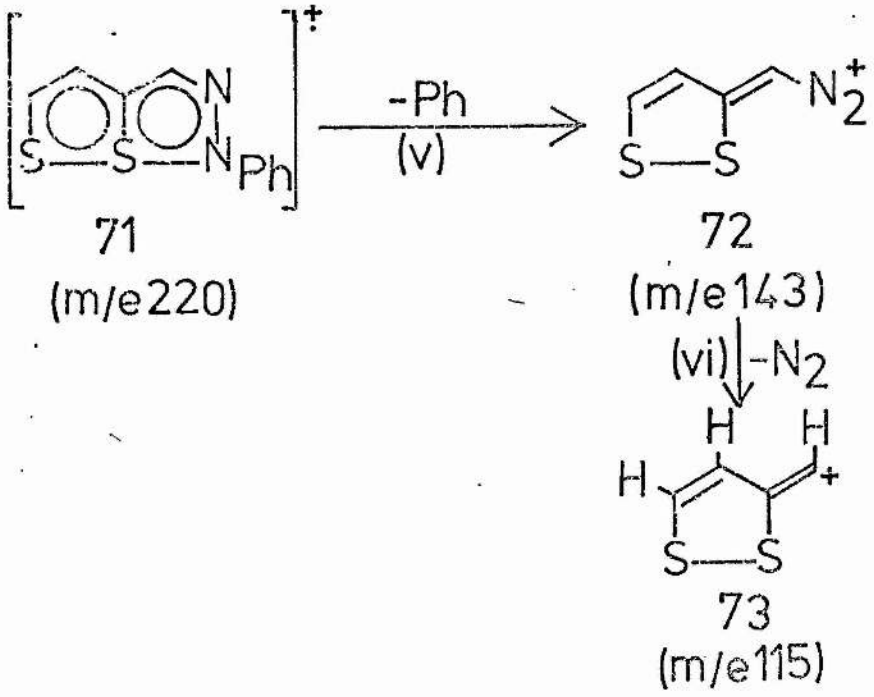


44h

Scheme V

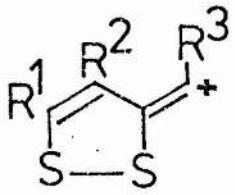


Scheme VI



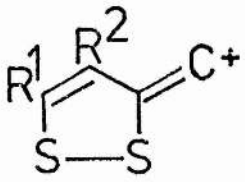
obtained were recorded, and their molecular ions were used to assist in the characterisation of the compounds. A detailed study of the breakdown pathways, however, was restricted to compounds containing only methyl and phenyl substituents, as more highly substituted compounds gave rise to very complex spectra which did not conform to a general pattern. The mass spectra of compounds (44b), (44c), (44e), (44f), (44g) and (44h) are shown in Figs I-VI respectively.

The base peak in the spectra of all the 6-phenyl-1,6a-dithia-5,6-diazapentalenes studied corresponds to the phenyl cation (m/e 77), and it is often very much more intense than any other peak in the spectra. The molecular ion peak is observed in all the spectra, and its intensity ranges from 6 to 29% of that of the base peak. The major breakdown pathway in the mass spectra of these systems is clearly established and is illustrated in Scheme V. The molecular ion (68), which is formed initially, decomposes to give the benzenediazonium cation (69) (m/e 105), which is observed in all the spectra, although the peak is often of very low intensity, probably because the ion decomposes very rapidly to form the phenyl cation, with accompanying loss of N_2. The phenyl cation then breaks down to a number of smaller $C_xH_y^+$ fragments, notably $C_4H_3^+$ (m/e 51), which arises from loss of C_2H_2 from the phenyl cation, and $C_3H_3^+$ (m/e 39). Metastable peaks corresponding to the transitions (i), (ii), and (iii) in Scheme V are observed in all cases, unless the peak is obscured by other more intense peaks. Another pathway which appears to be followed is the formation of the fragment R^1CS^+ (70) from the molecular ion [transition (iv) in Scheme V]. Compounds (44b), (44c), (44f) and (44h) give rise to the HCS^+ ion (m/e 45) and the peak intensity is in the region 7-37%, while compounds (44e) and (44g) form the $PhCS^+$ ion (m/e 121), which is stabilised by the phenyl group and whose peak is more intense (39% and 84% respectively). A metastable peak corresponding to the transition (iv) is observed



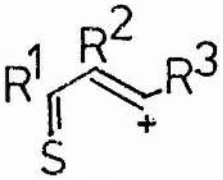
74

Cpd	m/e
44b	II5
44c	I43
44e	I9I
44g	205



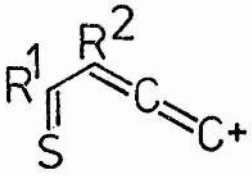
75

Cpd	m/e
44e	I90
44f	I90



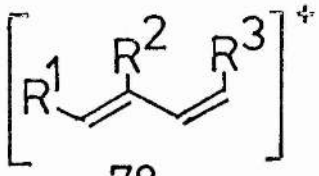
76

Cpd	m/e
44b	7I
44e	I47
44f	I47



77

Cpd	m/e
44e	I58
44f	I58



78

Cpd	m/e
44b	5I
44e	I27

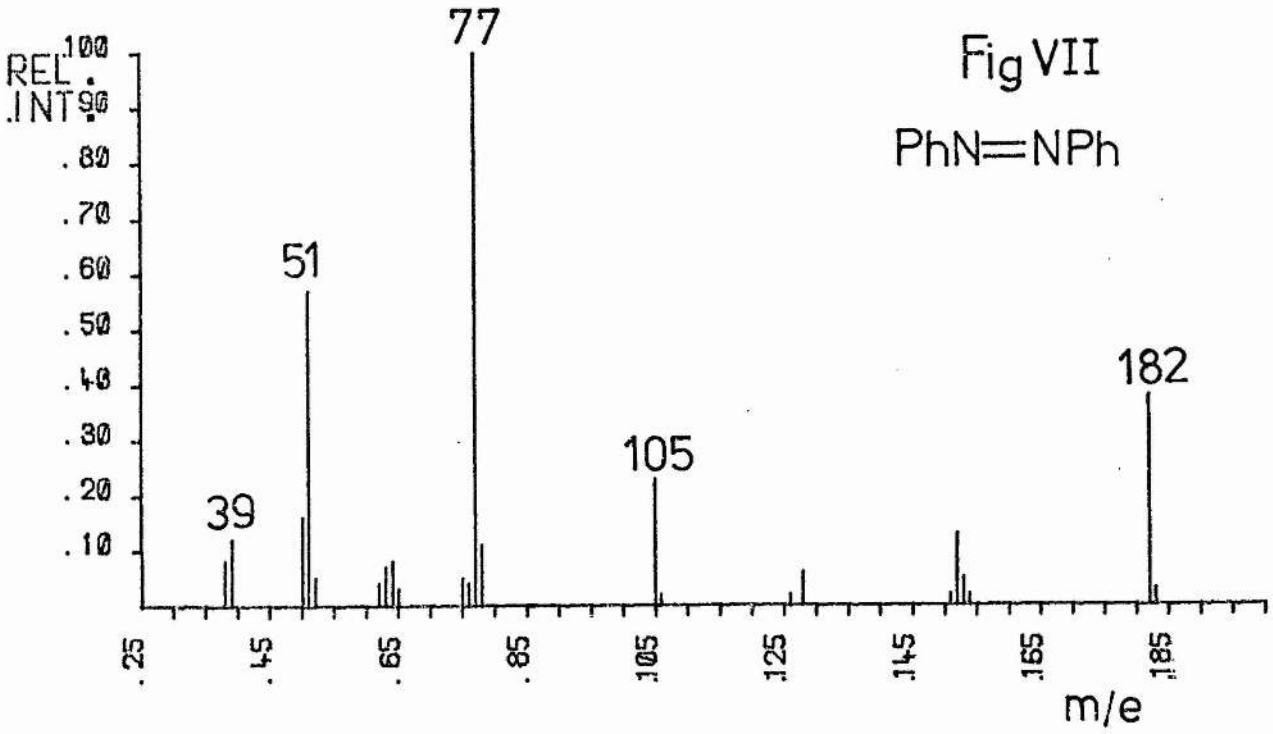
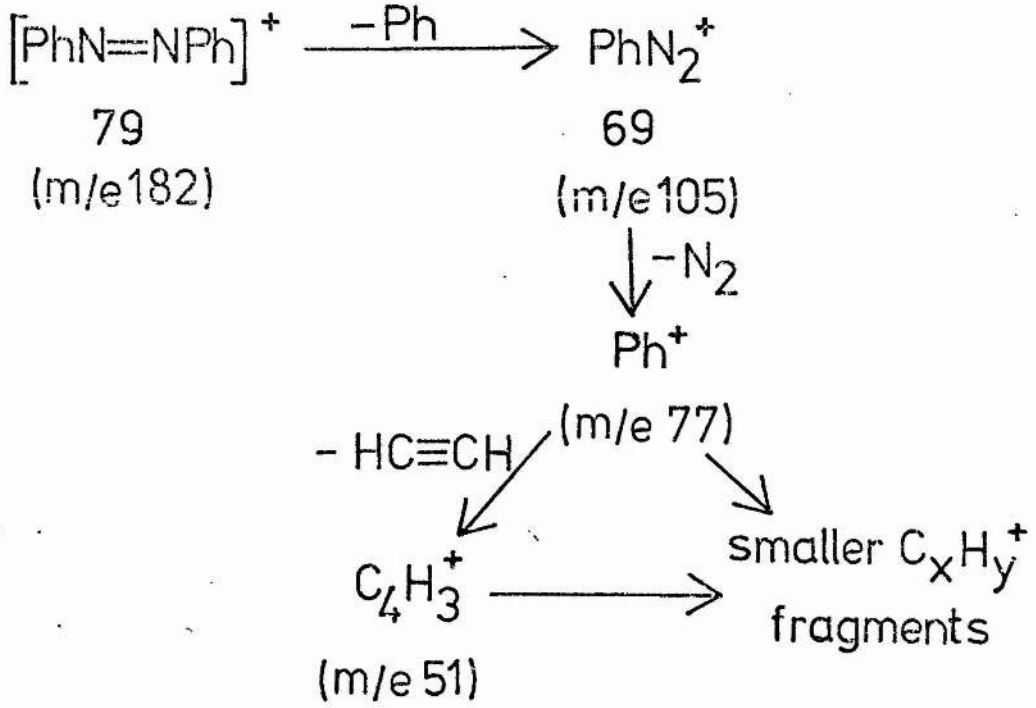


Fig VII

PhN=NPh

Scheme VII



in the spectrum of compound (44g). Other minor decomposition processes are observed, but they do not conform to any general pattern. Scheme VI, however, illustrates a third pathway for compound (44b), which is established by the presence of peaks arising from structures (72) (m/e 143) and (73) (m/e 115) together with a metastable peak corresponding to the transition (vi). Elimination of the phenyl group from the molecular ion (71) gives the ion (72), which subsequently loses N_2 to give the ion (73). Peaks corresponding to fragments for which structures (74)-(78) are tentatively proposed also occur in the spectra of these compounds, but the intensities are low (less than 15%), and they cannot be fitted into a general breakdown pattern.

The mass spectra of 1,6a-dithia-5,6-diazapentalenes are very unlike the spectra of 1,6,6a-trithiapentalenes[171]. The spectra of trithiapentalenes exhibit intense molecular ion peaks, which are frequently the base peaks, and the main fragmentation routes are loss of H and of SH from the molecular ions. The spectra of trithiapentalenes containing a 2-phenyl substituent, however, show an intense peak corresponding to $PhCS^+$ (m/e 121)[171], as do the spectra of compounds (44e) and (44g). The mass spectra of dithiadiazapentalenes are similar to those of aromatic azo compounds[172]. The base peak in the spectrum of azobenzene (Fig VII), for example, corresponds to the phenyl cation (m/e 77), and the major breakdown pathway, illustrated in Scheme VII, is analogous to the major breakdown pathway of dithiadiazapentalenes (Scheme V). Loss of a phenyl group from the molecular ion (79) gives rise to the benzenediazonium cation, which subsequently decomposes to give the phenyl cation with loss of N_2. Breakdown of the phenyl cation gives smaller $C_xH_y^+$ fragments, notably $C_4H_3^+$ (m/e 51) and $C_3H_3^+$ (m/e 39)[172].

D. Reactivity of 1,6a-Dithia-5,6-diazapentalenes

The results of the structural studies discussed in Part C demonstrate that, structurally, the 1,6a-dithia-5,6-diazapentalene system is closely related to the 1,6,6a-trithiapentalene system. It was of interest, therefore, to investigate whether 1,6a-dithia-5,6-diazapentalenes would undergo reactions similar to those of 1,6,6a-trithiapentalenes. The convenient synthesis of dithiadiazapentalenes from the reactions of 1,2-dithiolium salts with arenediazonium salts [see C,(a)] made a range of compounds available in quantities sufficient for a detailed study of their reactivity.

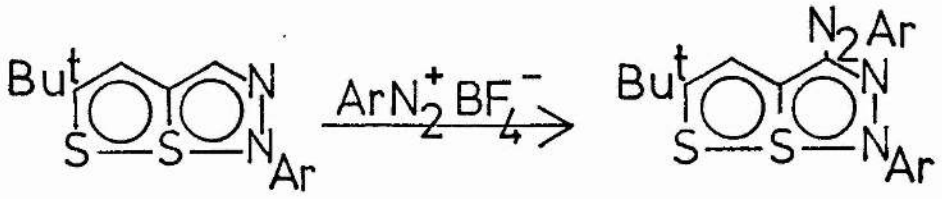
(a) Electrophilic Substitution

A number of electrophilic substitution reactions of 1,6a-dithia-5,6-diazapentalenes were carried out. Substitution at the 4-position was found to occur, in some cases to give the normal substitution product, and in some cases to give a rearranged product. Substitution at the para-position in the benzene ring was also observed in a few cases.

(i) Diazo-coupling

It has already been shown [see C,(a)] that in the synthesis of the dithiadiazapentalenes (44a), (44i), (44n), (44r), (44v) and (44w), further products (62a)-(62f) respectively were isolated. A number of reactions of dithiadiazapentalenes with arenediazonium salts were therefore carried out to investigate the formation of compounds (62) and to provide examples of the electrophilic substitution of the dithiadiazapentalene system.

Initially, the reaction of 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) with benzenediazonium fluoroborate and of 6-p-methoxyphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44n) with p-methoxybenzenediazonium fluoroborate were carried out with acetonitrile as reaction solvent, and gave compounds (62a) and (62c) respectively in low yield. When ethanol was used as solvent,

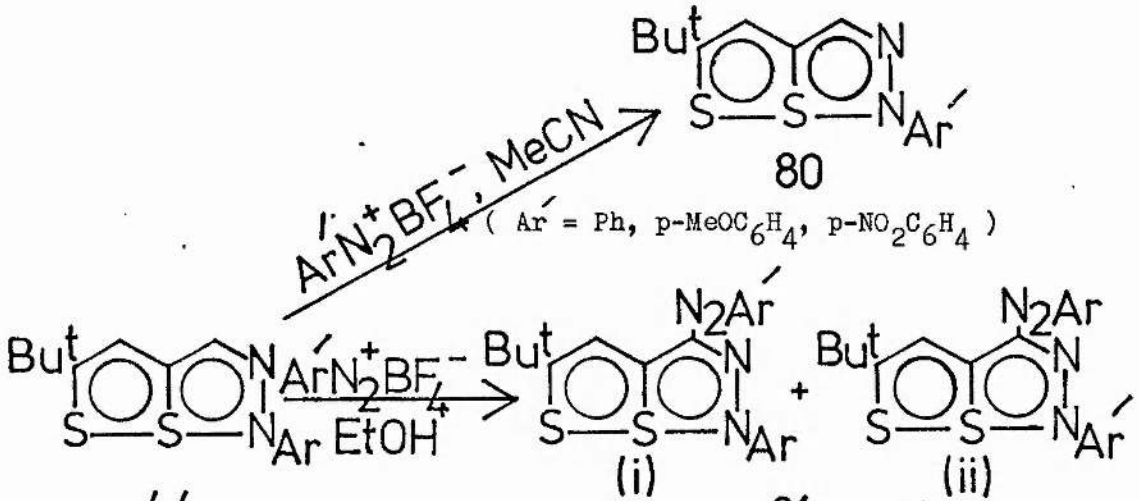


44

(a) Ar = Ph
(n) Ar = p-$MeOC_6H_4$
(r) Ar = p-$MeCOC_6H_4$
(v) Ar = p-MeC_6H_4
(w) Ar = p-BrC_6H_4

62

(a) Ar = Ph
(c) Ar = p-$MeOC_6H_4$
(d) Ar = p-$MeCOC_6H_4$
(e) Ar = p-MeC_6H_4
(f) Ar = p-BrC_6H_4



80

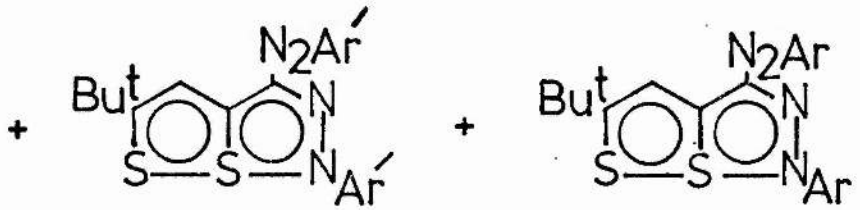
(Ar´ = Ph, p-$MeOC_6H_4$, p-$NO_2C_6H_4$)

44

(a) Ar = Ph
(n) Ar = p-$MeOC_6H_4$

81

(a) Ar = Ph, Ar´ = p-$MeOC_6H_4$
(b) Ar = Ph, Ar´ = p-$NO_2C_6H_4$
(c) Ar = p-$MeOC_6H_4$, Ar´ = p-$NO_2C_6H_4$



82

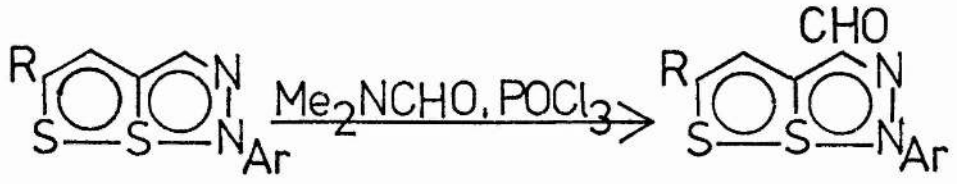
62

however, the coupled products (62a) and (62c)-(62f) were obtained from the reaction of the appropriate dithiadiazapentalenes and diazonium salts in high yield. This difference is attributed to the greater basicity of ethanol compared with acetonitrile. It is well-established that diazo-coupling reactions are facilitated by the presence of a base which removes a proton from the intermediate, failing which ejection of the diazonium ion competes successfully proton loss[173,174].

In the foregoing examples the aryl group in the substrate and in the arenediazonium salt were the same. A series of reactions were then carried out in which these groups were different. Again it was found that the reactions were solvent-dependent. When the reactions were carried out in acetonitrile, the diazonium group in the substrate was displaced by the incoming diazonium group to yield the new dithiadiazapentalene (80). Partial conversion occurred when the incoming group was less electrophilic than the displaced group, ie., $pMeOC_6H_4N_2^+$ displacing PhN_2^+, and complete conversion when the incoming group was more electrophilic, ie., $pNO_2C_6H_4N_2^+$ displacing PhN_2^+ and $pMeOC_6H_4N_2^+$, and PhN_2^+ displacing $pMeOC_6H_4N_2^+$. When the reactions were carried out in ethanol, however, a complex mixture of products resulted. The major product in each case was an inseparable mixture of isomers (81a)-(81c), the composition of which was estimated by nmr spectroscopy. Smaller amounts of the coupled products (82) and (62) in which the two aryl groups in the molecule are the same, were also obtained from the reactions. The formation of these species requires firstly an elimination reaction in which the new dithiadiazapentalene (80) is formed. Compound (82) then results from the reaction of compound (80) with the excess of the diazonium salt present. Compound (62) is formed by the reaction of the original substrate with the new arenediazonium cation formed in the elimination reaction. A few examples of the substitution of a diazonium group by a more

electrophilic diazonium ion have been reported previously[175,176].

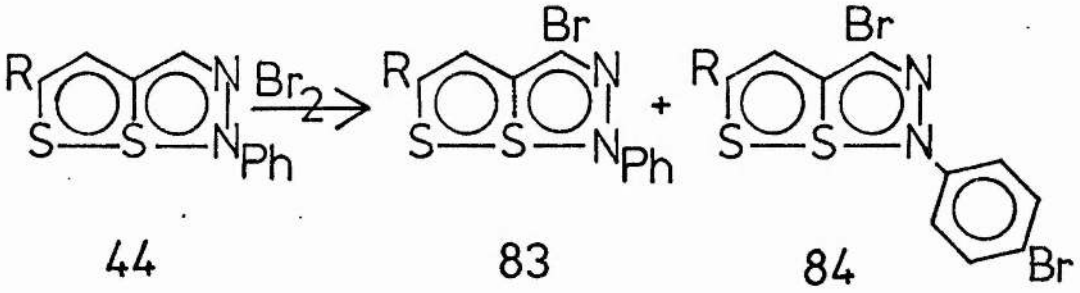
The nmr data for compounds (62a)-(62f) and (81a)-(81c) are contained in Table A4. The chemical shifts of the methyl groups in the 6-aryl ring and in the 4-arylazo ring in compounds (62c)-(62e) differ by 0.04-0.05 ppm. It is suggested that the signal at lower field is that of the methyl group in the arylazo ring, as this group will be experiencing the greatest deshielding effect due to the nitrogen-nitrogen double bond. The difference in these chemical shifts indicates that there is a S---S---N interaction present in these compounds. The nmr spectrum of compound (62c) in dimethylsulphoxide-d_6 showed two separate methoxy signals (δ3.80, δ3.85) at room temperature. As the temperature was raised these signals were seen to broaden until they coalesced at 86°, and at 120° a sharp singlet (δ3.84) remained. The benzene ring protons, which gave rise to two AA'BB' systems at room temperature, had collapsed to a single AA'BB' system at 120°. These results may be explained by the onset of rotation around the C(3a)-C(4) bond as the temperature is raised which makes the two aryl groups equivalent at high temperatures. The fact that the spectrum reverted to the original when the sample was allowed to cool to room temperature showed that the change was reversible. Unfortunately, compounds (62d) and (62e) were insoluble in dimethylsulphoxide-d_6 and dimethylformamide-d_7, and did not give separate methyl signals in nitrobenzene-d_5, bromobenzene-d_5 or deuteriobromoform. The nmr spectra of compounds (62c)-(62e) and (81a) in pyridine-d_5 showed non-equivalent methyl signals from room temperature up to 120°. From the integrals of the nmr spectra of the mixtures (81a)-(81c), the following isomer ratios were measured; (81a) (i):(ii) = 5:2, (81b) (i):(ii) = 2:3, and (81c) (i):(ii) = 1:4. The composition of the mixture (81a) was found to be independent of the method of preparation. Although the mixture (81c) was not obtained pure, as it could not be separated



44 20

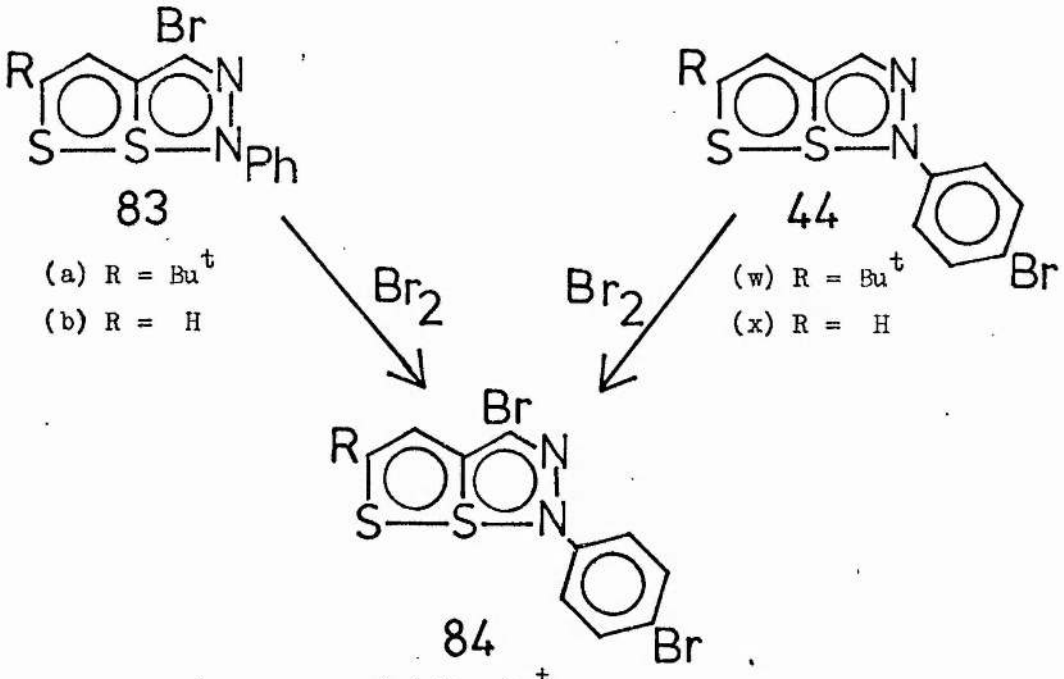
(a) R = Bu^t, Ar = Ph
(b) R = H , Ar = Ph
(i) R = Bu^t, Ar = p-$NO_2C_6H_4$
(j) R = H , Ar = p-$NO_2C_6H_4$

(d) R = Bu^t, Ar = Ph
(e) R = H , Ar = Ph
(a) R = Bu^t, Ar = p-$NO_2C_6H_4$
(b) R = H , Ar = p-$NO_2C_6H_4$



44 83 84

(a) R = Bu^t
(b) R = H



83
(a) R = Bu^t
(b) R = H

44
(w) R = Bu^t
(x) R = H

84
(a) R = Bu^t
(b) R = H

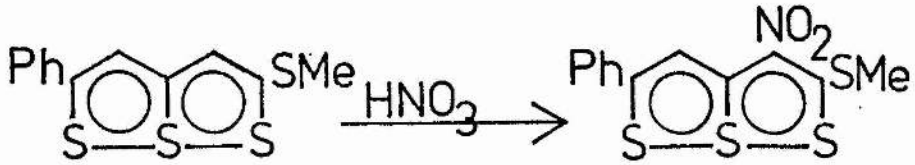
from compound (62b), its presence was demonstrated by nmr and mass spectrometry.

(ii) Formylation

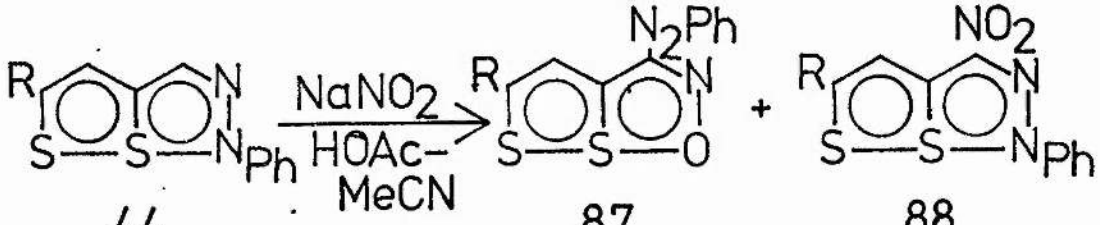
Vilsmeier-Haack formylation of the dithiadiazapentalenes (44a), (44b) and (44i) using phosphoryl chloride and dimethylformamide gave the aldehydes (20d),(20e) and (20a) respectively in yields of 57, 15 and 18%. These reactions provide further examples of electrophilic substitution at the 4-position of dithiadiazapentalenes. The aldehydes (20d),(20e) and (20a) had been obtained previously from the reaction of 1,6,6a-trithiapentalenes and related systems with arenediazonium fluoroborates [see B, (a)]. An attempt to formylate the dithiadiazapentalene (44j) was unsuccessful.

(iii) Bromination

Treatment of 6-phenyl-1,6a-dithia-5,6-diazapentalene (44b) with bromine in carbon tetrachloride gave two bromination products 4-bromo-6-phenyl-1,6a-dithia-5,6-diazapentalene (83b) (67%) and 4-bromo-6-p-bromophenyl-1,6a-dithia-5,6-diazapentalene (84b) (13%). The presence of an AB system (δ9.32 and δ7.92, J = 6.6Hz) attributed to the 2- and 3-protons, and the absence of a signal in the δ8.3-8.5 region in the nmr spectrum of compound (83b) indicated that bromination had taken place at the 4-position. In the same way, compound (44a) gave the monobromo compound (83a) (79%) and the dibromo compound (84a) (13%). The 6-p-bromophenyl compounds (44w) and (44x) and the 4-bromo compounds (83a) and (83b) each reacted with bromine, the latter less efficiently, to give the corresponding dibromo compounds (84a)and (84b). Compounds (84a) and (84b) may thus have resulted in the original reactions both from bromination of compounds (83a) and (83b) at the para-position in the benzene ring, and from prior para-bromination to give compounds (44w) and (44x) which subsequently reacted with the excess of bromine at the free 4-position.



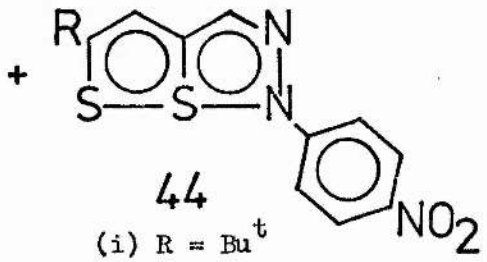
85 86



44 87 88

(a) R = Bu^t

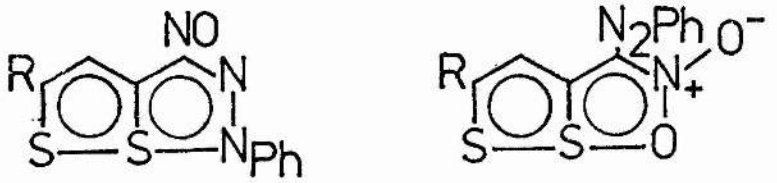
(b) R = H



44

(i) R = Bu^t

(j) R = H



89 90

(a) R = Bu^t

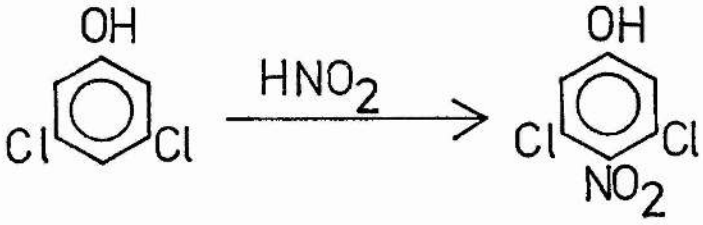
(b) R = H

(iv) Nitrosation and Nitration

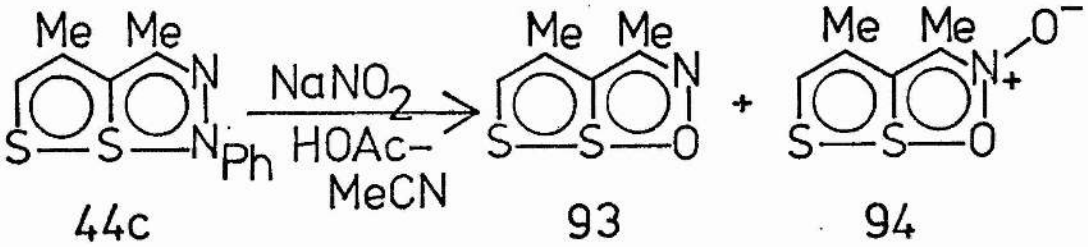
Bromination and formylation of 1,6a-dithia-5,6-diazapentalenes give the normal substitution products, in the same way as 1,6,6a-trithiapentalenes [see Part 1, C, (b)]. Nitrosation of trithiapentalenes, however, is accompanied by partial desulphurisation and rearrangement to derivatives of the 1-oxa-6,6a-dithia-2-azapentalene system[44-46], while attempted nitrations of trithiapentalenes generally lead to nitrosation products[42,45], although compound (85) was successfully converted into the nitro-compound (86)[45] by the action of nitric acid [See Part 1, C, (b)]. It was therefore of interest to investigate the reactions of 1,6a-dithia-5,6-diazapentalenes with nitrosating and nitrating reagents.

Three products were obtained from the reaction of the dithiadiazapentalene (44a) with sodium nitrite in acetic acid-acetonitrile 3-phenylazo-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene (87a), the major product, 4-nitro-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (88a) and 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i).

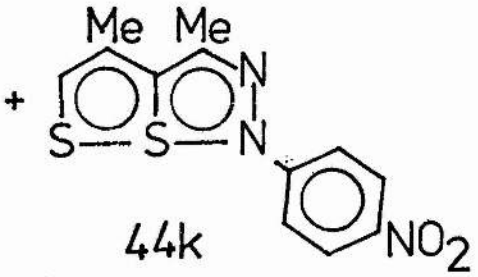
The structure of compound (87a) was confirmed by its uv spectrum. This was similar to the spectra of oxadithiaazapentalenes[68], and very unlike the spectra of dithiadiazapentalenes, a fact which rules out the isomeric structure (89a). Furthermore, the uv spectrum of a more concentrated solution of compound (87a) showed no N=O $n \longrightarrow \pi^*$ bands in the range (630-760 nm) which would have been expected of the spectrum of the structure (89a). On the other hand, structure (88a) was preferred to the isomeric 1-oxa-6,6a-dithia-2-azapentalene-2-oxide structure (90a), again on the basis of its uv spectrum, which shows the absorption bands characteristic of the dithiadiazapentalene system. The third product (44i) has already been prepared by the reaction of 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (61a) with p-nitrobenzenediazonium fluoroborate. Clearly, the major product (87a) resulted from nitrosation



91 92



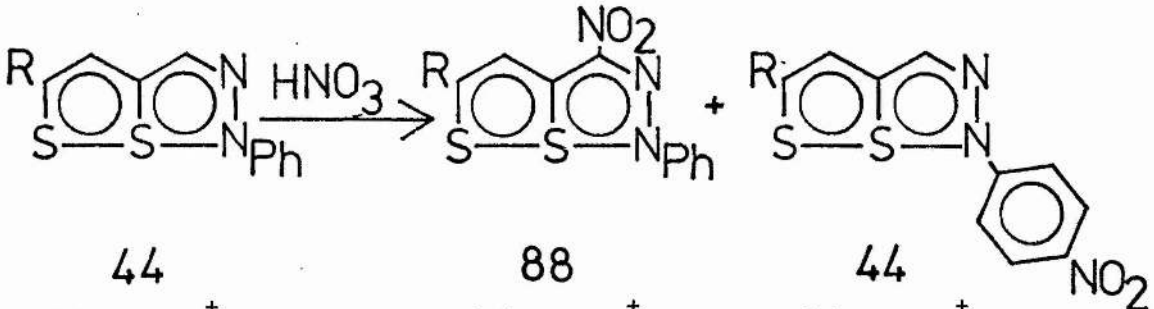
44c 93 94



44k

at the 4-position of the dithiadiazapentalene accompanied by a rearrangement to the oxadithiaazapentalene system. The possibility that the nitro compound (88a) had resulted from oxidation of compound (87a) was ruled out by the fact that compound (87a), when subjected to the nitrosation conditions, gave no trace of compound (88a) and was recovered almost quantitatively. It is probable, then, that compound (88a) resulted from direct nitration at the 4-position, and compound (44i) from nitration at the para-position in the benzene ring. Nitration by nitrous acid has been observed before. For example, attempted nitrosation of 3,5-dichlorophenol (91) gave 3,5-dichloro-4-nitrophenol (92)[177]. Treatment of 6-phenyl-1,6a-dithia-5,6-diazapentalene (44b) with sodium nitrite in acetic acid-acetonitrile also gave three products, namely the nitrosation product (87b), and, in small amount, the nitration products (88b) and (44j). The nmr spectrum of compound (88b) shows that the 2- and 3-protons give rise to an AB system (δ9.17 and 9.06, J = 6.6Hz), while, in the spectrum of compound (87b), a singlet (δ9.43) is attributed to the accidentally equivalent 4- and 5-protons.

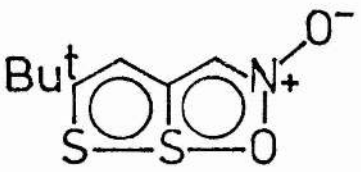
The reaction of 3,4-dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c), which carries a methyl group at the reactive 4-position, with sodium nitrite in acetic acid-acetonitrile afforded, as the major product, 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (93)[42], resulting from electrophilic attack by NO^+ at the 4-position and subsequent elimination of the benzenediazonium ion, together with small quantities of 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene-2-oxide (94)[42], from nitration with loss of the benzenediazonium ion, and 3,4-dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k), formed by nitration at the para-position in the benzene ring. As before, the formation of compound (94) by oxidation of compound (93) was discounted, because compound (93) was recovered nearly quantitatively when subjected to the reaction conditions. Diazonium cations have been



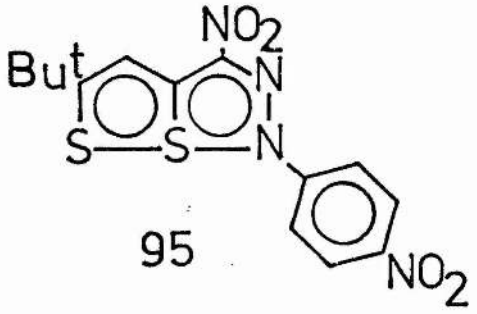
44 (a) R = Bu^t (b) R = H

88 (a) R = Bu^t (b) R = H

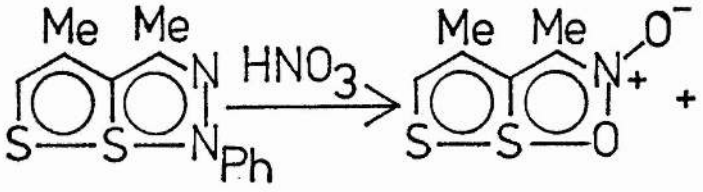
44 (i) R = Bu^t (j) R = H



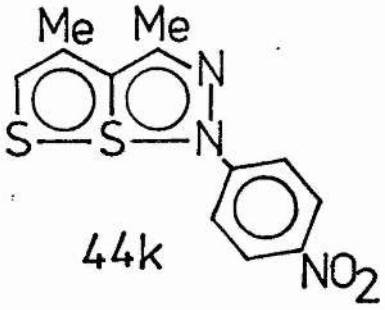
96



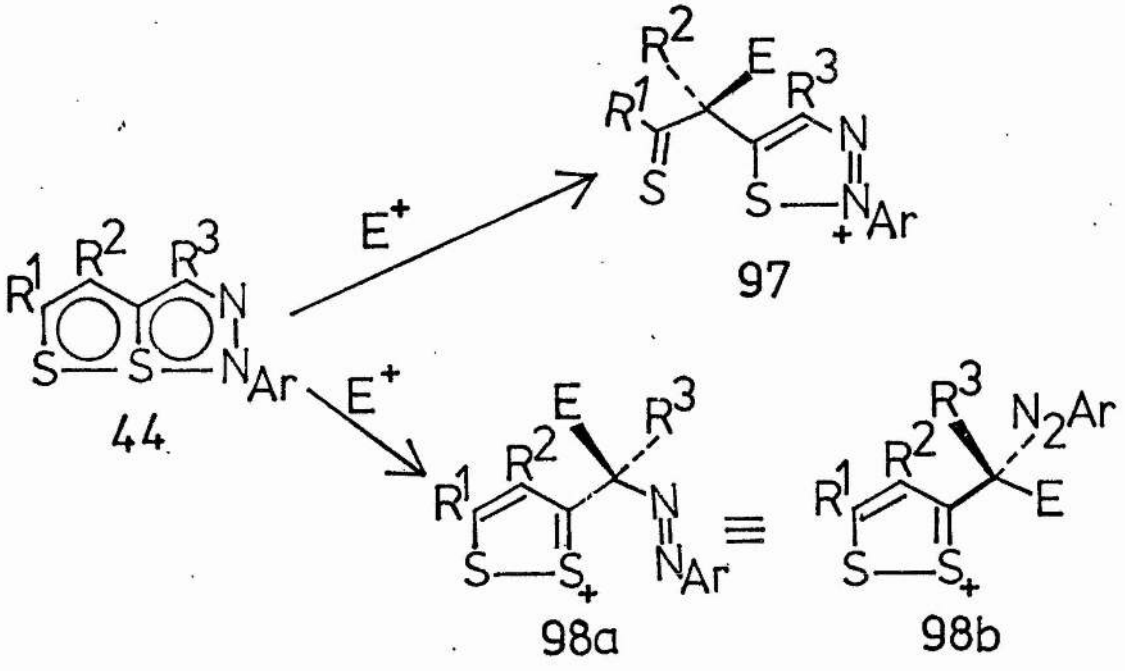
95



44c 94



44k



97

44

98a ≡ 98b

met with only infrequently as leaving groups in electrophilic substitution. A few examples of nitrosation[178] and nitration[176] reactions in which diazonium groups are lost have, however, been reported.

Because small amounts of nitration products were isolated from the reaction of dithiadiazapentalenes with nitrous acid, it seemed likely that nitration of dithiadiazapentalenes would be achieved using nitric acid. Brief treatment of the dithiadiazapentalenes (44a) and (44b) with nitric acid in acetic acid yielded compounds (88a) and (88b) respectively, formed by nitration at the 4-position, and compounds (44i) and (44j) respectively, from nitration at the para-position in the benzene ring. A third product, 4-nitro-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (95), was isolated from nitration of compound (44a). Compound (95) had previously been prepared by the reaction of 5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene-2-oxide (96) with p-nitrobenzenediazonium fluoroborate[69], while compounds (88a), (88b), (44i) and (44j) had previously been isolated as minor products in the reactions of compounds (44a) and (44b) with nitrous acid. The dinitro species (95) was formed by nitration of the mononitro compound (44i), whereas the mononitro compound (88a) was resistant to further nitration. This suggests that compound (95) resulted in the original reaction by nitration initially at the para-position in the benzene ring and subsequently at the 4-position. The dithiadiazapentalene (44c) was nitrated both at the 4-position with elimination of the benzenediazonium cation to give compound (94) and at the para-position in the benzene ring to yield compound (44k).

The various features of the electrophilic substitution of 1,6a-dithia-5,6-diazapentalenes are explained by a mechanism similar to that proposed for the electrophilic substitution of 1,6,6a-trithiapentalenes and related systems. Electrophilic attack at the 3-position, which would give rise to the monocyclic intermediate (97),

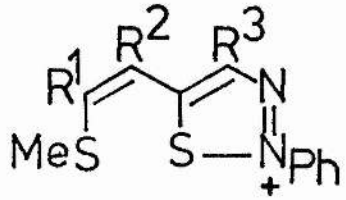
a derivative of the 1,2,3-thiadiazolium system, has so far not been encountered. Attack by an electrophile (E^+) at the 4-position of the dithiadiazapentalene (44) generates the 6π monocyclic intermediate (98), a derivative of the 1,2-dithiolium system. When the group R^3 is a proton, this may be eliminated either to give the normal substitution product via conformation (98a) or, if the group E is capable of interacting with the central sulphur atom, to give a rearranged product via conformation (98b). In the bromination and formylation of dithiadiazapentalenes, the group E (Br and $CH=\overset{+}{N}Me_2$) cannot interact with the central sulphur atom and the normal substitution product resulted. Nitration of dithiadiazapentalenes (44a) and (44b) led to the normal substitution products (88a) and (88b) respectively. Although, in principle, the nitro group is capable of interacting with the central sulphur to give the 1-oxa-6,6a-dithia-2-azapentalene-2-oxide structure (90), the dithiadiazapentalene structure (88) was preferred. Rearrangement to the 1-oxa-6,6a-dithia-2-azapentalene structure (87) was observed in the nitrosation of dithiadiazapentalenes, and rearrangements were also observed in some of the diazo-coupling reactions discussed in (i). When the group R^3 is methyl, nitrosation and nitration reactions involve elimination of the diazonium cation from conformation (98b) and a S--S--O interaction is generated. Bromination and nitration of 6-phenyl-1,6a-dithia-5,6-diazapentalenes gave small amounts of products arising from substitution at the para-position in the benzene ring. Substitution in the benzene ring was not observed in the diazo-coupling , formylation and nitrosation reactions, which involve weaker electrophiles.

(b) Methylation, and Synthesis of 6a-Thia-1,2,6-triazapentalenes

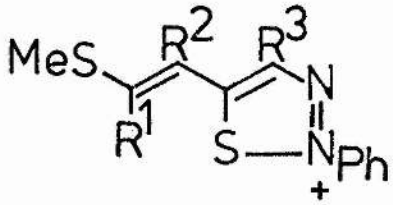
It has been shown [see Part 1, C, (a)] that 1,6a-dithia-6-azapentalenes[51,54-56] and 1,6,6a-trithiapentalenes[51] are methylated at sulphur by methyl iodide. Methylation of 1-oxa-6,6a-dithiapentalenes

44 99

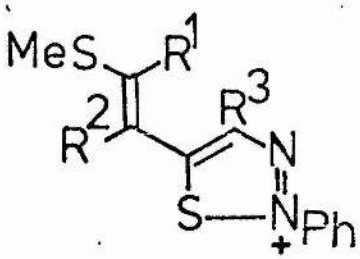
	R^1	R^2	R^3
(a)	Bu^t	H	H
(b)	H	H	H
(c)	H	Me	Me
(d)	H	$CH_2CH_2CH_2$	



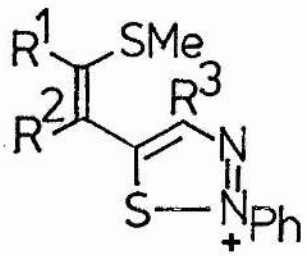
100a



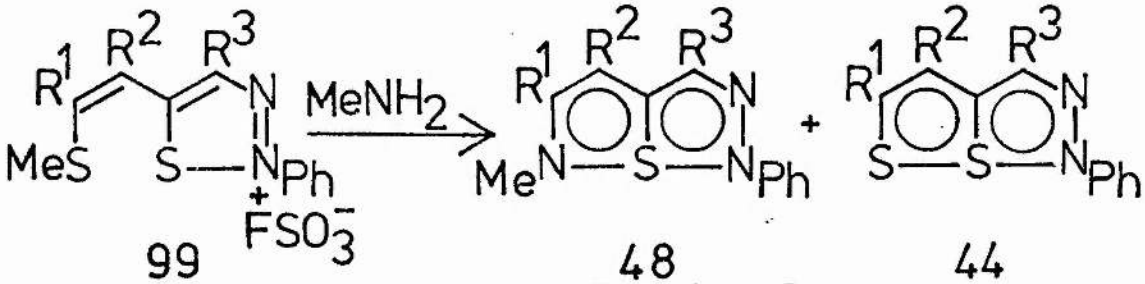
100b



100c



100d



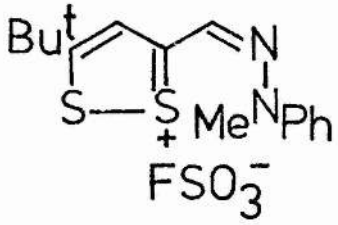
99 48 44

	R^1	R^2	R^3
(b)	H	H	H
(c)	H	Me	Me
(d)	H	$CH_2CH_2CH_2$	

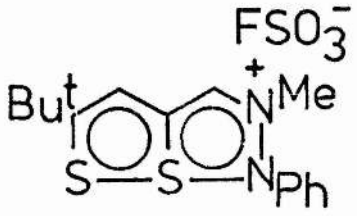
requires the use of the more powerful methylating agent, methyl fluorosulphonate, and takes place at oxygen[58]. It was of interest to investigate the methylation of 1,6a-dithia-5,6-diazapentalenes as part of a detailed study of the reactivity of this system.

Three possibilities for methylation were envisaged: S-1, N-5 or N-6. It was found that methylation of the dithiadiazapentalenes (44b)-(44d) took place at sulphur to give the 1,2,3-thiadiazolium salts (99b)-(99d) respectively. The reactions also required the use of methyl fluorosulphonate. There are four possible geometries (100a)-(100d) for these salts. Clearly, the bridged salt (99d) may only have the geometry(100a)or(100b) because of restrictions imposed by the trimethylene bridge. The trans configuration of the vinyl protons in 5-(2-methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium fluorosulphonate (99b) is indicated by the large coupling constant (15.4 Hz) for these protons, and either geometry (100b) or (100c) may be correct. The geometry of 4-methyl-5-(1-methyl-2-methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium fluorosulphonate (99c) cannot be deduced from its nmr spectrum. The chemical shifts of the methyl groups in compounds (99b)-(99d),(δ2.63, δ2.93 and δ2.93) are in the range expected for methylthio groups, and the absence of signals in the δ4 region demonstrates that N-methylation has not taken place. The occurrence of S-methylation was confirmed by treating the salts (99b)-(99d) with methylamine. This gave the 6a-thia-1,2,6-triazapentalenes (48b)-(48d), in a reaction analogous to that used for the synthesis of 6a-thia-1,6-diazapentalenes[55,56] [see Part 1, B, (c), (iii)]. The 1,6a-dithia-5,6-diazapentalenes (44c) and (44d), also isolated in small amount from the reaction of salts (99c) and (99d) with methylamine,arise by a demethylation reaction.

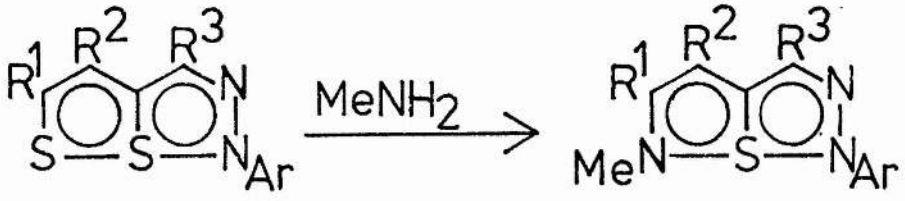
6-Phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) showed exceptional behaviour towards methyl fluorosulphonate. Complete methylation required a longer reaction time than that used for methylation of compounds (44b)-(44d), and the product was an oil



101a



101b

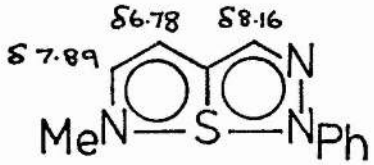


44

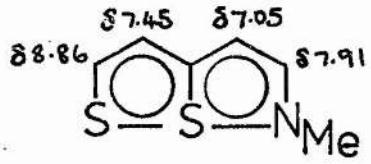
	R^1	R^2	R^3	Ar
(a)	Bu^t	H	H	Ph
(b)	H	H	H	Ph
(c)	H	Me	Me	Ph
(d)	H	$CH_2CH_2CH_2$		Ph
(k)	H	Me	Me	$p\text{-}NO_2C_6H_4$
(l)	H	$CH_2CH_2CH_2$		$p\text{-}NO_2C_6H_4$

48

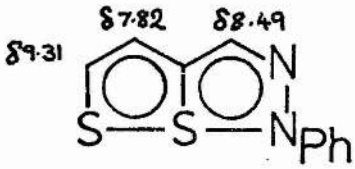
	R^1	R^2	R^3	Ar
(a)	Bu^t	H	H	Ph
(b)	H	H	H	Ph
(c)	H	Me	Me	Ph
(d)	H	$CH_2CH_2CH_2$		Ph
(e)	H	Me	Me	$p\text{-}NO_2C_6H_4$
(f)	H	$CH_2CH_2CH_2$		$p\text{-}NO_2C_6H_4$



48b



65



44b

which could not be induced to crystallise. The nmr spectrum of this oil showed the presence of two species in the ratio 5:2. The major species, which shows a singlet at δ2.67, attributable to a methylthio group, appears to be the thiadiazolium salt (99a). The minor species shows a singlet at δ4.27 which is in the region expected for an N-methyl group. At present, there is insufficient evidence to distinguish between the two possible structures (101a) (methylation at N-6) and (101b) (methylation at N-5) for the minor product. Methylation of 1,6a-dithia-5,6-diazapentalenes, then, appears to take place preferentially at sulphur, although partial N-methylation occurs when there is a bulky t-butyl group in the 2-position causing steric hindrance towards attack at sulphur. The oil obtained from methylation of compound (44a) gave only the demethylation product (44a) on reaction with methylamine, and no trace of the thiatriazapentalene (48a) was found, presumably due again to steric hindrance.

6a-Thia-1,2,6-triazapentalenes (48a)-(48f) were also prepared by treatment of the corresponding 1,6a-dithia-5,6-diazapentalenes (44a)-(44d), (44k) and (44 l) with methylamine, an example of the potential thiocarbonyl reactivity of the dithiadiazapentalene system. Nmr data for the thiatriazapentalenes are contained in Table A7. The chemical shift of the 5-proton (δ7.89) in 6-methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48b) is almost the same as that of the 5-proton (δ7.91)[53] in 6-methyl-1,6a-dithia-6-azapentalene (65), indicating that the 5-protons are in similar environments in the two systems. The 3- and 4-protons in compound (48b) are shielded relative to the corresponding protons in the dithiadiazapentalene (44b), due to the electron donating effect of the nitrogen atom in the 6-position, the chemical shift difference being greater for the 3-proton (1.04 ppm) than for the 4-proton (0.33 ppm).

The electronic spectra of the thiatriazapentalenes (48) show an intense visible absorption band (429-484 nm), which is responsible for the yellow to orange colour of the solutions of these compounds,

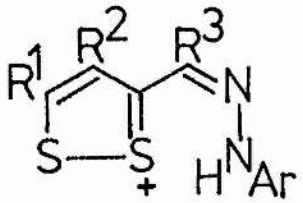
together with two slightly less intense bands in the ultraviolet region (201-203 nm) and (238-243 nm). Compounds (48e) and (48f) were previously obtained from the reactions of the dithiaazapentalenes (46a) and (46b) with p-nitrobenzenediazonium fluoroborate [see B, (b)], and this synthesis from dithiadiazapentalenes served as a proof of their structure.

(c) Protonation and Deuteration

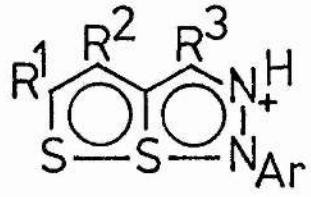
The protonation of 1,6,6a-trithiapentalenes and related systems in trifluoroacetic acid has been extensively studied in our laboratories[53,169]. It was therefore decided that a study of the reactivity of 1,6a-dithia-5,6-diazapentalenes should include an investigation into the protonation of the system using the techniques of nmr and ultraviolet spectroscopy. Initially the 6-phenyl compounds (44a)-(44c) were studied, and subsequently the 6-p-methoxyphenyl compounds (44n)-(44p) were included in the investigation.

The electronic spectra of compounds (44a)-(44c) and (44n)-(44p) in methanol (see Table B8) were almost identical to their spectra in cyclohexane (see Table B2). In methanol containing 2% perchloric acid, however, the spectra were very different. A broad band appeared in the visible region at considerably longer wavelength (505-570 nm) than the band in the visible region in the spectra of the dithiadiazapentalenes in methanol (479-502 nm). The spectra did not change further when the acidity of the solvent was increased (methanol/20% perchloric acid and acetic acid/10% perchloric acid). Solutions of the dithiadiazapentalenes in methanol were orange, whereas solutions in methanol containing 2% perchloric acid had a blue-purple colour, due no doubt to the presence of protonated species.

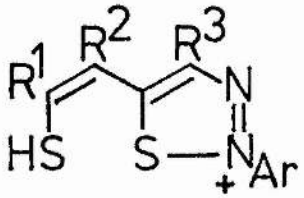
Five possible sites for protonation were envisaged: N-6, N-5, S-1, C-4 and C-3 giving rise to the structures (102)-(106) respectively. The nmr spectra of compounds (44a)-(44c) and



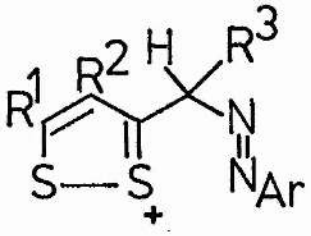
102



103



104



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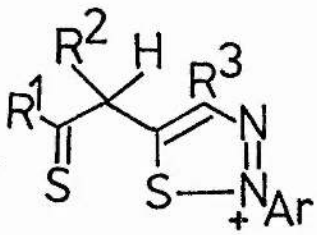
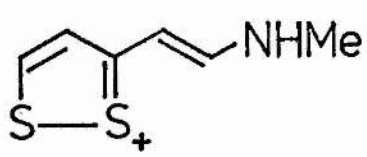


106

	R^1	R^2	R^3	Ar
(a)	Bu^t	H	H	Ph
(b)	H	H	H	Ph
(c)	H	Me	Me	Ph
(d)	Bu^t	H	H	p-$MeOC_6H_4$
(e)	H	H	H	p-$MeOC_6H_4$
(f)	H	Me	Me	p-$MeOC_6H_4$



107

(44$_n$)-(44p) in trifluoroacetic acid showed that, after a certain time, a single protonated species was present. Species (106) arising from protonation at C-3, seemed unlikely since electrophilic attack at the 3-position of the dithiadiazapentalene system has so far not been observed, and was excluded when it was shown from the spectra of compounds (44a), (44b), (44n) and (44o) in deuteriotrifluoroacetic acid that the 3-proton did not undergo H/D exchange. The 4-proton in compounds (44a), (44b), (44n) and (44o), however, did undergo H/D exchange, although very slowly. The species (105), therefore, was probably present, although in very low concentration, well below that detectable by nmr. Furthermore, since the nmr spectra of the protonated species obtained from compounds (44a)-(44c) were very different from the spectra of the S-methyl salts (99a)-(99c), the S-protonated species (104) was ruled out. It is believed that the species observed are those arising from protonation at N-6, ie., structures (102a)-(102f), derivatives of the 1,2-dithiolium system. Signals due to protons and substituents in the dithiole ring occur at lower field in the spectra of these protonated species, than the corresponding signals in the spectra of the dithiadiazapentalenes in deuteriochloroform, while the signals due to protons and substituents in the 4-position occur at higher field. Although chemical shifts obtained from the spectra of solutions in trifluoroacetic acid are not strictly comparable with those obtained from the spectra of solutions in deuteriochloroform because of solvent effects, the data are consistent with species (102) in which the positive charge is localised in the dithiolium ring. Better evidence for species (102) is that the dithiole ring proton coupling constant (5.3 Hz) in the protonated species derived from compound (44b) is almost the same as the corresponding coupling constant (5.4 Hz) in the species (107) derived from N-protonation of 6-methyl-1,6a-dithia-6-azapentalene (65)[53].

The nmr spectrum of compound (44a) in trifluoroacetic acid

showed that, initially, the species (102a) was the minor component in a two-component mixture. The signals due to the major species, however, rapidly diminished in intensity while the signals due to species (102a) increased in intensity. After ten minutes, only the signals due to the species (102a) remained. Clearly, there was a species present initially which was rapidly transformed into the species (102a). An analogous short-lived species was observed in the spectrum of compound (44b) in trifluoroacetic acid. The possibility that the short-lived species might have been unprotonated material was discounted since the 2-H,3-H coupling constant obtained from the spectrum of compound (44b) in deuteriochloroform (6.6 Hz) is significantly larger than the corresponding coupling constant in the short-lived species formed from compound (44b) in trifluoroacetic acid (6.1 Hz). The difference (0.5 Hz) is too large to be explained by a solvent effect. Again, the S-protonated species (104) was discounted, since the spectra of these short-lived species were very different from the spectra of the salts (99a) and (99b). It is tentatively suggested that these species have the structures (103a) and (103b), arising from protonation at N-5. Signals due to the dithiole ring protons and substituent in the species for which the structures (103a)and(103b) are proposed are at higher field than the corresponding signals of the species (102a) and (102b),while the 4-proton signal is at lower field. These effects are consistent with a positive charge localised largely on the nitrogen atom in the 5-position. Although the species (103c)-(103f) were not observed, it is possible that they may have been formed initially, but were transformed very rapidly into species (102c)-(102f) respectively.

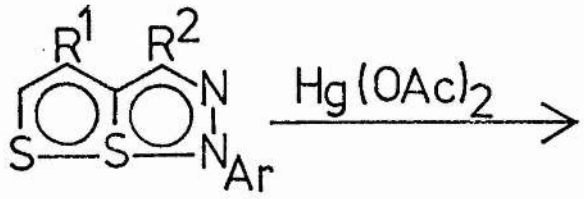
A further complication in the spectra of compounds (44n) and (44p) in trifluoroacetic acid was a broadening of the signals due to the 4-proton [compound (44n)] and 4-methyl [compound (44p)], the p-methoxyphenyl ring protons and the methoxy group. Because it was suspected that this broadening was due to restricted rotation about

the C(3a)-C(4) or C(4)-N(5) bond, a variable temperature nmr study of the solutions was undertaken. It was hoped that cooling might "freeze" separate geometrical isomers, and that raising the temperature might lead to sharper signals as barriers to rotation are overcome. The results of this investigation, however, were inconclusive. The trifluoroacetic acid solutions could only be subjected to the temperature range ($-12^{\circ} \longrightarrow +60^{\circ}$), and it is possible that better results might have been obtained, if it had been possible to observe the spectra over a wider temperature range. The spectra of compounds (44a)-(44c) and (44o) were unchanged over the temperature range ($-12^{\circ} \longrightarrow +60^{\circ}$). It was found that the broad signals from compound (44n) sharpened as the temperature was lowered, while those from compound (44p) sharpened, but only slightly, as the temperature was raised.

The spectra of compounds (44a), (44b), (44n), and (44o) in deuteriotrifluoric acid were initially identical to the spectra in trifluoroacetic acid. H/D exchange of the 4-proton in compounds (44n) and (44o) was detectable after a few hours. 95% exchange of the 4-proton took five weeks in the case of compound (44n) and seven weeks in the case of compound (44o). H/D exchange of the 4-proton in compounds (44a) and (44b), however, was much slower. After fourteen weeks, the 4-proton in compound (44a) had undergone 60% exchange, while, in the case of compound (44b), only 40% exchange was observed. It was also observed, after this time, that the phenyl ring protons in compounds (44a) and (44b) had undergone ca 50% exchange. No exchange of the p-methoxyphenyl ring protons in compounds (44n) and (44o) was observed.

(d) Synthesis of 1-Oxa-6a-thia-5,6-diazapentalenes and 6a-Thia-1,2,5,6-tetraazapentalenes

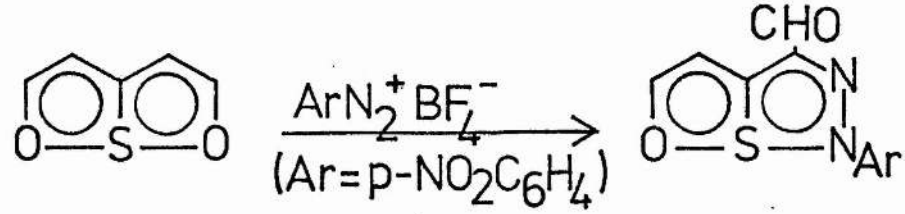
Mercury(II)acetate has been used to effect the replacement of a lateral sulphur atom of a 1,6,6a-trithiapentalene with oxygen[16].



44 108

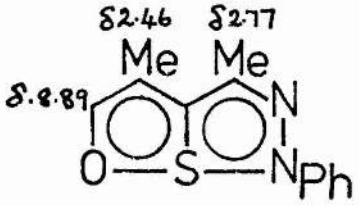
	R^I	R^2	Ar
(c)	Me	Me	Ph
(d)	$CH_2CH_2CH_2$		Ph
(k)	Me	Me	p-$NO_2C_6H_4$
(l)	$CH_2CH_2CH_2$		p-$NO_2C_6H_4$
(t)	Me	Me	p-$MeCOC_6H_4$
(u)	$CH_2CH_2CH_2$		p-$MeCOC_6H_4$

	R^I	R^2	Ar
(a)	Me	Me	Ph
(b)	$CH_2CH_2CH_2$		Ph
(c)	Me	Me	p-$NO_2C_6H_4$
(d)	$CH_2CH_2CH_2$		p-$NO_2C_6H_4$
(e)	Me	Me	p-$MeCOC_6H_4$
(f)	$CH_2CH_2CH_2$		p-$MeCOC_6H_4$

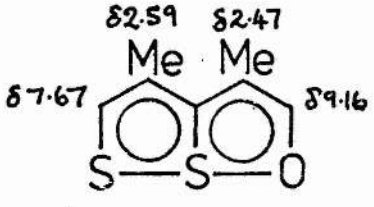


109 110

111



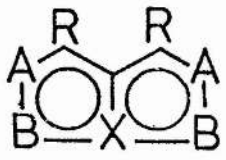
108a



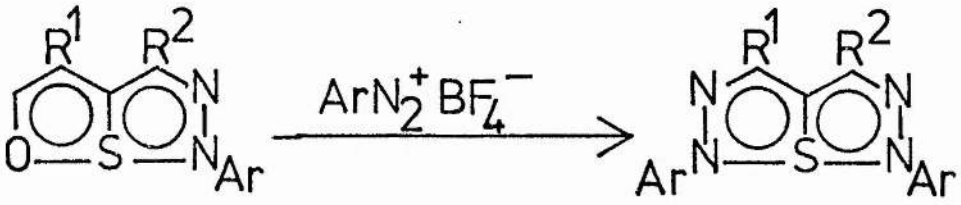
43a

It was found that this reagent could also be used to convert the 1,6a-dithia-5,6-diazapentalenes (44c), (44d), (44k), (44 l), (44t) and (44u) smoothly into the corresponding 1-oxa-6a-thia-5,6-diazapentalenes (108a)-(108f). The synthesis is restricted to compounds which contain substituents at the 4-position, and which are therefore not susceptible to electrophilic attack by mercury(II) acetate at this position. A derivative of the 1-oxa-6a-thia-5,6-diazapentalene system, compound (110), has previously been prepared by the reaction of 1,6-dioxa-6a-thiapentalene (109) with p-nitrobenzenediazonium fluoroborate[69]. This reaction, involving electrophilic attack by the diazonium cation at the 3-position of the dioxathiapentalene (109) accompanied by a rearrangement to the oxathiadiazapentalene (110), is analogous to the reactions of trithiapentalenes, oxadithiapentalenes and dithiaazapentalenes with diazonium salts [see B, (a)].

The electronic spectra of the oxathiadiazapentalenes (108a)-(108f) show an intense absorption band in the visible region (447-483 nm) which is responsible for the yellow to orange colour of the solutions of these compounds. The ultraviolet region shows an intense band (199-204 nm) and a band of medium intensity (233-247 nm). As in the infrared spectra of 1-oxa-6,6a-dithiapentalenes, there are no peaks in the normal carbonyl frequency region in the infrared of the oxathiadiazapentalenes (108a)-(108d), a fact which is inconsistent with the monocyclic structure (111) and which suggests that there is a sulphur-oxygen interaction in these systems. The spectra of compounds (108a)-(108d) show peaks in the region (1575-1590 cm^{-1}) which may be due to the carbon-oxygen stretching vibration. The infrared absorptions (1666 and 1668 cm^{-1} respectively) of compounds (108e) and (108f) are due to the para-acetyl groups. The signal due to the 2-proton in the nmr spectrum of 3,4-dimethyl-6-phenyl-1-oxa-6a-thia-5,6-diazapentalene (108a) (δ8.89) is at higher field than that due to the 2-proton in the spectrum of 3,4-dimethyl-1-oxa-6,6a-dithiapentalene (43a) (δ9.16)[19]. This indicates that there is a lower bond order of the carbon-oxygen bond, and consequently that

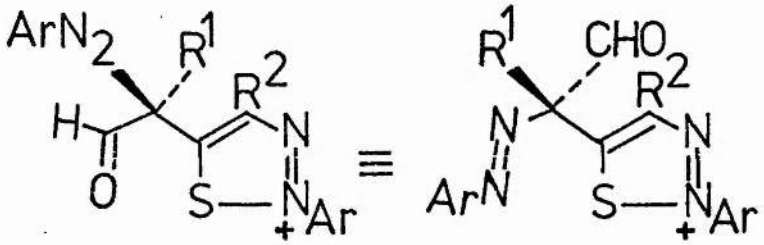


112

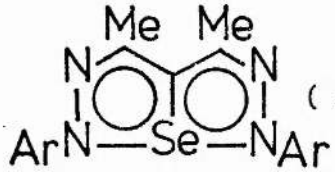


108 113

	R^1	R^2	Ar
(a)	Me	Me	Ph
(b)	$CH_2CH_2CH_2$		Ph
(c)	Me	Me	p-$NO_2C_6H_4$
(d)	$CH_2CH_2CH_2$		p-$NO_2C_6H_4$
(e)	Me	Me	p-$MeCOC_6H_4$
(f)	$CH_2CH_2CH_2$		p-$MeCOC_6H_4$

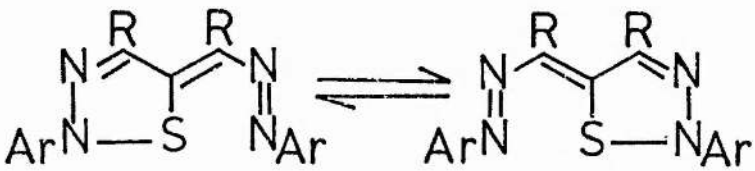


114a 114b



(Ar = 2,4-dinitrophenyl)

115



116a 116b

there is a stronger sulphur-oxygen interaction, in compound (108a) than in compound (43a).

A large number of compounds which may be represented by the general formula (112), where X is an element (S, Se, Te), theoretically capable of valence-shell expansion, have been synthesised (see Part 1, B). The nmr spectra of these compounds demonstrate that, in solution, the molecules possess real or time-averaged C_{2v} symmetry.

The oxathiadiazapentalenes (108a)-(108f) reacted with arenediazonium fluoroborates to give the corresponding 6a-thia-1,2,5,6-tetraazapentalenes (113a)-(113f). It is suggested that the reactions proceed by electrophilic attack by the diazonium cation at the 3-position of the oxathiadiazapentalene to give the monocyclic 1,2,3-thiadiazolium intermediate (114). Formal elimination of the formyl group from conformation (114b) then gives the thiatetraazapentalene. The reactions are analogous to the reactions of 1-oxa-6,6a-dithiapentalenes containing an alkyl group at the 3-position with arenediazonium salts [see B, (b)]. A derivative of the 6a-selena-1,2,5,6-tetraazapentalene system (115)[49] has been prepared [see Part 1, B, (c), (ii)], but compounds (113a)-(113f) are the first examples of the corresponding sulphur system. Because of the insolubility of compounds (113c) and (113d), their nmr spectra could not be recorded, but the spectra of compounds (113a), (113b), (113e) and (113f) show that, in solution, the molecules possess real or time-averaged C_{2v} symmetry about the central carbon-sulphur bond. The spectrum of 1,6-bis(p-acetylphenyl)-3,4-dimethyl-6a-thia-1,2,5,6-tetraazapentalene (113e), for example, shows the magnetic equivalence of the 3- and 4-methyl groups (δ2.86) and of the two acetyl groups (δ2.58), and the benzene ring protons give rise to a single AA'BB' system. Although this C_{2v} symmetry may be explained by a rapid valence isomerisation [116(i) $\rightleftharpoons$ 116(ii)], it seems more likely that, in common with trithiapentalenes and other related systems

this is a case of real equivalence corresponding to a symmetrical bonding pattern. The results of crystallographic studies of selected compounds, which are in progress, are awaited with interest. These will determine whether this C_{2v} symmetry is also present in the solid state, and the sulphur-nitrogen bond lengths will give a measure of the strength of the sulphur-nitrogen interactions, which doubtless exist in these systems.

PART THREE

EXPERIMENTAL

Introductory Notes

Melting points were determined on a Kofler hot-stage apparatus and are corrected.

Ultraviolet and visible spectra were measured with a Unicam SP800 spectrophotometer. Light absorption data refer to solutions in cyclohexane unless otherwise stated.

Infrared spectra were measured with a Perkin-Elmer 621 spectrophotometer. Samples were prepared as KBr discs. ^{1}H nmr spectra were measured at 31.4°C with a Varian HA100 spectrometer operating at 100 MHz. Chemical shifts (δ) are expressed in ppm downfield from the tetramethylsilane signal. Solutions in deuteriochloroform were 0.4 M, in hexadeuteriodimethylsulphoxide, pentadeuteriopyridine, trifluoroacetic and deuteriotrifluoroacetic acids, 0.5 M except where these concentrations could not be attained, when saturated solutions were employed. Chemical shift values given in the experimental section refer to singlet absorptions, unless otherwise stated, in which cases the symbols have their usual meanings.

Mass spectra were recorded on an AEI MS902 instrument. "Stick" diagrams were prepared with the aid of an IBM 360/44 computer.

Carbon, hydrogen and nitrogen microanalyses were carried out by Mr. J. Bews of this department. Sulphur and selenium microanalyses were carried out by Dr. A. Bernhardt, Mulheim, Germany.

Thin layer chromatography (tlc) was performed on silica (MN Kieselgel G) coated plates (0.25 mm thick), which were developed in iodine vapour. Yields quoted refer to material judged pure by tlc unless otherwise stated. Alumina for column chromatography was Spence type H (100/200 mesh) and silica was Sorbsil Silica Gel.

"Petrol" refers to 40/60 petroleum ether and "ether" to diethyl ether.

Acetic acid, acetic anhydride, methanol, ethanol, cyclohexane, n-hexane, petrol, acetone, and dimethylsulphoxide were all redistilled

commercial solvents.

Benzene, petrol, ether and xylene were refluxed over sodium wire for 1 hour and distilled to give the dry solvents. These solvents were stored over sodium wire. Where necessary, the crude solvents were pre-dried over calcium chloride for two days.

Benzene for chromatography was dried by azeotropic distillation, the first 25% of the distillate being used for extractions. Ether for chromatography was dried over calcium chloride, filtered and distilled.

Chloroform and methylene chloride were boiled over phosphoric anhydride for 1 hour, distilled, then percolated through a dry-packed column of alumina (12.5 x 2.5 cm) as required.

Acetonitrile was refluxed over sodium hydride (50% dispersion in oil, 2 g per litre) for 30 minutes and distilled. The distillate was then refluxed over phosphoric anhydride for 30 minutes, and distilled twice.

Dimethylformamide was allowed to stand over calcium hydride for 1 week and was then distilled under reduced pressure.

Dry ethanol was obtained by dissolving sodium in ethanol (7.5g per litre), adding diethyl succinate (25 g per litre) and boiling for two hours. Distillation then gave the dry solvent. Ethanolic ammonia was prepared by saturating dry ethanol with anhydrous ammonia.

Perchloric acid was 70% w/w and of Analar grade.

2M-Aqueous sodium hydrogen sulphide solutions were prepared by saturating 2M-aqueous sodium sulphide nonahydrate solutions with hydrogen sulphide (ca 2 hours).

Dimethyl sulphate, acetyl chloride, 2-methylthiophen, 5-methylisothiazole, aniline, carbon disulphide, ethyl formate, 2-methylbutan-2-ol, pinacolone, methyl iodide and methyl fluorosulphonate were redistilled commercial reagents.

Hydrogen disulphide was prepared by the method of Feher, Laue and Winkhaus[179,180]. Cyclohexanone-2-carboxylic acid was prepared

by the method of Gardner, Perkin and Watson[181].

Solutions were dried over anhydrous sodium sulphate, and solvents were evaporated at reduced pressure with a rotary film evaporator. Solids were dried in vacuo over phosphoric anhydride.

A. An Attempted Synthesis of 1,6-Dimethyl-6a-thia-1,6-diaza-pentalene from 2,5-Dimethylisothiazolium Perchlorate

2,5-Dimethylisothiazolium perchlorate[153]

A mixture of 5-methylisothiazole (4.960 g, 50 mmol) and dimethyl sulphate (6.08 ml, 65 mmol) was heated at 140°C for 20 minutes. The resulting dark oil was dissolved in hot ethanol (3 ml) and ether (350 ml) added. The ether layer was then decanted, the resulting oil dissolved in ethanol (35 ml) and 70% perchloric acid (10.11 ml, 120 mmol) added to the solution. Slow addition of ether precipitated the crude perchlorate as an oil which, after the ether layer was decanted, was taken up in boiling ethanol (25 ml) and screened twice with charcoal. 2,5-Dimethylisothiazolium perchlorate[153] (5.430 g, 51%) crystallised when the ethanolic solution was cooled. A further crop (2.395 g, 23%) was obtained by the addition of a large excess of ether to the mother liquors.

2,3-Dimethyl- and 2-methylisothiazolium perchlorates were obtained by established procedures.[185]

Treatment of 2,5-dimethylisothiazolium perchlorate with methylamine[153]

Aqueous methylamine (25-30%, 25 ml) was added to a solution of 2,5-dimethylisothiazolium perchlorate (2.135 g, 10 mmol) in methanol (60 ml), and the solution, which acquired an orange colour, was kept at room temperature for 30 minutes. The mixture was then poured into water, extracted with ether (3x) and the extracts washed with water (3x), dried and evaporated. The residue was chromatographed on a column of silica (30 x 2.0 cm) using benzene as eluant. Initial yellow eluates were evaporated and the residue rechromatographed on a column of silica (12 x 1.0 cm) using benzene-petrol (1:1) as eluant. Pale yellow eluates were evaporated to give sulphur (34 mg, 21%) identified by its mass spectrum. A second fraction from the original column afforded 5-methyl-2-(3-methylamino-1-thionopropenyl)thiophen (4a) (340 mg, 35%)[153].

Treatment of 2,5-dimethylisothiazolium perchlorate with N,N-dimethylhydrazine

A solution of N,N-dimethylhydrazine (6.00 g, 100 mmol) in methanol (50 ml) was added to a solution of 2,5-dimethylisothiazolium perchlorate (5.325 g, 25 mmol) in methanol (50 ml) and the mixture kept at room temperature for one hour. The solution was then poured into water, extracted with ether (3x), and the extracts washed successively with 0.5 M hydrochloric acid (500 ml) and water (2x), dried and evaporated. The resulting dark red oil was chromatographed on a column of alumina (20 x 2.5 cm), using benzene as eluant. Initial yellow eluates were evaporated and rechromatographed on a column of alumina (18 x 1.0 cm), using benzene-petrol (2:1) as eluant to give sulphur (24 mg, 6.0%). A second fraction from the original column afforded 2-(3-N,N-dimethylhydrazino-1-thionopropenyl)-5-methylthiophen (4c) (180 mg, 6.4%), after crystallisation from cyclohexane (red prisms, m.p. 138-139°) and rechromatography of the mother liquors on a column of alumina (15 x 1.0 cm) using benzene as eluant.

Found C 53.2; H 5.9; N 12.3%

$C_{10}H_4S_2N_2$ requires C 53.1; H 6.2; N 12.4%.

[Nmr spectrum: $CDCl_3$, δ2.43 d (3H, 5-Me), $J_{4,5}$=1.1 Hz, δ2.78 (6H, NMe_2), δ6.63dq (1H, 4-H), $J_{4,3}$=3.6 Hz, $J_{4,5}$=1.1 Hz, δ6.84d (1H, 2'-H), $J_{2,3}$=8.9 Hz, δ7.11d (1H, 3-H), $J_{3,4}$=3.6 Hz, δ7.19d (1H, 3'-H) $J_{3,2}$=8.9 Hz]. [UV spectrum: cyclohexane, λ_{max} (nm) 354 br, 264, 196 (log ε 4.22, 3.91, 4.04)]

A third fraction obtained from the original column on elution with benzene-ether (2:1) afforded 5-methyl-2-(3-methylamino-1-thionopropenyl)thiophen (4a) (19 mg, 0.8%) identical (nmr spectrum in $CDCl_3$) with an authentic sample[153].

2-Acetyl-5-methylthiophen (6)

To a solution of 2-methylthiophen (49.0 g, 0.5 mol) and acetyl chloride (37.5 ml, 0.525 mol) in dry benzene (400 ml), kept at 0°C

in an ice-salt bath, stannic chloride (61.3 ml, 0.525 mol) was added dropwise over two hours with efficient stirring, followed by stirring for a further hour. The purple complex which had separated was hydrolysed by the careful addition of 1M hydrochloric acid (200 ml), and then the mixture diluted with ether (500 ml). The acid layer was extracted again with ether (500 ml) and the combined extracts washed with water (4x), dried and evaporated. Fractional distillation of the residue gave three fractions: an initial fraction (11.3 g) (b.p. 113-116°/18 mm Hg) which was discarded, a second fraction (11.2 g) (b.p. 115-117°/18 mm Hg) and a bulk fraction, judged pure by GLC, of 2-acetyl-5-methylthiophen (6) (44.95 g, 64%) (b.p. 117-118°/18 mm Hg).

Found C 60.1; H 5.8%

C_7H_8OS requires C 60.0; H 5.8%

[Nmr spectrum: $CDCl_3$, δ2.47 (3H, COMe), δ2.50 dd (3H, 5-Me), $J_{5,4}$=1.0 Hz, $J_{5,3}$=0.4 Hz, δ6.77dq(1H, 4-H), $J_{4,3}$=3.6 Hz, $J_{4,5}$=1.0 Hz, δ7.49 dd (1H, 3-H) $J_{3,4}$=3.6 Hz, $J_{3,5}$=0.4 Hz].

A further quantity of product may be obtained by fractional distillation of the second fraction, discarding the first 30% and retaining the bulk fraction.

2-(3-hydroxy-1-oxopropenyl)-5-methylthiophen (7a)

2-Acetyl-5-methylthiophen (6) (28.0 g, 200 mmol) and ethyl formate (24.2 ml, 300 mmol) were added to dry ether (400 ml) containing sodium wire (4.6 g, 200 mmol). The reaction was initiated by the addition of dry ethanol (20 ml), and the mixture left overnight. The sodium salt of 2-(3-hydroxy-1-oxopropenyl)-5-methylthiophen (7) (32.36 g, 85%), a yellow solid, was filtered, washed with dry ether and dried.

A solution of the sodium salt (19.0 g, 100 mmol) in water (800 ml) was acidified with 0.5 M hydrochloric acid, extracted with benzene (2 x 800 ml), and the extracts washed with water (4x), dried and

evaporated. The brown residue was distilled at the oil-pump to give 2-(3-hydroxy-1-oxopropenyl)-5-methylthiophen (7a) (6.827 g, 41%) as a pale yellow liquid, b.p. 107-110°/0.8 mm Hg.

Found C 57.3; H 4.6%

$C_8H_8SO_2$ requires C 57.1; H 4.8%

[Nmr spectrum: $CDCl_3$, (enol form) δ2.54d (3H, 5-Me) $J_{5,4}$=1.0 Hz, δ5.98d (1H, 2'-H) $J_{2',3'}$=5.1 Hz, δ6.80dq (1H, 4-H) $J_{4,3}$=3.8 Hz, $J_{4,5}$=1.0 Hz, δ7.52d (1H, 3-H) $J_{3,4}$=3.8 Hz, δ7.67 (1H, 3'-H) $J_{3',2'}$=5.1 Hz, δ13.70b (1H, OH): (keto form) δ3.89d (2H, CH_2 $J_{CH_2,CHO}$=2.6 Hz, δ9.87t (1H, CHO) J_{CHO,CH_2}=2.6 Hz]

5-Methyl-2-(3-methylamino-1-oxopropenyl)thiophen (8)

Methylamine hydrochloride (2.025 g, 30 mmol) was added to a suspension of the sodium salt of 2-(3-hydroxy-1-oxopropenyl)-5-methylthiophen (7) (5.70 g, 30 mmol) in ethanol (35 ml) and the mixture heated for ten minutes on a boiling water bath. Water (10 ml) was then added and the solution screened with charcoal. Water (30 ml) was then added and the mixture chilled overnight. The yellow solid was filtered and recrystallised from cyclohexane-benzene (3:1) with charcoal-screening to give the product (2.646 g, 49%). 5-Methyl-2-(3-methylamino-1-oxopropenyl)thiophen (8) formed pale yellow needles, m.p. 87-89°.

Found C 59.7; H 6.2; N 7.4%

$C_9H_{11}SON$ requires C 59.6; H 6.1; N 7.7%

[Nmr spectrum: $CDCl_3$, δ2.49d (3H, 5-Me) $J_{5,4}$=0.9 Hz, δ3.01d (3H, NMe) $J_{NMe,NH}$=5.1 Hz, δ5.47d (1H, 2'-H) $J_{2',3'}$=7.1 Hz, δ6.70dq (1H, 4-H) $J_{4,3}$=3.6 Hz, $J_{4,5}$=0.9 Hz, δ6.80dd (1H,3'-H), $J_{3',NH}$=13.1 Hz, $J_{3',2'}$=7.1 Hz, δ7.34d (1H, 3-H) $J_{3,4}$=3.6 Hz, δ9.75b (1H,NH)]

M^+ at m/e 181

[UV spectrum: cyclohexane, λ_{max} (nm) 348, 344 infl, 294, 263, 257 infl, 214 infl (log ε 4.30, 4.30, 3.72, 3.77, 3.76, 3.68)]

5-Methyl-2-(3-methylamino-1-thionopropenyl)thiophen (4a)

Phosphorus pentasulphide (3.33 g, 15 mmol) was added to a solution of 5-methyl-2-(3-methylamino-1-oxopropenyl)thiophen (8) (1.81 g, 10 mmol) in carbon disulphide (20 ml), and the mixture, which rapidly acquired a red colour was stirred for 4 hours at room temperature. After evaporation of the solvent, the residue was extracted (8x) with benzene (50 ml) containing 33% ethanolic methylamine (6 ml), the extracts diluted with benzene (400 ml), washed with water (4x), dried and evaporated. Chromatography of the residue on a column of silica (35 x 2.0 cm) using benzene as eluant gave initially a red fraction, from which no useful material was obtained, followed by an orange fraction which was evaporated and rechromatographed on a column of silica (12 x 2.0 cm) using benzene as eluant to give 5-methyl-2-(3-methylamino-1-thionopropenyl) thiophen (4a) (471 mg, 24%), recrystallised from ethanol as orange-red needles, m.p. 150-152° (dec).

Found C 54.8; H 5.9; N 7.0%

$C_9H_{11}S_2N$ requires C 54.8; H 5.6; N 7.1%

[Nmr spectrum: $CDCl_3$, δ2.45d (3H, 5-Me) $J_{5,4}$ = 1.0 Hz, δ3.13d (3H, NMe) $J_{NMe,NH}$=5.2 Hz, δ6.44d (1H, 2'-H), $J_{2',3'}$=7.5 Hz, δ6.70dq (1H, 4-H) $J_{4,3}$=3.7 Hz, $J_{4,5}$=1.0 Hz, δ7.17dd (1H, 3'-H) $J_{3',NH}$=13.4 Hz, $J_{3',2'}$=7.5 Hz, δ7.34d (1H, 3-H) $J_{3,4}$=3.7 Hz, δ12.75b (1H, NH)]

M^+ at m/e 197.

3-(5-Methyl-2-thienyl)-1,2-dithiolium perchlorate (13)

The sodium salt of 2-(3-hydroxy-1-oxopropenyl)-5-methylthiophen (7) (19.0 g, 100 mmol) was added to a solution of hydrogen disulphide (6 ml) in acetic acid (200 ml) containing 70% perchloric acid (25 ml), and the resulting solution kept at 60-65° for 5 minutes. The cooled solution was filtered to remove a dark solid residue, and a large excess of ether was added to the filtrate. The salt (18.07 g, 61%) was filtered, washed with ether and dried. A sample of 3-(5-methyl-2-thienyl)-1,2-dithiolium perchlorate (13)

was recrystallised twice from ethanol with charcoal screening, and formed yellow plates, m.p. 149-150°.

Found C 32.3; H 2.4%.

$C_8H_7S_3ClO_4$ requires C 32.2; H 2.4%.

[Nmr spectrum; TFA, δ2.69 (3H, 5'-Me), δ7.16dq (1H, 4'-H) $J_{4',3'}$=4.1 Hz, $J_{4',5'}$=0.9 Hz, δ8.05d (1H, 3'-H), $J_{3',4'}$=4.1 Hz, δ8.43d (1H, 4-H) $J_{4,5}$=5.3 Hz, δ9.75d (1H, 5-H) $J_{5,4}$=5.3 Hz]

[UV spectrum; ethanol/1% $HClO_4$, λ_{max} (nm) 428, 283br, 251 (log ε 4.44, 3.57, 3.64)]

5-(5-Methyl-2-thienyl)isothiazole (14)

Ethanol saturated with ammonia (400 ml) was added slowly with stirring to 3-(5-methyl-2-thienyl)-1,2-dithiolium perchlorate (13) (35.86 g, 120 mmol). Anhydrous ammonia was then bubbled through the solution for 30 minutes at room temperature, and subsequently for 1 hour at reflux. The cooled mixture was then poured into water, extracted with ether (2x) and the extracts washed with water (4x), dried and evaporated. Distillation of the residue at the oil-pump gave an orange liquid which solidified (5.97 g, b.p. 107-110°/1.5 mm Hg). This was chromatographed on a column of silica (75 x 2.8 cm), using benzene as eluant, and initial eluates (700 ml) gave no useful material. Thereafter, fractions (10 x 100 ml) were collected and evaporated, and their compositions monitored by GLC. The first four such fractions were found to contain mixtures, while the subsequent six fractions afforded a homogeneous product. Rechromatography of the impure fractions in the same way gave a further quantity of pure product. 5-(5-Methyl-2-thienyl)isothiazole (14) (total yield 4.915 g, 23%) formed colourless plates, m.p. 74-75° (from n-hexane).

Found C 53.0; H 3.8; N 7.7%

$C_8H_7S_2N$ requires C 53.0; H 3.9; N 7.7%.

[Nmr spectrum; $CDCl_3$, δ2.49d (3H, 5'-Me) $J_{5',4'}$=1.0 Hz, δ6.61dq (1H, 4'-H), $J_{4',3'}$=3.4 Hz, $J_{4',5'}$=1.1 Hz, δ7.09d (1H, 3'-H)

$J_{3',4'}$=3.5 Hz, δ7.18d (1H, 4-H) $J_{4,3}$=1.7 Hz, δ8.34d (1H, 3-H) $J_{3,4}$=1.7 Hz]

M^+ at m/e 181

[UV spectrum; cyclohexane, λ_{max}(nm) 306, 254, 196 (log ε 4.11, 3.88, 3.96)]

2-Methyl-5-(5-methyl-2-thienyl)isothiazolium perchlorate (10a)

A mixture of 5-(5-methyl-2-thienyl)isothiazole (14) (4.525 g, 25 mmol) and dimethyl sulphate (2.80 ml, 30 mmol) was heated at 140° for 30 minutes. The resulting oil was dissolved in hot ethanol (10 ml) and ether (500 ml) was added. The ether layer was decanted, the resulting oil dissolved in ethanol (20 ml) and 70% perchloric acid (5.05 ml, 60 mmol) added to the solution. Slow addition of a large excess of ether gave a precipitate of 2-methyl-5-(5-methyl-2-thienyl)isothiazolium perchlorate (10a) (6.70 g, 91%). A sample was recrystallised from ethanol/1% perchloric acid as pale yellow needles, m.p. 130-132°.

Found C 36.5; H 3.3; N 4.7%

$C_9H_{10}S_2NClO_4$ requires C 36.6; H 3.4; N 4.7%.

[Nmr spectrum; TFA, δ2.61 (3H, 5'-Me), δ4.31 (3H, NMe), δ6.96dq (1H, 4'-H) $J_{4,3}$=2.8 Hz, δ7.56 (1H, 3'-H) $J_{3',4'}$=3.9 Hz, δ8.65dq (1H, 3-H) $J_{3,4}$=2.8 Hz, $J_{3,NMe}$=0.6 Hz]

[UV spectrum; ethanol/1% $HClO_4$, λ_{max} (nm) 364, 267br, 204 (log ε 4.28, 3.75, 3.86)]

Reaction of isothiazolium salts with Sodium Hydrogen Sulphide

(i) 2,5-Dimethylisothiazolium perchlorate (with A.R. Dunn)

2M aqueous sodium hydrogen sulphide (5 ml) was added to a solution of 2,5-dimethylisothiazolium perchlorate (1) (1.065 g, 5 mmol) in water (50 ml) and the mixture kept at room temperature for 10 minutes. The yellow mixture was then extracted repeatedly with benzene and the extracts were washed with water (3x), dried and

evaporated. Chromatography of the residue on a column of alumina (5 x 2.5 cm) using benzene as eluant gave 4-methylaminobutene-2-thione (18c) (470 mg, 82%) as an orange-red oil.

Found C 52.3; H 7.9; N 12.2%

C_5H_9NS requires C 52.2; H 7.9; N 12.2%.

[Nmr spectrum; $CDCl_3$, δ2.54 (3H, CSMe), δ3.13d (3H, NMe) $J_{NMe,NH}$= 5.0 Hz, δ6.03d (1H, 3-H) $J_{3,4}$=7.1 Hz, δ7.15qq (1H, 4-H) $J_{4,3}$=7.0 Hz, $J_{4,NH}$=13.0 Hz, $J_{4,NMe}$=0.6 Hz, δ13.14b (1H, NH). Shaking with D_2O causes the signal at δ13.14 to disappear, the signal at δ3.13 to collapse to a singlet, and the signal at δ7.15 to collapse to a double quartet]

M^+ at m/e 115.

(ii) 2,3-Dimethylisothiazolium perchlorate (with A.R. Dunn)

The above procedure was used, but with 2,3-dimethylisothiazolium perchlorate (11d) (1.065 g, 5 mmol), and 3-methylaminobut-2-enethial (18d) was obtained as a brown-yellow solid, m.p. 56.5-57.5°.

Found C 52.2; H 8.1; N 12.0%

C_5H_9NS requires C 52.2; H 7.9; N 12.2%.

[Nmr spectrum; $CDCl_3$, δ2.09 (3H, 3-Me), δ3.08d (3H, NMe) $J_{NMe,NH}$=5.3 Hz, δ6.16d (1H, 2-H) $J_{2,1}$=8.4 Hz, δ9.53d (1H, 1-H) $J_{1,2}$=8.4 Hz, δ13.82b (1H, NH). Shaking with D_2O causes the signal at δ13.82 to disappear and the signal at δ3.08 to collapse to a singlet]

M^+ at m/e 115

(iii) 2-methylisothiazolium perchlorate

Using 2-methylisothiazolium perchlorate (1.00 g, 5 mmol). Evaporation of the extracts gave an orange oil (320 mg) which rapidly decomposed to an insoluble tar.

(iv) 2-methyl-5-(5-methyl-2-thienyl)isothiazolium perchlorate (10a)

A similar procedure was used, involving the reaction of a solution of 2-methyl-5-(5-methyl-2-thienyl)isothiazolium perchlorate (10a) (592 mg, 2 mmol) in water (50 ml) with 2M aqueous sodium

hydrogen sulphide (2 ml). Work up as in (i) gave 5-methyl-2-(3-methylamino-1-thionopropenyl)thiophen (4a) (330 mg, 84%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

Reaction of 2-methyl-5-(5-methyl-2-thienyl)isothiazolium perchlorate with methylamine

Aqueous methylamine (25-30%, 12.5 ml) was added to a solution of 2-methyl-5-(5-methyl-2-thienyl)isothiazolium perchlorate (10a) (1.480 g, 5 mmol) in methanol (120 ml) and the solution was kept at room temperature for 30 minutes. The mixture was then extracted with benzene (2x), and the extracts washed with water (3x), dried and evaporated. A precipitate which formed during the extraction procedure was filtered and washed back into the extracts with hot benzene. The residue was chromatographed on a column of silica (26 x 2.2 cm) using benzene as eluant. Initial yellow eluates were evaporated and rechromatographed on a column of silica (20 x 1.5 cm) using petrol-benzene (1:1) as eluant to give sulphur (39 mg, 24%). A second fraction from the original column afforded 5-methyl-2-(3-methylamino-1-thionopropenyl)thiophen (4a) (223 mg, 23%), identical (nmr spectrum in $CDCl_3$) with the samples previously prepared.

Treatment of 5-methyl-2-(3-methylamino-1-thionopropenyl)thiophen with ethylamine

Aqueous ethylamine (70%, 5 ml) was added to a solution of 5-methyl-2-(3-methylamino-1-thionopropenyl)thiophen (4a) (197 mg, 1 mmol) in methanol (50 ml), and the solution kept at room temperature for 30 minutes. The mixture was then poured into water, extracted with benzene (2x) and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of silica (20 x 2.0 cm) using benzene as eluant yielded 2-(3-ethylamino-1-thionopropenyl)-5-methylthiophen (4b) (201 mg, 95%), identical (nmr spectrum in $CDCl_3$) with an authentic sample[153].

B. Reaction of 1,6,6a-Trithiapentalenes and Related Systems with Arenediazonium Fluoroborates

Benzenediazonium and p-toluenediazonium fluoroborates were prepared by established procedures[182]. Other arenediazonium fluoroborates were prepared by the following modification of the method of Starkey[183].

A solution of sodium nitrite (3.45 g, 50 mmol) in water (8 ml) was added dropwise with stirring to a solution of the amine (50 mmol) in 20% fluoroboric acid cooled in an ice-bath. When addition was complete, the mixture was stirred for a further 5 minutes, the salt filtered, washed with a little cold fluoroboric acid, twice with ethanol, several times with ether and dried. p-Nitrobenzenediazonium fluoroborate (11.153 g, 95%) was obtained from p-nitroaniline (6.906 g), p-acetylbenzenediazonium fluoroborate (8.63 g, 73%) from p-aminoacetophenone (6.76 g) and p-bromobenzenediazonium fluoroborate (10.86 g, 80%) from p-bromoaniline (8.60 g), all in fluoroboric acid (100 ml), while p-methoxybenzenediazonium fluoroborate (10.01 g, 90%) was obtained from p-anisidine (6.16 g) in fluoroboric acid (40 ml).

2-t-Butyl-[68], 2-phenyl-[22], 3,4-dimethyl-[53] and 3,4-trimethylene-1,6,6a-trithiapentalene[42], 1,6,6a-trithiapentalene[20], 5-t-butyl-[46], 5-phenyl-[22], 3,4-dimethyl-[46], 3-methyl-5-phenyl-[22] and 3,4-trimethylene-1-oxa-6,6a-dithiapentalene[42] and 1-oxa-6,6a-dithiapentalene[20] were prepared as in the references cited. 6-Methyl-2-t-butyl-, 6-methyl-2-phenyl-, 6-methyl-, 6-methyl-3,4-trimethylene- and 3,4,6-trimethyl-1,6a-dithia-6-azapentalene were also prepared by established procedures[53].

Synthesis of 2-Methylthio-5-t-butyl-1,6,6a-trithiapentalene (25a) and 2-Dimethylamino-5-t-butyl-1,6,6a-trithiapentalene (25b)

A mixture of sodium (46 g, 2 g atom), 2-methylbutan-2-ol (220 ml, 2 mol) and benzene (1 l) was refluxed overnight, then the solution decanted while still hot from unreacted sodium.

Pinacolone (125 ml, 1 mol) and then carbon disulphide (60 ml, 1 mol) were added to the stirred solution cooled to 5-10°, and the resulting mixture left for 4 hours at room temperature. Methyl iodide (62.5 ml, 1 mol) was added dropwise to the stirred mixture which was then set aside overnight before being extracted with water (2 x 500 ml). The extracts were acidified with 5M hydrochloric acid (250 ml) and the resulting mixture was extracted with ether (3 x). Distillation of the residue from the washed, dried and evaporated extracts gave methyl pivaloyldithioacetate (29) (80.7 g, 43%) as a yellow oil, b.p. 92-94°/2.0 mm Hg.

Found C 50.8; H 7.4%

$C_8H_{14}OS_2$ requires C 50.5; H 7.4%.

[Nmr spectrum; $CDCl_3$, (keto form, ca 10%) δ1.21 (9H, Bu^t), δ2.64 (3H, SMe), δ4.31 (2H, CH_2); (enol form, ca 90%) δ1.21 (9H, Bu^t), δ2.58 (3H, SMe), δ6.39 (1H, olefinic H), δ13.69 (1H, OH)]

The dithioester (29) (47.6 g, 250 mmol) in xylene (250 ml) was added over 20 minutes to a stirred suspension of phosphorus pentasulphide (166.5 g, 750 mmol) in xylene (750 ml) at room temperature. The mixture was boiled for 30 minutes, cooled and filtered. The solid was treated with water and the resulting mixture extracted with ether (2x). The combined ether extracts and xylene filtrate were washed with water(4x), dried and evaporated. Chromatography of the dark oil on a column of alumina (30 x 5.8 cm), initially with petrol-benzene (3:1) to remove residual xylene, and then with benzene, to give orange-yellow eluates. Evaporation, and crystallisation of the residual solid from n-hexane, gave 5-t-butyl-1,2-dithiole-3-thione (30) in two crops (33.14 g) as orange-yellow needles, m.p. 69-69.5° (lit[157], 70°).

Found C 44.2; H 5.4%

$C_7H_{10}S_3$ requires C 44.2; H 5.3%.

[Nmr spectrum; $CDCl_3$, δ1.42 (9H, Bu^t), δ7.11 (1H, 4-H)]

M^+ at m/e 190

[UV spectrum; cyclohexane, λ_{max} (nm) 412, 330, 259 infl, 251, 232 (log ε 3.94, 3.79, 3.98, 4.02, 3.94)]

Rechromatography of the residue from the mother liquors on a column of alumina (50 x 3.8 cm) with petrol-benzene (3:1) brought through red eluates which were discarded. Continued elution with benzene gave yellow eluates which yielded a further quantity (5.05 g) of the thione (total yield 38.19 g, 80%).

A mixture of the thione (30) (19.0 g, 100 mmol) and dimethyl sulphate (12.2 ml, 130 mmol) was heated at 130° for 20 minutes. The resulting oil was dissolved in ethanol (20 ml). Addition of ether precipitated a pink oil which slowly solidified. The ether layer was decanted and the methosulphate was redissolved in ethanol (30 ml). Addition of 70% perchloric acid (20.2 ml, 240 mmol) and subsequent gradual addition of much ether precipitated 3-methylthio-5-t-butyl-1,2-dithiolium perchlorate (31) (29.15 g, 96%), colourless spars (from ethanol containing 1% perchloric acid), m.p. 143.5-144.5°.

Found C 31.5; H 4.3%

$C_8H_{13}ClO_4S_3$ requires C 31.5; H 4.6%.

[Nmr spectrum; TFA, δ1.64 (9H, Bu^t), δ3.06 (3H, SMe), δ8.01 (1H,4-H)]

[UV spectrum; ethanol/1% $HClO_4$, λ_{max} (nm) 359, 278, 216 (log ε 4.28, 3.77, 3.76)]

A mixture of the perchlorate (31) (18.3 g, 60 mmol), the dithioester (29) (12.35 g, 65 mmol), pyridine (7 ml) and acetic acid (500 ml) was boiled for 4 hours, cooled, diluted with much water and extracted with benzene (2x). The extracts were washed successively with water(2x), aqueous 0.2 M sodium hydroxide, and water, dried and evaporated. Crystallisation of the solid from n-hexane gave 2-methylthio-3-pivaloyl-5-t-butyl-1,6,6a-trithiapentalene (32) (5.60 g), orange-red spars, m.p. 113-113.5°.

Found C 52.0; H 6.5%

$C_{15}H_{22}OS_4$ requires C 52.0; H 6.4%.

[Nmr spectrum; $CDCl_3$, δ1.33 (9H, 5-Bu^t), δ1.37 (9H, COBu^t), δ2.63 (3H, SMe), δ7.11 (1H, 4-H)]

M^+ at m/e 346.

ν_{max} ($CHCl_3$) 1680 (C=O) cm^{-1}.

[UV spectrum; cyclohexane, λ_{max} (nm), 485, 339, 252, 194 (log ε 4.09, 3.80, 4.63, 4.36)]

Chromatography of the residue from the hexane mother liquors on a column of alumina (50 x 3.8 cm) with petrol-benzene (3:1) gave orange eluates from which 2-methylthio-5-t-butyl-1,6,6a-trithiapentalene (25a) (278 mg, 1.8%) was isolated. Continued elution with petrol-benzene(1:1) brought through orange-red eluates from which more (5.28 g) of the ketone (32) was obtained (total yield 10.88 g, 52%).

A solution of the ketone (32) (10.38 g, 30 mmol) and 49% (w/w) aqueous hydrogen bromide (5 ml) in acetic acid (500 ml) was boiled for 45 minutes, cooled, poured into water, and extracted with ether (4x). The extracts were washed successively with water (2x), aqueous 2M sodium hydroxide (2x), and water, dried, and evaporated. Chromatography of the residual solid on a column of alumina (40 x 3.8 cm) with petrol-benzene (4:1) gave pale yellow eluates which were discarded, and subsequently orange eluates which afforded 2-methylthio-5-t-butyl-1,6,6a-trithiapentalene (25a) (5.888 g, 75%), orange-red spars from methanol, m.p. 114-115°.

Found C 50.7; H 6.4; N 5.3%

$C_{11}H_7NS_3$ requires C 50.9; H 6.6; N 5.4%.

[Nmr spectrum; $CDCl_3$, δ1.38 (9H, Bu^t), δ2.61 (3H, SMe), δ7.28 (1H, 4-H), δ7.63 (1H, 3-H)]

M^+ at m/e 262.

[UV spectrum; cyclohexane, λ_{max} (nm) 482, 340, 257, 237 (log ε 4.12, 3.81, 4.63, 4.47)]

The trithiapentalene (25a) (2.62 g, 10 mmol) in 33% (w/w) ethanolic dimethylamine (400 ml) was boiled under an ice condenser for 5 hours, cooled, and diluted with water. The mixture was extracted with ether (3x) and the extracts were washed with water (3x), dried and evaporated. Chromatography of the residual solid

on a column of silica (30 x 2.8 cm) with petrol-benzene (1:1) gave an orange fraction from which starting material (105 mg, 4%) was recovered. Continued elution with benzene-ether (4:1) brought through yellow eluates which yielded 2-dimethylamino-5-t-butyl-1,6,6a-trithiapentalene (25b) (2.46 g, 95%), yellow needles from n-hexane, m.p. 114-115°.

Found C 50.9; H 6.4; N 5.4%

$C_{11}H_{17}NS_3$ requires C 50.9; H 6.6; N 5.4%.

[Nmr spectrum: $CDCl_3$, δ1.34 (9H, Bu^t), δ3.25 (6H, NMe_2), δ6.88 (1H, 3-H), δ6.99 (1H, 4-H)]

M^+ at m/e 259

[UV spectrum; cyclohexane, λ_{max} (nm) 456, 336 br, 254, 232 (log ε 4.06, 3.79, 4.59, 4.50)]

2,3-tetramethylene-5-t-butyl-1-oxa-6,6a-dithiapentalene (56)

Cyclohexanone-2-carboxylic acid (15.60 g, 110 mmol) was dissolved in a 0.2 M ethanolic sodium ethoxide solution (500 ml) and 3-methylthio-5-t-butyl-1,2-dithiolium perchlorate (31) (15.25 g, 50 mmol) added. The resulting solution was heated at 50° for 15 minutes, and then cooled, poured into water, extracted with ether (3x), and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (50 x 2.8 cm) with petrol-benzene (3:1) gave pale yellow eluates which were discarded. Continued elution with benzene-petrol (2:1) gave a red fraction, and subsequently a homogeneous (tlc) yellow fraction was obtained with benzene-ether (4:1). Rechromatography of the residue from the red fraction in the same way gave red eluates which were discarded, followed by a yellow fraction. The combined yellow eluates were evaporated to give 2,3-tetramethylene-5-t-butyl-1-oxa-6,6a-dithiapentalene (56) (5.460 g, 43%), a yellow solid, m.p. 69.5-70°.

Found C 61.6; H 7.4%

$C_{13}H_{18}S_2O$ requires C 61.4; H 7.1%.

[Nmr spectrum; $CDCl_3$, δ1.34 (9H, Bu^t), δ1.82m (4H, $-CH_2CH_2-$), δ2.50m (2H, 3-C-CH_2)*, δ2.68m (2H, 2-C-CH_2)*, δ6.94 (1H, 4-H) (* tentative assignments)]

M^+ at m/e 254

[UV spectrum; cyclohexane, λ_{max} (nm) 432 infl, 420, 227 (log ε 4.11, 4.13, 4.29)]

Reactions of 1,6,6a-trithiapentalenes and Related Compounds with Arenediazonium salts

1. 1,6,6a-Trithiapentalenes

(a) with p-nitrobenzenediazonium fluoroborate

Method A

Filtered solutions of the trithiapentalene (5 mmol) in acetonitrile (150 ml) and p-nitrobenzenediazonium fluoroborate (1.775 g, 7.5 mmol) in acetonitrile (50 ml) were mixed and kept at room temperature for 1 hour. A red precipitate of the thioaldehyde polymer (2I) was filtered and washed with acetonitrile and hot benzene. The filtrate was then poured into water, extracted with benzene (2x), and the extracts washed with water (4x), dried and evaporated. Chromatography is described in individual cases.

Method A^1

As method A, except that water (9 ml, 500 mmol) was added to the solution of the trithiapentalene in acetonitrile.

(i) 2-t-butyl-1,6,6a-trithiapentalene (19a)

(1.080 g, 5 mmol), Method A.

6-p-Nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarbaldehyde polymer (2Ia) (28 mg, 1.5%) formed red prisms, m.p. 211-216°.

Found C 48.9; H 4.1; N 11.7; S 26.1%

$(C_{15}H_{15}N_3S_3O_2)_n$ requires C 49.3; H 4.1; N 11.5; S 26.3%.

Chromatography of the residue on a column of alumina (50 x 2.8 cm)

with benzene-petrol (3:1) gave orange eluates which afforded starting material (116 mg, 11%) and subsequently pink eluates which gave no useful material. Continued elution with benzene gave an orange fraction which was evaporated and rechromatographed in the same way to yield 4-formyl-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (20a) (140 mg, 8%), orange-red needles (from cyclohexane-benzene), m.p. 187-187.5°.

Found C 51.8; H 4.4; N 12.0%

$C_{15}H_{15}S_2N_3O_3$ requires C 51.6; H 4.3; N 12.0%.

M^+ at m/e 349. ν_{max} (KBr disc) 1683 (C=O) cm^{-1}.

(ii) 2-t-butyl-1,6,6a-trithiapentalene (19a)

(1.080 g, 5 mmol), Method A[1].

Method A[1] gave 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarbaldehyde polymer (22a) (294 mg, 16%), starting material (74 mg, 7%) and 4-formyl-6- p-nitrophenyl -2-t-butyl-1,6a-dithia-5,6-diazapentalene (20a) (391 mg, 22%).

(iii) 1,6,6a-trithiapentalene (19b)

(800mg, 5 mmol), Method A[1]

Method A[1] gave 6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene-4-thiocarbaldehyde polymer (22b) (7 mg, 0.5%), a red-brown powder, m.p. 212-222°.

Found C 42.1; H 2.4; N 13.3; S 30.9%

$(C_{11}H_7N_3O_2S_3)_n$ requires C 42.7; H 2.3; N 13.6; S 31.1%.

Chromatography of the residue on a column of silica (50 x 2.8 cm) with benzene gave orange eluates which afforded starting material (101 mg, 13%), followed by pale yellow eluates which were discarded. Continued elution with benzene-ether (9:1) brought through orange eluates which were evaporated to give 4-formyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (20b) (121 mg, 8.3%), red microneedles (from benzene), m.p. 275-276.5°.

Found C 45.0; H 2.7; N 14.5%

$C_{11}H_7N_3O_3S_2$ requires C 45.0; H 2.4; N 14.3%.

M^+ at m/e 293. ν_{max} (KBr disc) 1680 (C=O) cm^{-1}.

(iv) 2-phenyl-1,6,6a-trithiapentalene (19c)

(1.180 g, 5 mmol), Method A^1

Method A^1 did not in this case give a thioaldehyde polymer, although a cloudiness was observed in the reaction mixture. Chromatography as in (iii) gave starting material (125 mg, 11%) and 4-formyl-6-p-nitrophenyl-2-phenyl-1,6a-dithia-5,6-diazapentalene (20c) (129 mg, 7.0%), deep red prisms (from benzene), m.p. 214.5-215°.

Found C 55.1; H 3.0; N 11.4%

$C_{17}H_{11}N_3O_3S_2$ requires C 55.3; H 3.0; N 11.4%.

M^+ at m/e 369 ν_{max} (KBr disc) 1676 (C=O) cm^{-1}.

Method B

A solution of p-nitrobenzenediazonium fluoroborate (711 mg, 3 mmol) in acetonitrile (20 ml) was added to a solution of the trithiapentalene (2 mmol) in acetonitrile (60 ml), and the mixture kept at room temperature for 45 minutes. The mixture was then poured into water, extracted with benzene (3x), and the extracts washed with water (3x), dried and evaporated. Chromatography is described in individual cases.

(v) 2-methylthio-5-t-butyl-1,6,6a-trithiapentalene (25a)

(524 mg, 2 mmol), Method B

Chromatography on a column of alumina (60 x 2.2 cm) using petrol-benzene (1:1) as eluant afforded methyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-dithiocarboxylate (26a) (701 mg, 85%), red prisms (from cyclohexane), m.p. 137-137.5°.

Found C 46.4; H 4.0; N 9.9%

$C_{16}H_{17}N_3O_2S_4$ requires C 46.7; H 4.2; N 10.2%.

M^+ at m/e 411

(vi) 2-dimethylamino-5-t-butyl-1,6,6a-trithiapentalene (25b) (518 mg, 2 mmol), Method B

Chromatography on a column of alumina (40 x 2.2 cm) with benzene gave a deep red fraction, evaporated to give N,N-dimethyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarboxamide (26b), (745 mg, 91%), fine brown microneedles (from benzene-cyclohexane), m.p. 235-237.5°.

Found C 50.0; H 5.1; N 13.5%

$C_{17}H_{20}N_4O_2S_3$ requires C 50.0; H 5.0; N 13.7%. M^+ at m/e 408.

Continued elution with benzene-ether (4:1) brought through red eluates which afforded N,N-dimethyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-carboxamide (26e) (67 mg, 8.0%), brown microneedles (from cyclohexane) m.p. 176-177°.

Found C 52.0; H 5.2; N 14.4%

$C_{17}H_{20}N_4O_3S_2$ requires C 52.0; H 5.1; N 14.3%.

M^+ at m/e 392. ν_{max} (KBr disc) 1642 (C=O) cm^{-1}.

Method C

A solution of p-nitrobenenediazonium fluoroborate (2.370 g, 10 mmol) in acetonitrile (50 ml) was added to a solution of the trithiapentalene (5 mmol) in acetonitrile (150 ml), and the mixture kept at room temperature for 90 minutes. Benzene (200 ml) was then added, and the mixture adsorbed on a column of alumina (30 x 2.8 cm). Elution with ether gave red eluates, which were evaporated. Chromatography of the residue on a column of alumina (40 x 2.8 cm) with benzene, initially gave red eluates from which starting material was recovered and subsequently gave a deep red fraction which afforded the dithiadiazapentalene (44). Continued elution with benzene-ether (9:1) brought through a yellow fraction which was evaporated and rechromatographed on a column of alumina (30 x 2.2 cm) to afford the oxadithiapentalene (43).

(vii) 3,4-dimethyl-1,6,6a-trithiapentalene (42a)

(0.940 g, 5 mmol), Method C

Method C gave starting material (43 mg, 5%), 3,4-dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k) (203 mg, 14%), fine deep red microneedles (from benzene), m.p. 208.5-209°.

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%.

M^+ at m/e 293,

and 3,4-dimethyl-1-oxa-6,6a-dithiapentalene (43a) (36 mg, 4.2%), identical (nmr spectrum in $CDCl_3$) with an authentic sample[19].

(viii) 3,4-trimethylene-1,6,6a-trithiapentalene (42b)

(1.000 g, 5 mmol), Method C.

Method C gave starting material (39 mg, 3.9%), 3,4-trimethylene-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44 l) (315 mg, 21%), dark red prisms (from benzene-cyclohexane) m.p. 236-238°.

Found C 51.5; H 3.6; N 13.6%

$C_{13}H_{11}N_3O_2S_2$ requires C 51.1; H 3.6; N 13.8%.

M^+ at m/e 305,

and 3,4-trimethylene-1-oxa-6,6a-dithiapentalene (43b) (40 mg, 4.3%), identical (nmr spectrum in $CDCl_3$) with an authentic sample[42].

(b) with benzenediazonium fluoroborate

(i) 2-t-butyl-1,6,6a-trithiapentalene (19a)

A solution of benzenediazonium fluoroborate (1.920 g, 10 mmol) in acetonitrile (50 ml) was added to a solution of 2-t-butyl-1,6,6a-trithiapentalene (19a) (1.080 g, 5 mmol) in acetonitrile (150 ml) containing water (9 ml, 500 mmol), and the mixture kept at 50° for 2 hours. The cooled solution was poured into water, extracted with ether (2x) and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (30 x 2.8 cm) with benzene-petrol (1:1) gave orange-red eluates from which starting material (0.936 g, 87%) was obtained.

Further elution gave no useful material.

(ii) 2-methylthio-5-t-butyl-1,6,6a-trithiapentalene (25a)

A solution of benzenediazonium fluoroborate (786 mg, 4 mmol) in acetonitrile (20 ml) was added to a solution of 2-methylthio-5-t-butyl-1,6,6a-trithiapentalene (25a) (524 mg, 2 mmol) in acetonitrile (60 ml). The mixture was kept at room temperature for 90 minutes, a further quantity of the fluoroborate (768 mg, 4 mmol) added, and the mixture set aside for a further 90 minutes. The mixture was then poured into water, extracted with benzene (3x), and the extracts washed (3x), dried and evaporated. Chromatography of the residue on a column of alumina (40 x 2.2 cm) with petrol-benzene (2:1) gave orange eluates from which starting material (207 mg, 40%) was recovered. Further elution gave no useful material.

(iii) 2-dimethylamino-5-t-butyl-1,6,6a-trithiapentalene (25b)

A solution of benzenediazonium fluoroborate (768 mg, 4 mmol) in acetonitrile (20 ml) was added to a solution of 2-dimethylamino-5-t-butyl-1,6,6a-trithiapentalene (25b) (518 mg, 2 mmol) in acetonitrile (60 ml), and the mixture kept at room temperature for 1 hour. The solution was then poured into water, extracted with benzene (3x), and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (40 x 2.2 cm) with benzene gave orange eluates which afforded N,N-dimethyl 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarboxamide (26c), orange-red needles (from n-hexane) m.p. 119-121°.

Found C 55.9; H 5.6; N 11.6%

$C_{17}H_{21}N_3S_3$ requires C 56.2; H 5.8; N 11.5%.

M^+ at m/e 363

2. 1-oxa-6,6a-dithiapentalenes

(a) with p-nitrobenzenediazonium fluoroborate

(i) 5-t-butyl-1-oxa-6,6a-dithiapentalene (33a)

To a solution of 5-t-butyl-1-oxa-6,6a-dithiapentalene (33a) (1.000 g, 5 mmol) in acetonitrile (150 ml) was added a solution of p-nitrobenzenediazonium fluoroborate (1.775 g, 7.5 mmol) in acetonitrile (50 ml), and the mixture kept at room temperature for 30 minutes. The mixture, which immediately acquired a red colour and eventually precipitated a red solid was poured into water, extracted with benzene (2x), and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (35 x 2.8 cm) with benzene-ether (3:1) gave red eluates which afforded 4-formyl-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (20a) (1.590 g, 91%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(ii) 1-oxa-6,6a-dithiapentalene (33b)

The reaction conditions in (i) were used, with 1-oxa-6,6a-dithiapentalene (33b) (0.720 g, 5 mmol). Filtration of the red precipitate and crystallisation from benzene gave 4-formyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (20b) (1.246 g), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared. The filtrate was poured into water, extracted with benzene (2x), and the extracts washed with water (3x), dried, combined with the benzene mother liquors and evaporated. Chromatography of the residue on a column of silica (15 x 2.8 cm) with benzene-ether (19:1) gave red eluates which afforded a further quantity (192 mg) of the aldehyde (20b) (Total yield, 1.438 g, 98%).

(iii) 5-phenyl-1-oxa-6,6a-dithiapentalene (33c)

The procedure as in (i) was used, with 5-phenyl-1-oxa-6,6a-dithiapentalene (33c) (1.100 g, 5 mmol), and gave 4-formyl-6-p-nitrophenyl-2-phenyl-1,6a-dithia-5,6-diazapentalene (20c) (1.386 g, 75%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(iv) 3,4-dimethyl-1-oxa-6,6a-dithiapentalene (43a)

A solution of p-nitrobenzenediazonium fluoroborate (2.370 g, 10 mmol) in acetonitrile (50 ml) was added to a solution of 3,4-dimethyl-1-oxa-6,6a-dithiapentalene (43a) (0.860 g, 5 mmol) in acetonitrile (150 ml) and the mixture which acquired a red colour, kept at room temperature for 45 minutes. The mixture was then poured into water and extracted with benzene (2x), and the extracts washed with water (3x), dried and evaporated. The resulting red solid was chromatographed on a column of alumina (35 x 2.8 cm) with benzene to give red eluates which afforded 3,4-dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k) (1.222 g, 83%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(v) 3,4-trimethylene-1-oxa-6,6a-dithiapentalene (43b)

The procedure as in (iv) was used, with 3,4-trimethylene-1-oxa-6,6a-dithiapentalene (43b) (0.920 g, 5 mmol), and gave 3,4-trimethylene-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44 l) (1.211 g, 80%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(vi) 3-methyl-5-phenyl-1-oxa-6,6a-dithiapentalene (43c)

The procedure as in (iv) was used, with 3-methyl-5-phenyl-1-oxa-6,6a-dithiapentalene (43c) (1.250 g, 5 mmol) and gave 4-methyl-6-p-nitrophenyl-2-phenyl-1,6a-dithia-5,6-diazapentalene (44 m) (1.249 g, 70%), dark red needles (from benzene), m.p. 218-219°.

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%.

M^+ at m/e 355.

(vii) 2,3-tetramethylene-5-t-butyl-1-oxa-6,6a-dithiapentalene (56)

1. in acetonitrile

To a solution of 2,3-tetramethylene-5-t-butyl-1-oxa-6,6a-dithiapentalene (56) (1.270 g, 5 mmol) in acetonitrile (200 ml) was added p-nitrobenzenediazonium fluoroborate (2.370 g, 10 mmol) and the mixture stirred at room temperature for 45 minutes. The mixture

was then poured into water, extracted with benzene (2x), the extracts washed with water (2x) and then extracted with 0.1 M aqueous sodium hydroxide (300 ml). The red alkaline solution was then washed with benzene (300 ml) and acidified by careful additionof 2N hydrochloric acid. The resulting mixture was extracted with benzene (2x), and the extracts washed with water (2x), dried and evaporated to give 5-(6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalen-4-yl)-n-pentanoic acid (58) (1.791 g, 85%), deep red microneedles [from cyclohexane-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^+ at m/e 421, ν_{max} (KBr disc) 1712 (C=O) cm^{-1}.

2. in methanol

To a solution of 2,3-tetramethylene-5-t-butyl-1-oxa-6,6a-dithiapentalene (56) (1.270 g, 5 mmol) in methanol (200 ml) was added p-nitrobenzenediazonium fluoroborate (3.555 g, 15 mmol) and the mixture stirred at room temperature for 1 hour. The mixture was then poured into water, extracted with benzene (2x) and the extracts washed with water (2x), dried and evaporated. Chromatography of the residue on a column of silica (35 x 2.8 cm) with benzene gave pale orange eluates which were discarded. Further elution with benzene-ether (99:1) gave red eluates which afforded methyl 5-(6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalen-4-yl)-n-pentanoate (59) (2.031 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^+ at m/e 435 ν_{max} (KBr disc) 1730 (C=O) cm^{-1}.

(b) with benzenediazonium fluoroborate

(i) 5-t-butyl-1-oxa-6,6a-dithiapentalene (33a)

A solution of benzenediazonium fluoroborate (1.920 g, 10 mmol) in acetonitrile (50 ml) was added to a solution of 5-t-butyl-1-oxa-6,6a-dithiapentalene (33a) (1.000 g, 5 mmol) in acetonitrile (150 ml), and the mixture, which acquired a red colour, was kept at room

temperature for 1 hour. The solution was then poured into water, extracted with ether (2x) and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (30 x 2.8 cm) with benzene gave orange eluates, which afforded 4-formyl-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (20d) (1.141 g, 74%), orange prisms (from n-hexane), m.p. 111.5-112.5°.

Found C 59.4; H 5.2; N 9.4%

$C_{15}H_{16}N_2OS_2$ requires C 59.2; H 5.3; N 9.2%.

M^+ at m/e 304. ν_{max} (KBr disc) 1689 (C=O) cm^{-1}.

(ii) 1-oxa-6,6a-dithiapentalene (33b)

The procedure as in (i) was used, with 1-oxa-6,6a-dithiapentalene (33b) (0.720 g, 5 mmol), except that a column of silica (30 x 2.8 cm) was used for the chromatography, with benzene as eluant. 4-Formyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (20e) (704 mg, 57%) was obtained, as red needles (from cyclohexane-benzene), m.p. 139.5-140°.

Found C 53.2; H 3.2; N 11.2%

$C_{11}H_8N_2OS_2$ requires C 53.2; H 3.3; N 11.3%.

M^+ at m/e 248. ν_{max} (KBr disc) 1672 (C=O) cm^{-1}.

(iii) 5-phenyl-1-oxa-6,6a-dithiapentalene (33c)

The procedure as in (i) was used, with 5-phenyl-1-oxa-6,6a-dithiapentalene (33c) (1.100 g, 5 mmol), and gave 4-formyl-2,6-diphenyl-1,6a-dithia-5,6-diazapentalene (20f) (0.860 g, 53%), fine orange-red needles (from cyclohexane), m.p. 154.5-155°.

Found C 62.8; H 3.8; N 8.7%

$C_{17}H_{12}N_2OS_2$ requires C 62.9; H 3.7; N 8.6%.

M^+ at m/e 324. ν_{max} (KBr disc) 1680 (C=O) cm^{-1}.

3. 1,6a-Dithia-6-azapentalenes

(a) with p-nitrobenzenediazonium fluoroborate

Method A

A solution of p-nitrobenzenediazonium fluoroborate (1.775 g ,7.5 mmol)

in acetonitrile (50 ml) was added to a solution of the dithiaaza-pentalene (5 mmol) in acetonitrile (150 ml) and the mixture was kept at room temperature for 45 minutes. The mixture, which had acquired a deep red colour, was then poured into water, extracted with benzene (2x), and the extracts washed with water (3x), dried and evaporated. Chromatography is described in individual cases.

(i) 6-Methyl-2-t-butyl-1,6a-dithia-6-azapentalene (34a)

(1.065 g, 5 mmol), Method A

Chromatography on a column of alumina (35 x 2.8 cm) with benzene-ether (4:1) gave red eluates, which afforded 4-formyl-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (20a) (1.440 g, 83%); identical (nmr spectrum in $CDCl_3$) with the samples previously prepared.

(ii) 6-Methyl-1,6a-dithia-6-azapentalene (34b)

(0.786 g, 5 mmol), Method A

Chromatography on a column of silica (25 x 2.8 cm) using benzene as eluant initially gave pale yellow eluates which were discarded and subsequently gave an orange fraction which afforded 4-formyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (20b) (155 mg, 10.6%) identical (nmr spectrum in $CDCl_3$) with samples previously prepared. Further elution with benzene-ether (19:1) brought through deep orange eluates which were evaporated. TLC indicated that a mixture of products was present which could not be separated by further chromatography or crystallisation.

(iii) 6-Methyl-2-phenyl-1,6a-dithia-6-azapentalene (34c)

(1.165 g, 5 mmol), Method A

Chromatography as in (ii) gave 4-formyl-6-p-nitrophenyl-2-phenyl-1,6a-dithia-5,6-diazapentalene (20c) (76 mg, 4.1%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared. Later eluates showed traces of three orange compounds (tlc) not separable by further chromatography.

Method B

To a solution of the dithiaazapentalene (5 mmol) in acetonitrile (150 ml) was added a solution of p-nitrobenzenediazonium fluoroborate (2.370 g, 10 mmol) in acetonitrile (50 ml), and the mixture kept at room temperature for 2 hours. Benzene (200 ml) was then added to the mixture, and the solution adsorbed on a column of alumina (30 x 2.8 cm). Elution with ether gave deep red eluates which were evaporated. Chromatography of the residue on a column of alumina (40 x 2.8 cm) with benzene gave red eluates which afforded the dithiadiazapentalene. Elution with benzene-ether (9:1) gave orange eluates from which no useful material was obtained. Elution with benzene-ether (1:1) then gave a deep orange fraction from which the thiatriazapentalene was obtained.

(iv) 3,4,6-Trimethyl-1,6a-dithia-6-azapentalene (46a)

(0.925 g, 5 mmol), Method B

3,4-Dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k) (122 mg, 8.3%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared, was obtained from initial eluates. Subsequent eluates afforded 3,4,6-trimethyl-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (48e) (334 mg, 23%), deep red spars (from benzene-cyclohexane), m.p. 227-229°.

Found C 53.5; H 4.9; N 19.2%

$C_{13}H_{14}SN_4O_2$ requires C 53.8; H 4.9; N 19.3%.

M^+ at m/e 290.

(v) 6-Methyl-3,4-trimethylene-1,6a-dithia-6-azapentalene (46b)

(0.985 g , 5 mmol), Method B

3,4-Trimethylene-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44 l) (275 mg, 18%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared, was obtained from initial eluates. Subsequent eluates afforded 6-methyl-3,4-trimethylene-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (48f) (91 mg, 6.0%), deep red needles (from benzene-cyclohexane), m.p. 244-246.5°.

Found C 55.7; H 4.7; N 18.6%

$C_{14}H_{14}N_4O_2S_2$ requires C 55.6; H 4.7; N 18.5%.

M^+ at m/e 302.

(b) with benzenediazonium fluoroborate

Method C

To a solution of the dithiaazapentalene (5 mmol) in acetonitrile (150 ml) was added a solution of benzenediazonium fluoroborate (1.920 g, 10 mmol) in acetonitrile (50 ml), and the mixture kept at room temperature for 1 hour. The mixture was then poured into water, extracted with ether (2x) and the extracts washed, dried and evaporated. Chromatography of the residue is described in individual cases.

(i) 6-Methyl-2-t-butyl-1,6a-dithia-6-azapentalene (34a)

(1.065 g, 5 mmol), Method C

Chromatography on a column of alumina (30 x 2.8 cm) with benzene gave orange eluates which afforded 4-formyl-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (20d) (1.351 g, 89%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(ii) 6-Methyl-1,6a-dithia-6-azapentalene (34b)

(0.785 g, 5 mmol), Method C

Chromatography on a column of silica (25 x 2.8 cm) with benzene gave a pale orange fraction from which no useful material was obtained. Continued elution with benzene gave a yellow fraction from which starting material (251 mg, 32%) was recovered.

(iii) 6-Methyl-2-phenyl-1,6a-dithia-6-azapentalene (34c)

(1.165 g, 5 mmol), Method C

Chromatography as in (ii) gave orange eluates which afforded 4-formyl-2,6-diphenyl-1,6a-dithia-5,6-diazapentalene (20f) (551 mg, 34%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared. Continued elution with benzene gave yellow eluates from which

starting material (102 mg, 8.7%) was obtained.

Selective Desulphurisation of Dithioester (26a) and of Thioamides (26b) and (26c)

(i) Desulphurisation of Methyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-dithiocarboxylate (26a)

Mercury(II) acetate (1.274 g, 4 mmol) was added to a solution of methyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-dithiocarboxylate (26a) (822 mg, 2 mmol) in chloroform (75 ml), and the mixture stirred at room temperature for 15 minutes. A further quantity (1.274 g, 4 mmol) of mercury(II) acetate was then added and the mixture stirred for a further 15 minutes. The mixture was then filtered, benzene (500 ml) added to the filtrate, and the resulting red solution washed with water(3x) dried and evaporated. Chromatography of the residue on a column of alumina (25 x 2.2 cm) with benzene gave red eluates which afforded S-methyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarboxylate (26d) (774 mg, 98%), red microneedles (from cyclohexane), m.p. 184-186°.

Found C 48.7; H 4.3; N 10.6%

$C_{16}H_{17}N_3O_3S_3$ requires C 48.6; H 4.3; N 10.6%.

M^+ at m/e 395, ν_{max} (KBr disc) 1650 (C=O) cm^{-1}.

(ii) Desulphurisation of N,N-dimethyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarboxamide (26b)

(a) with mercury(II) acetate

The procedure as in (i) was used, with the thioamide (26b) (816 mg, 2 mmol), and gave N,N-dimethyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-carboxamide (26e) (778 mg, 99%), identical with the sample previously prepared.

(b) with p-nitrobenzenediazonium fluoroborate

To a solution of the thioamide (26b) (408 mg, 1 mmol) in acetonitrile (60 ml), was added a solution of p-nitrobenzenediazonium fluoroborate (237 mg, 1 mmol) in acetonitrile (10 ml), and the mixture kept at room temperature for 45 minutes. The solution was then poured into water, extracted with benzene (2x), and the extracts washed with water (2x), dried and evaporated. Chromatography of the residue on a column of alumina (40 x 2.2 cm) with benzene gave red eluates from which starting material (304 mg, 75%) was recovered. Subsequent elution with benzene-ether (4:1) gave red eluates which afforded N,N-dimethyl 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-carboxamide (26e) (75 mg, 19%), identical (nmr spectrum in $CDCl_3$) with the samples previously prepared.

(c) with fluoroboric acid

The procedure as in (b) was used, but with 40% fluoroboric acid (0.17 ml, 1 mmol) in place of the diazonium salt. Starting material (403 mg, 99%) was recovered, and no trace of the amide (26e) was found.

(iii) Desulphurisation of N,N-dimethyl 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarboxamide (26c)

The procedure as in (i) was used, with N,N-dimethyl 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-thiocarboxamide (26c) (726 mg, 2 mmol), and gave N,N-dimethyl 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene-4-carboxamide (26f) (680 mg, 98%), orange-red prisms (from n-hexane), m.p. 92-93°.

Found C 58.9; H 6.2; N 12.3%

$C_{17}H_{21}N_3OS_2$ requires C 58.8; H 6.1; N 12.1%.

M^+ at m/e 347. ν_{max} (KBr disc) 1640 (C=O) cm^{-1}.

C. Synthesis of 1,6a-Dithia-5,6-diazapentalenes and 1,6a-Diselena-5,6-diazapentalenes

3-Methyl-5-t-butyl-[23], 3-methyl-[22], 3-ethyl-4-methyl-[53], 3-methyl-5-phenyl-[22], 3-methyl-4-phenyl-[22], 3-ethyl-5-phenyl-[22], and 4,5,6,7-tetrahydrobenzo[c][1,2]dithiolium perchlorate[42] and 3-benzyl-4-phenyl-1,2-dithiolium bromide[124] were prepared as in the references cited. 3-Ethyl-4-methyl- and 3,5-dimethyl-1,2-diselenolium perchlorate were also prepared by established procedures[168].

(a) From benzenediazonium fluoroborate

Method A

To a solution of the 1,2-dithiolium salt (5 mmol) in ethanol (120 ml) was added a solution of benzenediazonium fluoroborate (1.005 g, 5.25 mmol) in water (50 ml), and the mixture stirred at room temperature for 40 minutes. The resulting deep red solution was then diluted with water, extracted with benzene (2x), and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (50 x 2.8 cm) with petrol-benzene (2:1) gave orange eluates, which were evaporated and the residue rechromatographed on a column of alumina (30 x 2.8 cm) with petrol-benzene (2:1) to give the 1,6a-dithia-5,6-diazapentalene (44). A second fraction from the original column, obtained by elution with benzene, was evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with benzene to give the 4-arylazo-1,6a-dithia-5,6-diazapentalene (62) from deep red eluates.

Method A'

As Method A, except that a single product, the dithiadiaza-pentalene (44) was obtained.

Method A"

The procedure as in Method A' was used, but with the diselenolium

salt (63). Chromatography gave purple eluates which afforded the diselenadiazapentalene (64).

(i) 6-Phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a)

Method A was used, with 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (61a) (1.365 g, 5 mmol), 6-Phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) (616 mg, 45%) formed red plates (from n-hexane), m.p. 115-115.5°.

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%.

M^+ at m/e 285.

6-Phenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62a) (189 mg, 10%) formed deep red prisms (from cyclohexane), m.p. 183-184°.

Found C 63.3; H 5.4; N 14.5%

$C_{20}H_{20}N_2S_2$ requires C 63.1; H 5.3; N 14.7%.

M^+ at m/e 380.

(ii) 6-Phenyl-1,6a-dithia-5,6-diazapentalene (44b)

Method A' was used, with 3-methyl-1,2-dithiolium perchlorate (61b) (1.085 g, 5 mmol) and gave 6-phenyl-1,6a-dithia-5,6-diazapentalene (44b) (345 mg, 31%), red needles (from n-hexane), m.p. 95-96°.

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; S 29.1%.

M^+ at m/e 220.

(iii) 3,4-Dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c)

Method A' was used, with 3-ethyl-4-methyl-1,2-dithiolium perchlorate (61c) (1.225 g, 5 mmol) and gave 3,4-dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c) (1.116 g, 90%), red needles (from cyclohexane), m.p. 136-137°.

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%.

M^+ at m/e 248.

(iv) 3,4-Trimethylene-6-phenyl-1,6a-dithia-5,6-diazapentalene (44d)

Method A' was used, with 4,5,6,7-tetrahydrobenzo[c][1,2]dithiolium perchlorate (61d) (1.283 g, 5 mmol) and gave 3,4-trimethylene-6-phenyl-1,6a-dithia-5,6-diazapentalene (44d) (1.246 g, 99%), red spars (from n-hexane), m.p. 100-100.5°.

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%.

M^+ at m/e 296.

(v) 2,6-Diphenyl-1,6a-dithia-5,6-diazapentalene (44e)

Method A' was used, with 3-methyl-5-phenyl-1,2-dithiolium perchlorate (61e) (1.465 g, 5 mmol), and gave 2,6-diphenyl-1,6a-dithia-5,6-diazapentalene (44e) (1.064g, 72%), red plates (from benzene-cyclohexane), m.p. 163-163.5°.

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%.

M^+ at m/e 296.

(vi) 3,6-Diphenyl-1,6a-dithia-5,6-diazapentalene (44f)

Method A' was used, with 3-methyl-4-phenyl-1,2-dithiolium perchlorate (61f) (1.465 g, 5 mmol), and gave 3,6-diphenyl-1,6a-dithia-5,6-diazapentalene (44f) (1.157 g, 78%), red needles (from cyclohexane), m.p. 111.5-112.5°.

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%.

M^+ at m/e 296.

(vii) 4-Methyl-2,6-diphenyl-1,6a-dithia-5,6-diazapentalene (44g)

Method A' was used, with 3-ethyl-5-phenyl-1,2-dithiolium perchlorate (61g) (1.533 g, 5 mmol), and gave 4-methyl-2,6-diphenyl-1,6a-dithia-5,6-diazapentalene (44g) (1.481 g, 96%), fine deep red needles (from cyclohexane), m.p. 108-109°.

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%.

M^+ at m/e 310.

(viii) 3,4,6-Triphenyl-1,6a-dithia-5,6-diazapentalene (44h)

Method A' was used, with 3-benzyl-4-phenyl-1,2-dithiolium bromide (61h) (1.745 g, 5 mmol), and gave 3,4,6-triphenyl-1,6a-dithia-5,6-diazapentalene (44h) (1.775 g, 96%), deep red prisms (from cyclohexane), m.p. 207-208.5°.

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%.

(ix) 2-Methyl-6-phenyl-1,6a-diselena-5,6-diazapentalene (64a)

Method A" was used, with 3,5-dimethyl-1,2-diselenolium perchlorate (63a) (1.623 g, 5 mmol), and gave 2-methyl-6-phenyl-1,6a-diselena-5,6-diazapentalene (64a) (533 mg, 33%), deep purple needles (from n-hexane), m.p. 109-110°.

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%.

M^+ at m/e 324-328.

(x) 3,4-Dimethyl-6-phenyl-1,6a-diselena-5,6-diazapentalene (64b)

Method A" was used, with 3-ethyl-4-methyl-1,2-diselenolium perchlorate (63b) (1.690 g, 5 mmol), and gave 3,4-dimethyl-6-phenyl-1,6a-diselena-5,6-diazapentalene (64b) (700 mg, 41%) deep purple needles (from n-hexane), m.p. 82-83°.

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%.

M^+ at m/e 340-346.

(b) From p-nitrobenzenediazonium fluoroborate

Method B

To a solution of the dithiolium salt (5 mmol) in ethanol

(120 ml) was added a solution of p-nitrobenzenediazonium fluoroborate (1.245 g, 5.25 mmol) in aqueous ethanol (1:1, 150 ml), and the mixture stirred at room temperature for 1 hour. The mixture was then poured into water, extracted with benzene (2x), and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (50 x 2.8 cm) with benzene gave red eluates, which were evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with benzene to give the dithiadiazapentalene (44). A second fraction of deep red eluates from the original column was evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with benzene-ether (9:1) to give the arylazodithiadiazapentalene (62).

Method B'

As Method B, except that a single product, the dithiadiazapentalene (44), was obtained.

Method B''

As Method B', but using the diselenolium salt (5 mmol). Chromatography gave purple eluates from which the diselenadiazapentalene (64) was obtained.

(i) 6-p-Nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i)

Method B was used, with 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (61a) (1.365 g, 5 mmol). 6-p-Nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i) (557 mg, 35%) formed deep red spars (from benzene), m.p. 267-268°.

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%.

M^+ at m/e 321.

6-p-Nitrophenyl-4-p-nitrophenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62b) (105 mg, 4.5%) formed red-brown microneedles (from benzene), m.p. 296-297°.

Found C 50.8; H 3.8; N 17.9%

$C_{20}H_{18}N_6O_4S_2$ requires C 51.1; H 3.9; N 17.9%.

M^+ at m/e 470.

(ii) 6-p-Nitrophenyl-1,6a-dithia-5,6-diazapentalene (44j)

Method B' was used, with 3-methyl-1,2-dithiolium perchlorate (61b) (1.085 g, 5 mmol) and gave 6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44j) (321 mg, 24%), orange-red prisms, (from benzene-cyclohexane), m.p. 198-199°.

Found C 45.1; H 2.7; N 15.4%

$C_{10}H_7N_3O_2S_2$ requires C 45.3; H 2.7; N 15.8%.

M^+ at m/e 265.

(iii) 3,4-Dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k)

Method B' was used, with 3-ethyl-4-methyl-1,2-dithiolium perchlorate (61c) (1.225 g, 5 mmol), and gave 3,4-dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k) (1.392 g, 95%), identical (nmr spectrum in $CDCl_3$) with the samples previously prepared.

(iv) 3,4-Trimethylene-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44 l)

Method B' was used, with 4,5,6,7-tetrahydrobenzo[c][1,2]dithiolium perchlorate (61d) (1.283 g, 5 mmol), and gave 3,4-trimethylene-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44 l) (1.287 g, 84%), identical (nmr spectrum in $CDCl_3$) with the samples previously prepared.

(v) 4-Methyl-6-p-nitrophenyl-2-phenyl-1,6a-dithia-5,6-diazapentalene (44m)

Method B' was used, with 3-ethyl-5-phenyl-1,2-dithiolium perchlorate (61g) (1.533 g, 5 mmol), and gave 4-methyl-6-p-nitrophenyl-2-phenyl-1,6a-dithia-5,6-diazapentalene (44m) (1.536 g, 87%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(vi) 2-Methyl-6-p-nitrophenyl-1,6a-diselena-5,6-diazapentalene (64c)

Method B" was used, with 3,5-dimethyl-1,2-diselenolium perchlorate (63a) (1.623 g, 5 mmol), and gave 2-methyl-6-p-nitrophenyl-1,6a-diselena-5,6-diazapentalene (64c) (361 mg, 19%), deep violet needles (from benzene-cyclohexane), m.p. 225-227°.

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%.

M^+ at m/e 370-376.

(vii) 3,4-Dimethyl-6-p-nitrophenyl-1,6a-diselena-5,6-diazapentalene (64d)

Method B" was used, with 3-ethyl-4-methyl-1,2-diselenolium perchlorate (63b) (1.690 g, 5 mmol), and gave 3,4-dimethyl-6-p-nitrophenyl-1,6a-diselena-5,6-diazapentalene (64d) (804 mg, 42%), fine deep violet microneedles (from benzene-cyclohexane), m.p. 207-208°.

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%.

M^+ at m/e 384-390.

(c) From p-methoxybenzenediazonium fluoroborate

Method C

To a solution of the dithiolium salt (5 mmol) in ethanol (120 ml) was added a solution of p-methoxybenzenediazonium fluoroborate (1.220 g, 5.5 mmol) in ethanol-water (2:1, 150 ml), and the mixture stirred at room temperature for 1 hour. The mixture was then poured into water, extracted with ether (2x), and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (50 x 2.8 cm) with benzene gave orange eluates which were evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with benzene to give the dithiadiazapentalene (44). A second fraction obtained from the original column by elution with benzene-ether (4:1) was evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with

benzene-ether (4:1) to yield the arylazodithiadiazapentalene (62).

Method C'

As method C, except that a single product, the dithiadiazapentalene (44) was obtained.

Method C''

As method C', but with the diselenolium salt (5 mmol). Chromatography gave deep violet eluates from which the diselenadiazapentalene (64) was obtained.

(i) 6-p-Methoxyphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44n)

Method C was used, with 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (61a) (1.365 g, 5 mmol). 6-p-Methoxyphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44n) (1.161 g, 76%) formed orange-red plates (from n-hexane), m.p. 144-144.5°.

Found C 58.9; H 6.3; N 9.5%

$C_{15}H_{18}N_2O_2S_2$ requires C 58.8; H 5.9; N 9.1%.

M^+ at m/e 306.

6-p-Methoxyphenyl-4-p-methoxyphenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62c) (60 mg, 2.7%) formed red-brown needles (from n-hexane), m.p. 110-111.5°.

Found C 59.8; H 5.8; N 12.8%

$C_{22}H_{24}N_4O_2S_2$ requires C 60.0; H 5.5; N 12.7%.

M^+ at m/e 440.

(ii) 6-p-Methoxyphenyl-1,6a-dithia-5,6-diazapentalene (44o)

Method C' was used, with 3-methyl-1,2-dithiolium perchlorate (61b) (1.085 g, 5 mmol), and gave 6-p-methoxyphenyl-1,6a-dithia-5,6-diazapentalene (44o) (350 mg, 28%), orange-red spars (from n-hexane), m.p. 110-110.5°.

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%.

M^+ at m/e 250.

(iii) 6-p-Methoxyphenyl-3,4-dimethyl-1,6a-dithia-5,6-diaza-pentalene (44p)

Method C' was used, with 3-ethyl-4-methyl-1,2-dithiolium perchlorate (61c) (1.225 g, 5 mmol), and gave 6-p-methoxyphenyl-3,4-dimethyl-1,6a-dithia-5,6-diazapentalene (44p) (1.378 g, 99%), fine red microneedles (from cyclohexane), m.p. 153-153.5°.

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%.

M^+ at m/e 278,

(iv) 6-p-Methoxyphenyl-3,4-trimethylene-1,6a-dithia-5,6-diaza-pentalene (44q)

Method C' was used, with 4,5,6,7-tetrahydrobenzo[c][1,2] dithiolium perchlorate (61d) (1.283 g, 5 mmol), and gave 6-p-methoxyphenyl-3,4-trimethylene-1,6a-dithia-5,6-diazapentalene (44q) (1.430 g, 99%), deep red needles (from n-hexane), m.p. 118.5-119.5°.

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%.

M^+ at m/e 290.

(v) 6-p-Methoxyphenyl-2-methyl-1,6a-diselena-5,6-diazapentalene (64e)

Method C" was used, with 3,5-dimethyl-1,2-diselenolium perchlorate (63a) (1.623 g, 5 mmol), and gave 6-p-methoxyphenyl-2-methyl-1,6a-diselena-5,6-diazapentalene (64e) (451 mg, 25%), deep purple plates (from n-hexane), m.p. 121-122.5°.

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%.

M^+ at m/e 356-361.

(d.) From p-acetylbenzenediazonium fluoroborate

Method D

The reaction conditions and extraction procedure as in Method C were used, with p-acetylbenzenediazonium fluoroborate (1.285 g, 5.5 mmol). Chromatography of the residue on a column of alumina

(50 x 2.8 cm) with benzene-ether (4:1) gave red eluates which were evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with benzene-ether (4:1) to give the dithiadiazapentalene (44). A second fraction of deep red eluates obtained from the original column, with ether-benzene (2:1) as eluant, was evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with ether-benzene (2:1) to give the arylazodithiadiazapentalene (62).

Method D'

As Method D, except that a single product, the dithiadiazapentalene (44), was obtained.

(i) 6-p-Acetylphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44r)

Method D was used, with 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (61a) (1.365 g, 5 mmol). 6-p-Acetylphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44r) (477 mg, 30%) formed orange plates (from cyclohexane), m.p. 140-141°.

Found C 60.6; H 5.6; N 8.9%

$C_{16}H_{18}N_2OS_2$ requires C 60.4; H 5.7; N 8.8%.

M^+ at m/e 318. ν_{max} (KBr disc) 1680 (C=O) cm^{-1}.

6-p-Acetylphenyl-4-p-acetylphenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62d) (213 mg, 9.2%) formed dark red needles (from benzene-cyclohexane), m.p. 234-235°.

Found C 62.2; H 5.3; N 12.0%

$C_{24}H_{24}N_4O_2S_2$ requires C 62.1; H 5.2; N 12.1%.

M^+ at m/e 464. ν_{max} (KBr disc) 1672 (C=O) cm^{-1} and 1680 (C=O) cm^{-1}.

(ii) 6-p-Acetylphenyl-1,6a-dithia-5,6-diazapentalene (44s)

Method D' was used, with 3-methyl-1,2-dithiolium perchlorate (61b) (1.085 g, 5 mmol), and gave 6-p-acetylphenyl-1,6a-dithia-5,6-diazapentalene (44s) (238 mg, 18%), orange-red plates [from cyclohexane-benzene (1:1)], m.p. 180-180.5°.

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%.

M^+ at m/e 262, ν_{max} (KBr disc) 1680 (C=O) cm^{-1}.

(iii) 6-p-Acetylphenyl-3,4-dimethyl-1,6a-dithia-5,6-diazapentalene (44t)

Method D' was used, with 3-ethyl-4-methyl-1,2-dithiolium perchlorate (61c) (1.225 g, 5 mmol), and gave 6-p-acetylphenyl-3,4-dimethyl-1,6a-dithia-5,6-diazapentalene (44t) (1.439 g, 99%), red needles [from cyclohexane-benzene (1:1)], m.p. 158-160°.

Found C 58.1; H 4.9; N 9.4%

$C_{14}H_{14}N_2OS_2$ requires C 58.0; H 4.9; N 9.7%.

M^+ at m/e 290. ν_{max} (KBr disc) 1665 (C=O) cm^{-1}.

(iv) 6-p-Acetylphenyl-3,4-trimethylene-1,6a-dithia-5,6-diazapentalene (44u)

Method D' was used, with 4,5,6,7-tetrahydrobenzo[c][1,2] dithiolium perchlorate (61d) (1.283 g, 5 mmol), and gave 6-p-acetylphenyl-3,4-trimethylene-1,6a-dithia-5,6-diazapentalene (44u) (1.389 g, 92%), red needles [from cyclohexane-benzene (1:1)], m.p. 149-150°.

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%.

M^+ at m/e 302. ν_{max} (KBr disc) 1666 (C=O) cm^{-1}.

(e) From p-toluenediazonium fluoroborate

Method E

As Method A, but with p-toluenediazonium fluoroborate (1.086 g, 5.25 mmol).

(i) 2-t-butyl-6-p-tolyl-1,6a-dithia-5,6-diazapentalene (44v)

Method E was used, with 3-methyl-5-t-butyl-1,2-dithiolium perchlorate(61a) (1.365 g, 5 mmol). 2-t-Butyl-6-p-tolyl-1,6a-dithia-5,6-diazapentalene (44v) (0.988 g, 68%) formed orange-red plates (from

n-hexane), m.p. 129.5-130.5°.

Found C 62.2; H 6.1; N 9.8%

$C_{15}H_{18}N_2S_2$ requires C 62.0; H 6.2; N 9.7%.

M^+ at m/e 290.

2-t-Butyl-6-p-tolyl-4-p-tolylazo-1,6a-dithia-5,6-diazapentalene (62e) (138 mg, 6.8%) formed red-brown spars (from cyclohexane), m.p. 167.5-170°.

Found C 64.6; H 6.1; N 13.8%

$C_{22}H_{24}N_4S_2$ requires C 64.7; H 5.9; N 13.7%.

M^+ at m/e 408.

(f) From p-bromobenzenediazonium fluoroborate

Method F

The reaction conditions and extraction procedure as in Method C were used, but with p-bromobenzenediazonium fluoroborate (1.489 g, 5.5 mmol). Chromatography of the residue on a column of alumina (50 x 2.8 cm) with petrol-benzene (3:1) gave an orange fraction, which was evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with petrol-benzene (3:1) to give the dithiadiazapentalene (44). A second fraction of red eluates obtained from the original column, with benzene as eluant, was evaporated and rechromatographed on a column of alumina (30 x 2.8 cm) with benzene to give the arylazodithiadiazapentalene (62).

Method F'

As Method F, except that a single product, the dithiadiazapentalene (44), was obtained.

(i) 6-p-Bromophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44w)

Method F was used, with 3-methyl-5-t-butyl-1,2-dithiolium perchlorate (61a) (1.365 g, 5 mmol). 6-p-Bromophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44w) (730 mg, 41%) formed orange-red needles (from n-hexane), m.p. 163.5-165°.

Found C 47.4; H 4.5; N 7.9%

$C_{14}H_{15}N_2S_2Br$ requires C 47.3; H 4.3; N 7.9%.

M^+ at m/e 354, 356 (1:1).

6-p-Bromophenyl-4-p-bromophenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62f) (398 mg, 15%) formed fine red microneedles (from cyclohexane), m.p. 217.5-220°.

Found C 44.7; H 3.6; N 10.4%

$C_{20}H_{18}N_4S_2Br_2$ requires C 44.6; H 3.4; N 10.4%.

M^+ at m/e 536, 538, 540 (1:2:1).

(ii) 6-p-Bromophenyl-1,6a-dithia-5,6-diazapentalene (44x)

Method F' was used, with 3-methyl-1,2-dithiolium perchlorate (61b) (1.085 g, 5 mmol), and gave 6-p-bromophenyl-1,6a-dithia-5,6-diazapentalene (44x) (324 mg, 22%), orange-red needles (from n-hexane), m.p. 126-127°.

Found C 40.0; H 2.2; N 9.3%

$C_{10}H_7S_2N_2Br$ requires C 40.1; H 2.4; N 9.4%.

M^+ at m/e 298, 300 (1:1).

D. Reactivity of 1,6a-Dithia-5,6-diazapentalenes

1. Electrophilic Substitution

(a) Diazo-coupling Reactions of 1,6a-dithia-5,6-diazapentalenes

The following general procedure was used. To a solution of the dithiadiazapentalene (2 mmol) in acetonitrile or ethanol (75 ml) was added the arenediazonium fluoroborate (quantities given in individual cases), and the mixture stirred at 60° for 1 hour. The cooled mixture was then poured into water, extracted with ether (4x) and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue is described in individual cases.

1. With benzenediazonium fluoroborate

6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a)

(i) (552 mg, 2 mmol) in acetonitrile, with benzenediazonium fluoroborate (768 mg, 4 mmol). Chromatography on a column of alumina (40 x 2.2 cm) with petrol-benzene (3:1) gave orange eluates from which starting material (486 mg, 88%) was recovered. Continued elution with benzene brought through red eluates which afforded 6-phenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62a) (79 mg, 10%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(ii) Reaction (i) was repeated in ethanol, and gave starting material (79 mg, 14%) and 6-phenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62a) (558 mg, 74%).

6-p-methoxyphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44n)

(iii) (612 mg, 2 mmol) in acetonitrile, with benzenediazonium fluoroborate (768 mg, 2 mmol). Chromatography on a column of alumina (35 x 2.2 cm) with petrol-benzene (2:1) gave orange eluates which afforded 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) (540 mg, 98%), identical (nmr spectrum in $CDCl_3$) with the

sample previously obtained.

(iv) Reaction (iii) was repeated in ethanol. Chromatography on a column of alumina with petrol-benzene (2:1) gave orange eluates which afforded 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) (133 mg, 24%). Continued elution with petrol-benzene (2:1) brought through red eluates which afforded 6-phenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62a) (158 mg, 21%), followed by a deep red fraction, on elution with benzene-petrol (2:1) which yielded a mixture of 4-p-methoxyphenylazo-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene [81a (i)] and 6-p-methoxyphenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene [81a (ii)] (5:2, 294 mg, 36%), red-brown prisms (from cyclohexane), m.p. 151-155.5°.

Found C 61.7; H 5.6; N 13.9%

$C_{21}H_{22}N_4OS_2$ requires C 61.4; H 5.4; N 13.7%.

$M^{+\cdot}$ at m/e 410

Elution with benzene-ether (9:1) then gave red eluates which afforded 6-p-methoxyphenyl-4-p-methoxyphenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62c) (47 mg, 5.3%). Compounds (44a), (62a) and (62c) were identical (nmr spectrum in $CDCl_3$) with the samples previously prepared.

2. With p-nitrobenzenediazonium fluoroborate

6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a)

(i) (552 mg, 2 mmol) in acetonitrile, with p-nitrobenzenediazonium fluoroborate (0.948 g , 4 mmol). Chromatography on a column of alumina (40 x 2.2 cm) with benzene-petrol (2:1) gave pale orange eluates which were discarded. Elution with benzene then brought through red eluates which afforded 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i) (440 mg, 69%). Finally, elution with benzene-ether (9:1) gave a deep red fraction from which 6-p-nitrophenyl-4-p-nitrophenylazo-2-t-butyl-1,6a-dithia-5,6-diaza-pentalene (62b) (144 mg, 15%) was obtained. The products were

identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

(ii) Reaction (i) was repeated in ethanol. Chromatography of the residue on a column of alumina (60 x 2.2 cm) with benzene gave orange eluates which were evaporated and rechromatographed on a column of alumina (30 x 2.2 cm) with petrol-benzene (3:1) to give 6-phenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62a) (27 mg, 3.8%). A second fraction of red eluates from the original column, obtained by elution with benzene, was evaporated and rechromatographed on a column of silica (60 x 2.2 cm). Elution with benzene-petrol (3:1) gave red eluates from which 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i) (108 mg, 17%) was obtained. Subsequent elution with benzene-ether (9:1) brought through deep red eluates which afforded a mixture of 4-p-nitrophenylazo-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene [81b (i)] and 6-p-nitrophenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene [81b (ii)] (2:3, 466 mg, 55%), red-brown needles (from benzene), m.p. 192-194°.

Found C 56.8; H 4.8; N 16.6%

$C_{20}H_{19}N_5O_2S_2$ requires C 56.5; H 4.5; N 16.5%.

$M^{+\cdot}$ at m/e 425.

A third red fraction obtained from the original column, by elution with benzene-ether (9:1), afforded 6-p-nitrophenyl-4-p-nitrophenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62b) (58 mg, 6.2%). Compounds (62a), (44i) and (62b) were identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

6-p-methoxyphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44n)

(iii) (612 mg, 2 mmol), in acetonitrile with p-nitrobenzenediazonium fluoroborate (948 mg, 4 mmol). Chromatography as in [2, (i)] gave 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i) (472 mg, 74%) and 6-p-nitrophenyl-4-p-nitrophenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62b) (146 mg, 15%). The products were

identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

(iv) Reaction (iii) was repeated in ethanol. Chromatography on a column of alumina (40 x 2.2 cm) with benzene-petrol (4:1) gave pale yellow eluates which were discarded. Elution with benzene then gave red eluates from which 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i) (420 mg, 66%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared, was obtained. Subsequent elution with benzene-ether (4:1) then gave a deep red fraction which was evaporated to give a red-brown solid (311 mg) shown (nmr and mass spectra) to be a mixture of 6-p-methoxyphenyl-4-p-nitrophenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene [81c (i)] and 4-p-methoxyphenylazo-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene [81c (ii)] (1:4) and 6-p-nitrophenyl-4-p-nitrophenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62b).

Molecular weight 455.1088

$C_{21}H_{18}N_5O_3S_2$ (81c) requires 455.1086.

Molecular weight 470.0835

$C_{20}H_{18}N_6O_4S_2$ (62b) requires 470.0831.

3. With p-methoxybenzenediazonium fluoroborate

6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a)

(i) (552 mg, 2 mmol) in acetonitrile, with p-methoxybenzenediazonium fluoroborate (1.332 g, 6 mmol). Chromatography on a column of alumina (35 x 2.2 cm) with petrol-benzene (2:1) gave orange eluates from which starting material (295 mg, 53%) was obtained. Further elution with petrol-benzene (1:1) gave an orange fraction which afforded 6-p-methoxyphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44n) (231 mg, 38%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

(ii) Reaction (i) was repeated in ethanol. Chromatography as in [1, (iv)] gave starting material (34 mg, 6.2%),

6-phenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62a) (82 mg, 11%), a mixture of 4-p-methoxyphenylazo-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene [81a (i)] and 6-p-methoxyphenyl-4-phenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene [81a (ii)] (5:2, 359 mg, 44%), and 6-p-methoxyphenyl-4-p-methoxyphenylazo-2-t-butyl-1,6-dithia-5,6-diazapentalene (62c) (195 mg, 22%). The products were identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

6-p-methoxyphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44n)

(iii) (612 mg, 2 mmol) in acetonitrile, with p-methoxybenzenediazonium fluoroborate (1.332 g, 6 mmol). Chromatography on a column of alumina (35 x 2.2 cm) with benzene-petrol (1:1) gave orange eluates from which starting material (286 mg, 47%) was recovered. Continued elution with benzene gave red eluates which afforded 6-p-methoxyphenyl-4-p-methoxyphenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62c) (65 mg, 7.4%).

(iv) Reaction (iii) was repeated in ethanol, and gave starting material (18 mg, 2.9%) and 6-p-methoxyphenyl-4-p-methoxyphenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62c) (785 mg, 89%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

4. With p-acetylbenzenediazonium fluoroborate

6-p-acetylphenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44r)

(636 mg, 2 mmol) in ethanol, with p-acetylbenzenediazonium fluoroborate (936 mg, 4 mmol). Chromatography on a column of alumina (30 x 2.2 cm) with benzene-ether (4:1) gave orange eluates from which starting material (42 mg, 6.6%) was recovered. Continued elution with benzene-ether (1:1) gave deep red eluates which afforded 6-p-acetylphenyl-4-p-acetylphenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62d) (835 mg, 90%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

5. With p-toluenediazonium fluoroborate

2-t-butyl-6-p-tolyl-1,6a-dithia-5,6-diazapentalene (44v)

(580 mg, 2 mmol) in ethanol, with p-toluenediazonium fluoroborate (823 mg, 4 mmol). Chromatography as in [1, (i)] gave starting material (107 mg, 17%) and 2-t-butyl-6-p-tolyl-4-p-tolylazo-1,6a-dithia-5,6-diazapentalene (62e) (623 mg, 76%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

6. With p-bromobenzenediazonium fluoroborate

6-p-bromophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44w)

(711 mg, 2 mmol) in ethanol, with p-bromobenzenediazonium fluoroborate (1.083 g, 4 mmol). Chromatography as in [1, (i)] gave starting material (32 mg, 9%) and 6-p-bromophenyl-4'-p-bromophenylazo-2-t-butyl-1,6a-dithia-5,6-diazapentalene (62f) (827 mg, 77%) identical (nmr spectrum in $CDCl_3$) with the sample previously obtained.

(b) Formylation of 1,6a-Dithia-5,6-diazapentalenes

Method A

A solution of phosphoryl chloride (1.82 ml, 20 mmol) in dry dimethylformamide (10 ml) was added over 15 minutes to a solution of the dithiadiazapentalene (2 mmol) in dry dimethylformamide (10 ml) and the mixture heated at 60° for 2 hours. The mixture was then allowed to cool, poured into 1M aqueous sodium hydroxide (200 ml), extracted with benzene (3x), and the extracts washed with water (5x), dried and evaporated. Chromatography is described in individual cases.

Method B

A solution of phosphoryl chloride (1.82 ml, 20 mmol) in dry dimethylformamide (10 ml) was added over 15 minutes to a solution of the dithiadiazapentalene (2 mmol) in dry dimethylformamide

(150 ml). The mixture was then heated at 60° for 1 hour and at 80° for a further hour. The solution was allowed to cool, poured into 1M aqueous sodium hydroxide (200 ml), extracted with benzene (3x), and the extracts washed with water (5x), dried and evaporated. Chromatography of the residue is described in individual cases.

(i) 6-Phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a)

(552 mg, 2 mmol), Method A

Chromatography on a column of alumina (40 x 2.2 cm) with benzene-petrol (1:1) gave orange eluates from which starting material (190 mg, 34%) was recovered. Continued elution with benzene-ether (9:1) then brought through orange eluates which afforded 4-formyl-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (20d) (345 mg, 57%), identical (nmr spectrum in $CDCl_3$) with the samples previously prepared.

(ii) 6-Phenyl-1,6a-dithia-5,6-diazapentalene (44b)

(440 mg, 2 mmol), Method A

Chromatography on a column of silica (40 x 2.2 cm) with benzene gave pale pink eluates which were discarded. Elution with benzene-ether (9:1) then gave an orange fraction which afforded 4-formyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (20e) (74 mg, 15%) identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(iii) 6-p-Nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i)

(642 mg, 2 mmol), Method B

Chromatography on a column of alumina (50 x 2.8 cm) with benzene gave red eluates from which starting material (171 mg, 27%) was recovered. Continued elution with benzene-ether (9:1) gave an orange fraction which was evaporated to give 4-formyl-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (20a) (125 mg, 18%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

(iv) 6-p-Nitrophenyl-1,6a-dithia-5,6-diazapentalene (44j)

(530 mg, 2 mmol), Method B

Chromatography on a column of silica (30 x 2.2 cm), initially with benzene and subsequently with benzene-ether (1:1) gave no trace of starting material or product.

(c) Bromination of 1,6a-Dithia-5,6-diazapentalene

Method A

To a solution of the dithiadiazapentalene (5 mmol) in carbon tetrachloride (150 ml) was added a 1M solution of bromine in carbon tetrachloride (10 ml, 10 mmol), and the mixture stirred at room temperature for ten minutes. The mixture was then poured into water, extracted with ether (2x) and the extracts washed with water (3x), dried and evaporated. Chromatography of the residue is described in individual cases.

Method B

As method A, but on a smaller scale, with the dithiadiazapentalene (1 mmol) in carbon tetrachloride (30 ml), and a 1M solution of bromine in carbon tetrachloride (2 ml, 2 mmol).

(i) 6-Phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a)

(1.380 g, 5 mmol), Method A

The residue was chromatographed on a column of silica (60 x 2.2 cm) with petrol-benzene (4:1) and the eluates examined by TLC. Initial red eluates (400 ml) contained a single red compound and a second red fraction (200 ml) contained two components. A third fraction of orange eluates (400 ml) contained a single orange compound. The second fraction was evaporated and rechromatographed in the same way to effect a complete separation of the two components. Evaporation of the combined red eluates yielded 4-bromo-6-p-bromophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (84a) (291 mg, 13%), red prisms (from n-hexane), m.p. 143.5-144.5°.

Found C 39.1; H 3.3; N 6.5%

$C_{14}H_{14}N_2S_2Br_2$ requires C 38.7; H 3.3; N 6.5%.

M^+ at m/e 432, 434, 436 (1:2:1)

Evaporation of the combined orange eluates gave 4-bromo-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (83a) (1.396 g, 79%), orange-red needles (from n-hexane), m.p. 104-105.5°.

Found C 47.3; H 4.2; N 7.7%

$C_{14}H_{15}N_2S_2Br$ requires C 47.3; H 4.3; N 7.9%.

M^+ at m/e 354, 356 (1:1)

(ii) 6-Phenyl-1,6a-dithia-5,6-diazapentalene (44b)

(1.100 g, 5 mmol), Method A

Chromatography as in (i) gave initial red eluates which afforded 4-bromo-6-p-bromophenyl-1,6a-dithia-5,6-diazapentalene (84b) (244 mg, 13%), red-brown needles (from n-hexane), m.p. 146-147°.

Found C 31.8; H 1.6; N 7.3%

$C_{10}H_6N_2S_2Br_2$ requires C 31.8; H 1.6; N 7.4%.

M^+ at m/e 376, 378, 380 (1:2:1)

Subsequent orange eluates afforded 4-bromo-6-phenyl-1,6a-dithia-5,6-diazapentalene (83b) (1.008 g, 67%), orange-red spars (from n-hexane), m.p. 97-99°.

Found C 40.4; H 2.4; N 9.4%

$C_{10}H_7S_2N_2Br$ requires C 40.1; H 2.4; N 9.4%.

M^+ at m/e 298, 300 (1:1)

(iii) 4-Bromo-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (83a)

(355 mg, 1 mmol), Method B

Chromatography on a column of silica (60 x 2.2 cm) with petrol-benzene (4:1) gave initially red eluates which afforded 4-bromo-6-p-bromophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (84a) (226 mg, 52%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared. Continued elution brought through orange eluates from

which starting material (99mg, 28%) was recovered.

(iv) 6-p-Bromophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44w)

(355 mg, 1 mmol), Method B

Chromatography as in (iii) gave 4-bromo-6-p-bromophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (84a)(420 mg, 97%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared. No starting material was recovered.

(v) 4-Bromo-6-phenyl-1,6a-dithia-5,6-diazapentalene (83b)

(299 mg, 1 mmol), Method B

Chromatography as in (iii) gave initially 4-bromo-6-p-bromophenyl-1,6a-dithia-5,6-diazapentalene (84b) (85 mg, 23%), identical (nmr spectrum in $CDCl_3$) with the sample previously obtained, and subsequently starting material (73 mg, 37%).

(vi) 6-p-Bromophenyl-1,6a-dithia-5,6-diazapentalene (44x)

(299 mg, 1 mmol), Method B

Chromatography as in (iii) gave 4-bromo-6-p-bromophenyl-1,6a-dithia-5,6-diazapentalene (84b) (280 mg, 74%), identical (nmr spectrum in $CDCl_3$) with the samples previously prepared. No starting material was recovered.

(d) Nitrosation of 1,6a-Dithia-5,6-diazapentalenes

The following general procedure was used:

Sodium nitrite (0.690 g, 10 mmol) was added to a solution of the dithiadiazapentalene (5 mmol) in acetonitrile-acetic acid (1:1, 150 ml), and the mixture stirred at room temperature for 15 minutes. A further quantity of sodium nitrite (0.345 g, 5 mmol) was then added and the stirring continued for a further 15 minutes. The solution was then poured into water, extracted with benzene (3x), and the extracts washed successively with water (2x), saturated sodium bicarbonate solution (2x) and water (2x), dried and

evaporated. Chromatography of the residue is described in individual cases.

(i) 6-Phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a)

(1.380 g, 5 mmol)

Chromatography on a column of alumina (40 x 2.8 cm) with benzene-petrol (1:1) gave pale yellow eluates which were discarded. Elution with benzene then gave red eluates, which were evaporated and rechromatographed on a column of silica (55 x 2.2 cm). Initial red eluates, obtained by elution with benzene-petrol (1:1) afforded 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i) (24 mg, 1.5%), identical(nmr spectrum in $CDCl_3$) with the samples previously prepared. Subsequent red eluates, obtained by elution with benzene afforded 4-nitro-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (88a) (70 mg, 4.4%), 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^+ at m/e 321

A second fraction of deep orange-yellow eluates, obtained from the original column by elution with benzene-ether (4:1), was evaporated to give 3-phenylazo-5-t-butyl-1-oxa-6,6a-dithia-2-aza-pentalene (87a) (1.322 g, 87%), fine orange-yellow microneedles (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^+ at m/e 305

(ii) 6-Phenyl-1,6a-dithia-5,6-diazapentalene (44b)

(1.100 g, 5 mmol)

Chromatography as in (i) gave the following three products; 6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44j) (16 mg, 1.2%), identical (nmr spectrum in $CDCl_3$) with the sample previously

prepared, 4-nitro-6-phenyl-1,6a-dithia-5,6-diazapentalene (88b) (85 mg, 6.4%), red prisms (fromcyclohexane-benzene) m.p. 151-151.5°

Found C 45.4; H 2.6; N 15.6%

$C_{10}H_7N_3O_2S_2$ requires C 45.3; H 2.7; N 15.8%.

M^+ at m/e 265,

and 3-phenylazo-1-oxa-6,6a-dithia-2-azapentalene (87b) (624 mg, 50%), fine brown-yellow microneedles (from cyclohexane-benzene), 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^+ at m/e 249

(iii) 3,4-Dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c)

(1.240 g, 5 mmol)

Chromatography on a column of alumina (50 x 2.8 cm) with benzene-petrol (2:1) gave pale orange eluates which were discarded. Elution with benzene-petrol (3:1) then gave red eluates which afforded 3,4-dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k) (87 mg, 6.0%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared. Elution with benzene-ether (4:1) then gave a yellow fraction, which was evaporated to give 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (93) (336 mg, 39%), identical (nmr spectrum in $CDCl_3$) with an authentic sample[42]. Finally, elution with ether-ethanol (99:1) gave yellow eluates which afforded 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene-2-oxide (94) (102 mg, 11%), identical (nmr spectrum in $CDCl_3$) with an authentic sample[42].

Attempted Oxidations with Nitrous Acid

(i) 3-Phenylazo-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene (87a)

Sodium nitrite (276 mg, 4 mmol) was added to a solution of 3-phenylazo-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene (87a) (610 mg, 2 mmol) in acetonitrile-acetic acid (1:1 , 100 ml), and the

mixture stirred at room temperature for 15 minutes. A further portion of sodium nitrite (138 mg, 2 mmol) was then added and the stirring continued for a further 15 minutes. The mixture was then poured into water, extracted with benzene (2x), and the extracts washed successively with water (2x), saturated sodium bicarbonate solution (2x) and water (2x), dried and evaporated. Chromatography of the residue on a column of alumina (35 x 2.2 cm) with benzene gave colourless eluates which were discarded. Elution with benzene-ether (4:1) then brought through orange eluates from which starting material (601 mg, 99%) was recovered.

(ii) 3,4-Dimethyl-1-oxa-6,6a-dithia-2-azapentalene (93)

The reaction conditions and extraction procedure as in (i) were used, but with 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (93) (346 mg, 2 mmol) in acetonitrile-acetic acid(1:1, 50 ml). Chromatography of the residue on a column of alumina (30 x 2.2 cm) with benzene-ether (4:1) gave yellow eluates from which starting material (339 mg, 98%) was recovered. Continued elution with ether-ethanol(99:1) gave no useful material.

(e) Nitration of 1,6a-Dithia-5,6-diazapentalenes

Method A

To a solution of the dithiadiazapentalene (5 mmol) in acetic acid (150 ml) was added concentrated nitric acid (0.50 ml), and the mixture kept at room temperature for 2 minutes. The mixture was then poured into water, extracted with benzene (2x) and the extracts washed successively with water (2x), saturated sodium bicarbonate solution (2x), and water (2x), dried and evaporated. Chromatography is described in individual cases.

Method B

As Method A, but on a smaller scale, with the dithiadiaza-pentalene (1 mmol) in acetic acid (150 ml), and concentrated nitric

acid (0.10 ml). Chromatography is described in individual cases.

(i) 6-Phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) (1.380 g, 5 mmol), Method A

Chromatography of the residue on a column of alumina (40 x 2.8 cm) with benzene-petrol (2:1) gave pale yellow eluates which were discarded. Elution with benzene then gave a red fraction which was evaporated and rechromatographed on a column of silica (60 x 2.2 cm). Elution with benzene-petrol (1:1) gave an orange-red fraction which afforded 6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i) (120 mg, 7.5%), and subsequent elution with benzene brought through orange eluates which were evaporated to give 4-nitro-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (88a) (889 mg, 55%). The products were identical (nmr spectrum in $CDCl_3$) with samples previously obtained. A final fraction from the original column, obtained by elution with benzene-ether (4:1) was evaporated and the residue crystallised from cyclohexane-benzene to give 4-nitro-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (95) (174 mg, 9.5%), identical (nmr spectrum in $CDCl_3$) with an authentic sample[69,184].

(ii) 6-Phenyl-1,6a-dithia-5,6-diazapentalene (44b) (1.100 g, 5 mmol), Method A

The chromatographic procedure as in (i) was used, except that a dinitro compound [analogous to compound (95)] was not obtained. Initial eluates afforded 6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44j) (160 mg, 12.1%), and later eluates yielded 4-nitro-6-phenyl-1,6a-dithia-5,6-diazapentalene (88b) (638 mg, 48%). The products were identical (nmr spectrum in $CDCl_3$) with samples previously prepared.

(iii) 3,4-Dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c) (1.240 g, 5 mmol), Method A

Chromatography on a column of alumina (35 x 2.8 cm) with benzene gave red eluates which afforded 3,4-dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k) (213 mg, 14.6%), identical (nmr spectrum in $CDCl_3$) with samples previously prepared. Subsequent elution with ether-ethanol (99:1) gave yellow eluates which were evaporated to give 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene-2-oxide (94) (330 mg, 35%), identical (nmr spectrum in $CDCl_3$) with an authentic sample[42].

(iv) 6-p-Nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44i) (321 mg, 1 mmol), Method B

Chromatography on a column of alumina (50 x 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 4-nitro-6-p-nitrophenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (95) (91 mg, 25%), identical (nmr spectrum in $CDCl_3$) with an authentic sample[69,184].

(v) 4-Nitro-6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (88a) (321 mg, 1 mmol), Method B

Chromatography as in (iv) gave starting material (311 mg, 97%). No trace of compound (95) was found.

2. Methylation of 1,6a-Dithia-5,6-diazapentalenes

The following general procedure was used:

To a solution of the dithiadiazapentalene (5 mmol) in methylene chloride (25 ml) was added methyl fluorosulphonate (0.80 ml, 10 mmol), and the mixture kept at room temperature for 7 hours. Ether (500 ml) was then added and the mixture allowed to settle. The ether layer was then decanted, and the resulting red oil dissolved in acetonitrile

(25 ml). The solution was filtered and ether (500 ml) added slowly to reprecipitate the salt.

(i) 6-Phenyl-1,6a-dithia-5,6-diazapentalene (44b)

(1.100 g, 5 mmol)

The general procedure gave 5-(2-methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium fluorosulphonate (99b) (1.115 g, 71%), red-brown needles, m.p. 149-151° (dec).

Found C 39.9; H 3.6; N 8.5%

$C_{11}H_{11}N_2O_3S_3F$ requires C 39.5; H 3.3; N 8.4%.

(ii) 3,4-Dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c)

(1.758 g, 5 mmol)

The general procedure gave 4-methyl-5-(1-methyl-2-methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium fluorosulphonate (99c) (1.758 g, 97%), red prisms, m.p. 136-138.5°.

Found C 42.7; H 4.3; N 7.5%

$C_{13}H_{15}N_2O_3S_3F$ requires C 43.1; H 4.2; N 7.7%.

(iii) 3,4-Trimethylene-6-phenyl-1,6a-dithia-5,6-diazapentalene (44d)

(1.300 g, 5 mmol)

The general procedure gave 4,5,6,7-tetrahydro-7-methylthiomethylene-2-phenylbenzo[d][1,2,3]thiadiazolium fluorosulphonate (99d) (1.637 g, 88%), red plates, m.p. 127-129.5°.

Found C 44.6; H 4.1; N 7.4%

$C_{14}H_{15}N_2O_3S_3F$ requires C 44.9; H 4.0; N 7.5%.

(iv) 6-Phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a)

(1.380 g, 5 mmol)

The general procedure was used except that a longer reaction time (14 hours) was required. A dark red oil (0.990 g), was obtained, which could not be induced to crystallise. The composition of this oil is discussed in Part 2, D, (b).

3. Synthesis of 6a-Thia-1,2,6-triazapentalenes

(a) From the 1,2,3-Thiadiazolium Salts (99)

(i) 6-Methyl-1-phenyl-5-t-butyl-6a-thia-1,2,6-triazapentalene (48a) (Attempted Synthesis)

The red oil obtained from methylation of 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) (1.380 g, 5 mmol) [see 2,(iv)] was dissolved in acetonitrile (40 ml), and aqueous methylamine (25-30%, 15 ml) added. The solution was diluted with water immediately, extracted with benzene (2x) and the extracts washed with water (2x), dried and evaporated. The residue was chromatographed on a column of silica (40 x 2.2 cm) with benzene to give orange eluates which afforded 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) [153 mg, 11% overall yield from compound (44a)], identical (nmr spectrum in $CDCl_3$) with samples previously obtained. Further elution with benzene-ether (19:1) gave no useful material.

(ii) 6-Methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48b)

To a solution of 5-(2-methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium fluorosulphonate (99b) (668 mg, 2 mmol) in acetonitrile (25 ml) was added aqueous methylamine (25-30%, 10 ml), the solution diluted immediately with water and extracted with benzene (2x). The extracts were washed with water (2x), dried and evaporated, and the residue chromatographed on a column of silica (40 x 2.2 cm). Elution with benzene gave pale orange eluates which were discarded. Subsequent elution with benzene-ether (19:1) gave a yellow fraction which afforded 6-methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48b) (65 mg, 15%), fine orange-yellow needles (from 40-60 petrol), m.p.90-92°.

Found C 60.9; H 5.1; N 19.3; S 14.9%

$C_{11}H_{11}N_3S$ requires C 60.8; H 5.1; N 19.3; S 14.8%.

M^+ at m/e 217

(iii) 3,4,6-Trimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48c)

The procedure as in (ii) was used, but with 4-methyl-5-(1-methyl-2-methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium fluorosulphonate (99c)(724 mg, 2 mmol). Elution with benzene gave orange eluates which yielded 3,4-dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c) (97 mg, 20%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared. Subsequent elution with benzene-ether (19:1) gave yellow eluates which afforded 3,4,6-trimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48c) (197 mg, 40%), orange-yellow spars (from 40-60 petrol), m.p. 70.5-71.5°.

Found C 63.7; H 6.3; N 17.0%

$C_{13}H_{15}N_3S$ requires C 63.6; H 6.2; N 17.1%.

M^+ at m/e 243

(iv) 6-Methyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (48d)

The procedure as in (iii) was used, but with 4,5,6,7-tetrahydro-7-methylthiomethylene-2-phenylbenzo[d][1,2,3]thiadiazolium fluorosulphonate (99d) (748 mg, 2 mmol). Initial eluates afforded 3,4-trimethylene-6-phenyl-1,6a-dithia-5,6-diazapentalene (44d) (18 mg, 3.5%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared. Subsequent eluates afforded 6-methyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (48d) (390 mg, 76%), orange-red spars (from n-hexane), m.p. 102-103.5°.

Found C 65.3; H 5.7; N 16.2%

$C_{14}H_{15}N_3S$ requires C 65.4; H 5.9; N 16.3%.

M^+ at m/e 257

(b) From 1,6a-Dithia-5,6-diazapentalenes

(i) 6-Methyl-1-phenyl-5-t-butyl-6a-thia-1,2,6-triazapentalene (48a)

To a solution of 6-phenyl-2-t-butyl-1,6a-dithia-5,6-diazapentalene (44a) (552 mg, 2 mmol) in dimethylformamide (60 ml) was

added ethanolic methylamine (33%, 20 ml) and the mixture was heated at 60° for 5 hours. A further portion of ethanolic methylamine (33%, 20 ml) was then added and the heating continued for another 5 hours. A third portion of ethanolic methylamine (33%, 20 ml) was then added and the temperature maintained at 60° for a further 10 hours. The cooled solution was then poured into water, extracted with benzene (2x), and the extracts washed with water (6x), dried and evaporated. Chromatography of the residue on a column of alumina (30 x 2.2 cm) with benzene-petrol (1:1) gave orange eluates from which starting material (230 mg, 42%) was recovered. Elution with benzene then brought through yellow eluates which afforded 6-methyl-1-phenyl-5-t-butyl-6a-thia-1,2,6-triazapentalene (48a) (143 mg, 26%), orange-yellow plates (from methanol), m.p. 98-99°.

Found C 65.8; H 7.0; N 15.3%

$C_{15}H_{19}N_3S$ requires C 65.9; H 7.0; N 15.4%.

M^+ at m/e 273

(ii) 6-Methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48b)

Ethanolic methylamine (33%, 10 ml) was added to a solution of 6-phenyl-1,6a-dithia-5,6-diazapentalene (44b) (440 mg, 2 mmol) in dimethylformamide (60 ml) and the mixture kept at room temperature for 5 minutes. Extraction and chromatography as in (i) gave starting material (17 mg, 3.9%), and 6-methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48b) (86 mg, 20%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(iii) 3,4,6-Trimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48c)

Ethanolic methylamine (33%, 10 ml), was added to a solution of 3,4-dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c) (496 mg, 2 mmol) in dimethylformamide (60 ml) and the mixture kept at room temperature for 20 minutes. Extraction and chromatography as in (i) gave starting material (25 mg, 5.0%) and 3,4,6-trimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (48c) (61 mg, 12.4%),

identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(iv) 6-Methyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (48d)

Ethanolic methylamine (33%, 20 ml) was added to a solution of 3,4-trimethylene-6-phenyl-1,6a-dithia-5,6-diazapentalene (48d) (520 mg, 2 mmol) and the mixture heated at 60° for 3 hours. Extraction and chromatography as in (i) gave starting material (27 mg, 5.2%) and 6-methyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (48d) (336 mg, 65%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(v) 3,4,6-Trimethyl-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (48e)

Ethanolic methylamine (33%, 10 ml) was added to a solution of 3,4-dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k) (586 mg, 2 mmol) in dimethylformamide (150 ml) and the mixture kept at room temperature for 15 minutes. The solution was then poured into water, extracted with benzene (2x), and the extracts washed with water (6x), dried and evaporated. Chromatography of the residue on a column of alumina (20 x 2.2 cm) with benzene gave pink eluates which were discarded. Continued elution with benzene-ether (4:1) gave deep red eluates which afforded 3,4,6-trimethyl-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (48e) (145 mg, 25%), identical (nmr spectrum in $CDCl_3$) with the sample previously prepared.

(vi) 6-Methyl-3,4-trimethylene-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (48f)

Ethanolic methylamine (33%, 10 ml) was added to a solution of 3,4-trimethylene-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44.1) (610 mg, 2 mmol) in dimethylformamide (150 ml) and the mixture kept at 60° for 2 hours. Extraction and chromatography as in (v) gave 6-methyl-3,4-trimethylene-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (48f) (255 mg, 42%), identical (nmr spectrum

in $CDCl_3$) with the sample previously prepared.

4. Synthesis of 1-Oxa-6a-thia-5,6-diazapentalenes

The following general procedure was used:

To a solution of the 1,6a-dithia-5,6-diazapentalene (5 mmol) in chloroform (150 ml) was added mercury(II) acetate (3.187 g, 10 mmol), and the mixture refluxed with stirring for 30 minutes. The mixture was then cooled, filtered and the filtrate diluted with benzene (500 ml). The resulting orange solution was washed with water (3x), dried and evaporated. Chromatography of the residue on a column of alumina (30 x 2.8 cm) with benzene gave pale orange-red eluates which were discarded. Elution with benzene-ether (4:1) then brought through an orange fraction from which the 1-oxa-6a-thia-5,6-diazapentalene was obtained.

(i) 3,4-Dimethyl-6-phenyl-1-oxa-6a-thia-5,6-diazapentalene (108a)

From 3,4-dimethyl-6-phenyl-1,6a-dithia-5,6-diazapentalene (44c) (1.240 g, 5 mmol). The general procedure gave 3,4-dimethyl-6-phenyl-1-oxa-6a-thia-5,6-diazapentalene (108a) (1.152 g, 99%), orange needles (from cyclohexane), m.p. 129-129.5°.

Found C 62.0; H 5.1; N 12.1; S 13.9%

$C_{12}H_{12}N_2OS$ requires C 62.0; H 5.2; N 12.1; S 13.8%.

M^+ at m/e 232. ν_{max} (KBr disc) 1590 cm^{-1}.

(ii) 3,4-Trimethylene-6-phenyl-1-oxa-6a-thia-5,6-diazapentalene (108b)

The general procedure was used, with 3,4-trimethylene-6-phenyl-1,6a-dithia-5,6-diazapentalene (44d) (1.300 g, 5 mmol), and gave 3,4-trimethylene-6-phenyl-1-oxa-6a-thia-5,6-diazapentalene (108b) (1.167 g, 96%), orange-red spars (from n-hexane), m.p. 81.5-83°.

Found C 64.0; H 4.8; N 11.2%

$C_{13}H_{12}N_2OS$ requires C 63.9; H 4.9; N 11.5%.

M^+ at m/e 244. ν_{max} (KBr disc) 1576 cm^{-1}.

(iii) 3,4-Dimethyl-6-p-nitrophenyl-1-oxa-6a-thia-5,6-diazapentalene (108c)

The general procedure was used, with 3,4-dimethyl-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44k) (1.465 g, 5 mmol), and gave 3,4-dimethyl-6-p-nitrophenyl-1-oxa-6a-thia-5,6-diazapentalene (108c) (1.299 g, 94%), orange-red needles (from benzene-cyclohexane), m.p. 226-227.5°.

Found C 51.9; H 4.0; N 15.4%

$C_{12}H_{11}N_3O_3S$ requires C 51.9; H 4.0; N 15.2%.

M^+ at m/e 277. ν_{max} (KBr disc) 1590 cm^{-1}.

(iv) 3,4-Trimethylene-6-p-nitrophenyl-1-oxa-6a-thia-5,6-diazapentalene (108d)

The general procedure was used, with 3,4-trimethylene-6-p-nitrophenyl-1,6a-dithia-5,6-diazapentalene (44 l) (1.525 g, 5 mmol), and gave 3,4-trimethylene-6-p-nitrophenyl-1-oxa-6a-thia-5,6-diazapentalene (108 d) (1.284 g, 89%), red prisms (from benzene-cyclohexane), m.p. 198-199°.

Found C 54.2; H 4.0; N 14.8%

$C_{13}H_{11}N_3O_3S$ requires C 54.0; H 3.8; N 14.5%.

M^+ at m/e 289. ν_{max} (KBr disc) 1587 cm^{-1}.

(v) 6-p-Acetylphenyl-3,4-dimethyl-1-oxa-6a-thia-5,6-diazapentalene (108e)

The general procedure was used, with 6-p-acetylphenyl-3,4-dimethyl-1,6a-dithia-5,6-diazapentalene (44t) (1.450 g, 5 mmol), and gave 6-p-acetylphenyl-3,4-dimethyl-1-oxa-6a-thia-5,6-diazapentalene (108e) (1.328 g, 97%), fine orange microneedles [from cyclohexane-benzene (1:1)], m.p. 142.5-144°.

Found C 61.3; H 5.0; N 10.0%

$C_{14}H_{14}N_2O_2S$ requires C 61.3; H 5.1; N 10.2%.

M^+ at m/e 274. ν_{max} (KBr disc) 1666 (C=O) cm^{-1}.

(vi) 6-p-Acetylphenyl-3,4-trimethylene-1-oxa-6a-thia-5,6-diazapentalene (108f)

The general procedure was used, with 6-p-acetylphenyl-3,4-trimethylene-1,6a-dithia-5,6-diazapentalene (44u) (1.510 g, 5 mmol), and gave 6-p-acetylphenyl-3,4-trimethylene-1-oxa-6a-thia-5,6-diazapentalene (108f) (1.341 g, 94%), orange microprisms [from cyclohexane-benzene (1:1)], m.p. 173-174°.

Found C 62.9; H 4.8; N 9.7%

$C_{15}H_{14}N_2OS$ requires C 62.9; H 4.9; N 9.8%.

M^+ at m/e 286. ν_{max} (KBr disc) 1668 (C=O) cm^{-1}.

5. Synthesis of 6a-Thia-1,2,5,6-tetraazapentalenes

(i) 3,4-Dimethyl-1,6-diphenyl-6a-thia-1,2,5,6-tetraazapentalene (113a)

To a solution of 3,4-dimethyl-6-phenyl-1-oxa-6a-thia-5,6-diazapentalene (108a) (464 mg, 2 mmol), in ethanol (150 ml) was added benzenediazonium fluoroborate (1.152 g, 6 mmol), and the mixture stirred at 60° for 1 hour. The cooled mixture was then poured into water, extracted with ether (2x), and the extracts washed with water (2x), dried and evaporated. Chromatography of the residue on a column of alumina (36 x 2.2 cm) with benzene-petrol (1:1) gave red eluates which afforded 3,4-dimethyl-1,6-diphenyl-6a-thia-1,2,5,6-tetraazapentalene (113a) (602 mg, 98%), deep red needles from cyclohexane, m.p. 157-158°.

Found C 66.2; H 5.2; N 18.4; S 10.4%

$C_{17}H_{16}N_4S$ requires C 66.2; H 5.2; N 18.2; S 10.4%.

M^+ at m/e 308

(ii) 3,4-Trimethylene-1,6-diphenyl-6a-thia-1,2,5,6-tetraazapentalene (113b)

The procedure as in (i) was used, with 3,4-trimethylene-6-phenyl-1-oxa-6a-thia-5,6-diazapentalene (108b) (488 mg, 2 mmol) and gave 3,4-trimethylene-1,6-diphenyl-6a-thia-1,2,5,6-tetraazapentalene (113b) (632 mg, 99%), deep red needles (from

cyclohexane), m.p. 204.5-205°.

Found C 67.5; H 4.9; N 17.5%

$C_{18}H_{16}N_4S$ requires C 67.5; H 5.0; N 17.5%.

M^+ at m/e 320

(iii) 3,4-Dimethyl-1,6-bis(p-nitrophenyl)-6a-thia-1,2,5,6-tetraazapentalene (113c)

To a solution of 3,4-dimethyl-6-p-nitrophenyl-1-oxa-6a-thia-5,6-diazapentalene (108c) (554 mg, 2 mmol) in ethanol (250 ml) was added p-nitrobenzenediazonium fluoroborate (948 mg, 4 mmol), and the mixture stirred at 60° for 30 minutes. The solution was allowed to cool, and the product (764 mg, 96%) filtered. 3,4-Dimethyl-1,6-bis(p-nitrophenyl)-6a-thia-1,2,5,6-tetraazapentalene (113c)formed fine deep red needles (from xylene), which did not melt below 350°.

Found C 51.2; H 3.5; N 21.2%

$C_{17}H_{14}N_6O_4S$ requires C 51.3; H 3.5; N 21.1%.

M^+ at m/e 398

(iv) 3,4-Trimethylene-1,6-bis(p-nitrophenyl)-6a-thia-1,2,5,6-tetraazapentalene (113d)

The procedure as in (iii) was used, with 3,4-trimethylene-6-p-nitrophenyl-1-oxa-6a-thia-5,6-diazapentalene (108d) (578 mg, 2 mmol), and gave 3,4-trimethylene-1,6-bis(p-nitrophenyl)-6a-thia-1,2,5,6-tetraazapentalene (113d) (708 mg, 86%), deep green needles (from xylene), which did not melt below 350°.

Found C 52.7; H 3.5; N 20.4%

$C_{18}H_{14}N_6O_4S$ requires C 52.7; H 3.4; N 20.5%.

M^+ at m/e 410

(v) 1,6-bis(p-acetylphenyl)-3,4-dimethyl-6a-thia-1,2,5,6-tetraazapentalene (113e)

To a solution of 6-p-acetylphenyl-3,4-dimethyl-1-oxa-6a-thia-5,6-diazapentalene (108e) (548 mg, 2 mmol) in ethanol (150 ml) was added p-acetylbenzenediazonium fluoroborate (936 mg, 4 mmol) and

the mixture stirred at 60° for 30 minutes. The cooled mixture was then poured into water, extracted with benzene (2x) and the extracts washed with water (2x), dried and evaporated. Crystallisation of the solid residue from benzene-cyclohexane (2:1) gave 1,6-bis(p-acetylphenyl)-3,4-dimethyl-6a-thia-1,2,5,6-tetraazapentalene (113e) (640 mg) as deep red microneedles, m.p. 234-236°.

Found C 64.4; H 5.1; N 14.3%

$C_{21}H_{20}N_4O_2S_2$ requires C 64.2; H 5.1; N 14.3%.

M^+ at m/e 392. ν_{max} (KBr disc) 1670 (C=O) cm^{-1}.

The mother liquors were evaporated and rechromatographed on a column of alumina (15 x 2.8 cm) with benzene-ether (2:1) to give pale yellow eluates which were discarded. Elution with ether then gave deep red eluates which afforded a further quantity (101 mg) of compound (113e) (Total yield 741 mg, 95%).

(vi) 1,6-bis(p-acetylphenyl)-3,4-trimethylene-6a-thia-1,2,5,6-tetraazapentalene (113f)

The procedure as in (v) was used, with 6-p-acetylphenyl-3,4-trimethylene-1-oxa-6a-thia-5,6-diazapentalene (108f) (572 mg, 2 mmol), and gave 1,6-bis(p-acetylphenyl)-3,4-trimethylene-6a-thia-1,2,5,6-tetraazapentalene (113f) (689 mg, 85%), deep green needles needles [from benzene-cyclohexane (2:1)], m.p. 242-242.5°.

Found C 65.3; H 4.8; N 13.9%

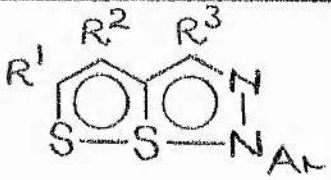
$C_{22}H_{20}N_4O_2S$ requires C 65.3; H 5.0; N 13.9%.

M^+ at m/e 404. ν_{max} (KBr disc) 1770 (C=O) cm^{-1}.

APPENDIX A : NMR SPECTRA DATA

Solutions were in deuteriochloroform unless otherwise stated. Signals are singlets unless otherwise stated; b = broad, d = doublet, dd = double doublet , t = triplet, q = quartet, dq = two quartets, qq = four quartets, qn = quintet, m = multiplet. J values are in Hz, δ values are in ppm downfield from TMS.

Table A1 : 1,6a-Dithia-5,6-diazapentalenes from Diazo-coupling reactions of 1,6,6a-trithiapentalenes and related compounds



Cpd	R^1	R^2	R^3	Ar ortho	Ar meta	Ar para
20a	1.53	9.23	10.03	7.88-8.04	8.22-8.36	
*20b	9.39d J = 6.5 Hz	9.23d	10.03	8.01-8.16	8.31-8.48	
20c	a,b	9.58	10.11	7.95-8.12[a]	8.27-8.41[b]	
20d	1.47	9.09	10.00	7.72-7.89		7.22-7.53
20e	9.19[c]	9.19[c]	10.07	7.79-7.99		7.21-7.59
20f	a,d	9.36	10.02	7.70-7.94[a]		7.26-7.54[d]
26a	1.47	9.84	2.71	7.85-8.00	8.12-8.28	
26b	1.43	8.14	3.27,3.70[e]	7.81-7.96	8.17-8.32	
26c	1.41	8.05	3.23,3.67[e]	7.66-7.87		7.16-7.52
26d	1.51	9.16	2.45	7.83-8.00	8.17-8.34	
26e	1.47	8.31[f]	3.23b	7.81-7.97	8.19-8.38[f]	
26f	1.45	8.28	3.20	7.70-7.88		7.21-7.54
58	1.47	7.77	3.10m[g] 1.92m[h] 2.49m[j]	7.80-7.97	8.20-8.32	
59	1.49	7.77	3.07m[g] 1.88m[h] 2.43m[j] 3.68 [k]	7.77-7.96	8.11-8.34	

*CAT spectrum a - ortho proton multiplets overlap, b - meta and para proton multiplet and meta proton multiplet overlap, c - signals accidentally equivalent, d - meta and para proton multiplets overlap, e - NMe_2 group gives separate methyl signals, f - signals overlap, g - $-\underline{CH_2}-$ ring, h - $-\underline{CH_2}\underline{CH_2}-$, j - $-\underline{CH_2}-CO_2R$, k - $CO_2\underline{Me}$

Table A2 : 1,6a-Dithia-5,6-diazapentalenes

Cpd	R^1	R^2	R^3	Ar ortho	Ar meta	Ar para
44a	1.43	7.69	8.37	7.72-8.84	7.20-7.47	
44b	9.31d J = 6.6 Hz	7.82d	8.49	7.66-7.96	7.15-7.62	
44c	8.95q J = 0.8 Hz	2.82d	2.87	7.70-7.83	7.10-7.49	
44d	8.91t	3.02t[a], 2.08m, 3.06t[a] J = 0.8 Hz		7.62-7.85	7.07-7.50	
44e	[b]	8.08	8.49	7.74-7.96[b]	7.24-7.56[b]	
44f	9.15	7.48[a]	8.42	7.70-7.91	7.12-7.58[a]	
44g	[b]	7.89[a]	2.65	7.65-7.98[a,b]	7.06-7.45[b]	
44h	9.27	6.97	7.04	7.85-8.01	7.28-7.60	
*44i	1.46	7.78	8.40	7.80-8.02	8.16-8.35	
*44j	9.37d J = 6.5 Hz	7.94d[a]	8.53	7.86-8.03[a]	8.20-8.36	
*44k	9.17 J = 0.8 Hz	2.94d	2.94	7.77-8.00	8.17-8.32	
44 l	9.01	3.16m[a], 2.23m, 3.16m[a]		7.73-7.94	8.11-8.23	
44m	7.40-7.52[c,d]	8.09	2.75	7.80-8.00[d]	8.20-8.35	
44n	1.42	7.82[a]	8.33	7.58-7.74[a]	6.85-6.99	3.79
44o	9.18d J = 6.7 Hz	7.74d	8.43	7.61-7.76	6.87-7.02	3.80
44p	8.87q J = 0.8 Hz	2.83d	2.89	7.59-7.74	6.86-7.00	3.79
44q	8.83t J = 0.8 Hz	3.09t, 2.08m, 3.03t		7.56-7.77	6.82-7.02	3.79
44r	1.44	7.70	8.32	7.70-8.01		2.54
44s	9.38d J = 6.2 Hz	7.91d	8.53	7.82-7.99	7.99-8.17	2.61
44t	9.05q J = 0.7 Hz	2.83d	2.85	7.69-7.84	7.85-8.04	2.54
44u	9.03t J = 0.7 Hz	3.01t[a], 2.12m, 3.01t[a]		7.72-7.88	7.90-8.05	2.55
44v	1.43	7.66	8.35	7.56-7.74	7.11-7.28	2.33b
44w	1.43	7.70	8.36	7.57-7.73	7.44-7.57	
44x	9.26d J = 6.6 Hz	7.82d	8.45	7.58-7.73	7.42-7.58	

* CAT SPECTRUM

a. overlap of signals

b. ortho proton and meta and para proton multiplets overlap

c. meta and para multiplet

d. ortho proton multiplets overlap

Table A3 : 1,6a-Diselena-5,6-diazapentalenes

Cpd	R^1	R^2	R^3	Ar ortho	Ar meta	Ar para
64a	2.71d J = 0.8Hz	7.95q	8.47	7.73-7.87	7.21-7.49	
64b	9.71q J = 0.8Hz	2.94d	2.96	7.76-7.88	7.22-7.49	
*64c	2.77	8.11	8.49	7.79-7.99	8.14-8.30	
*64d	10.12	3.04	3.03	7.87-8.05	8.14-8.35	
64e	2.69d J = 0.9Hz	7.86q	8.44	7.65-7.79	6.81-6.98	3.79

* CAT spectrum

Table A4 : Products of the Reaction of 1,6a-Dithia-5,6-diazapentalenes with Arenediazonium Salts

(a) in $CDCl_3$

Cpd	Bu^t	3-H	Ar ortho	Ar meta	Ar para
62a	1.51	9.24	7.91-8.06	7.24-7.56	
*62b	1.55	9.26	7.97-8.16	8.25-8.48	
62c	1.48	9.09	7.78-8.03	6.87-7.07	3.80,3.85
62d	1.52	9.24	7.91-8.16		2.60,2.64
62e	1.49	9.19	7.78-7.99	7.15-7.40	2.36,2.42
62f	1.49	9.13	7.70-7.89	7.45-7.70	
81a (i)[c]	1.49	9.17	7.81-8.07	6.91-7.10[a]	3.87
(ii)		7.16		7.29-7.56[b]	3.83
*81b (i)[d]	1.53	9.21	7.82-8.12	8.14-8.43[a]	
(ii)		9.25		7.13-7.67[b]	
*81c (i)[e,f]	1.53	9.20[g]	7.86-8.15	6.92-7.21[h]	3.87
(ii)				8.19-8.38[j]	3.91

(b) in DMSO-d_6[k]

62c (40°)	1.42	9.06	7.80-8.10	6.95-7.25	3.80,3.85
(120°)	1.42	9.04	7.80-8.05	6.95-7.25	3.84

(c) in pyridine-d_5[k]

62c	1.52	9.32	7.91-8.31	6.97-7.23	3.69,3.73
62d	1.50	9.40	8.17-8.30		2.58,2.62
62e	1.48	9.37	7.85-8.25	7.12-7.58	2.25,2.30
81a (i)[c]	1.49	9.32	7.93-8.33	6.96-7.17[a]	3.72
(ii)				7.20-7.62[b]	3.69

* CAT spectrum

a meta protons in substituted ring (both isomers)

b meta and para protons in phenyl ring (both isomers)

c Isomer ratio (i):(ii) = 5:2

d/

d Isomer ratio (i) : (ii) = 2:3

e Isomer ration (i):(ii) = 1:4

f not obtained pure; contamined with a trace of compound (62b)

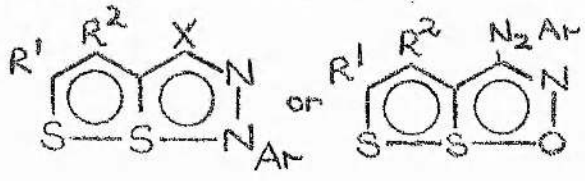
g signal not observed above background noise

h meta protons in $pMeOC_6H_4$ ring (both isomers)

j meta protons in $pNO_2C_6H_4$ ring (both isomers)

k spectra measured with a Perkin-Elmer R.10 spectrometer operating at 60 MHz

Table A5: Products of Electrophilic Substitution of 1,6a-dithia-5,6-diazapentalenes



Cpd	R^1	R^2	Ar ortho	Ar meta	Ar para
83a	1.46	7.83	7.68-7.82	7.18-7.55	
83b	9.32d J = 6.6 Hz	7.92d	7.65-7.84	7.13-7.57	
84a	1.47	7.84	7.57-7.76	7.43-7.57	
84b	9.33d J = 6.6 Hz	7.99d	7.60-7.76	7.46-7.59	
87a	1.54	9.32	7.92-8.06	7.42-7.60	
87b	9.43[a]	9.43[a]	7.92-8.10	7.42-7.61	
88a	1.51	8.99	7.80-7.97	7.30-7.58	
88b	9.17d J = 6.6 Hz	9.06d	7.72-7.99	7.24-7.58	

a accidentally equivalent

Table A6 : Salts obtained by Methylation of 1,6a-Dithia-5,6-diaza-pentalenes

(in trifluoroacetic acid)

(a) 5-(2-Methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium Fluoro-sulphonates

Cpd	R^1	R^2	R^3	MeS	Ph ortho	Ph meta+para
99a[b]	1.49	[a]	9.09	2.67	7.90-8.14[c]	7.20-7.82[c]
99b	8.39d J = 15.4 Hz	6.88d	8.91	2.63	7.82-8.00	7.55-7.78
99c	[a]	2.72d J = 1.1 Hz	3.14	2.93	7.87-8.10	7.58-7.80
99d	[a]	3.01m, 2.24m, 3.43t		2.93	7.88-8.09	7.57-7.79

(b) N-methyl salt

[b]	1.68	8.59[d]	4.27	[c]	[c]

a. signal obscured by meta and para multiplet

b. isomer ratio. [(a)99a]:(b) = 5:2

c/

c. ortho multiplets and meta and para multiplets in the two species overlap

d. the signal observed cannot be assigned unambiguously to a particular proton. The other signal is presumably obscured by the phenyl multiplets.

Table A7 : 6a-Thia-1,2,6-triazapentalenes

Cpd	NMe	R^1	R^2	R^3	Ar ortho	Ar meta	Ar para
48a	3.65	1.38	6.84	8.13	7.62-7.80	7.00-7.46	
48b	3.57d J = 0.7Hz,	7.89dq J = 4.0Hz	6.78	8.16	7.62-7.80	6.95-7.50	
48c	3.51d J = 0.7Hz,	[a] J = 0.6Hz	2.51d	2.78	7.58-7.78[a]	6.88-7.47	
48d	3.58d J = 0.8Hz	7.73b	2.76t,2.08m,3.02t		7.63-7.70	6.84-7.45	
48e	3.66	7.85	2.59	2.79	7.60-7.75	8.07-8.22	
48f	3.72	7.91	2.85m,2.13m,3.04m		7.51-7.67	8.08-8.21	

a, signal obscured by ortho multiplet

Table A8 : 1,6a-Dithia-5,6-diazapentalenes in TFA

Cpd	R^1	R^2	R^3	ortho	Ar meta	Ar para
44a (i)	1.61	8.08	8.24	7.50-7.72	7.12-7.50	
(ii)	1.64	7.93	8.18		7.12-7.48	
44b (i)	9.02d J = 6.1Hz	8.24d	8.42	7.56-7.77	7.24-7.56	
(ii)	9.43d J = 5.3Hz	8.05d	8.29		7.10-7.58	
44c	9.19	2.93	2.61		7.14-7.58	
44n	1.65	7.90	8.17b[a]	7.30-7.54b[a]	7.01-7.24[a]	3.99[a]
44o	9.35d J = 5.8Hz	8.00d	8.27	7.37-7.58	7.05-7.25	4.00
44p	9.14	2.93	2.61b	7.30-7.66b	7.02-7.27b	4.01b

a. signals become broader after 4 hours

(i) species present initially

(ii) species present after ca 20 minutes

Table A9 : 1-Oxa-6a-thia-5,6-diazapentalenes

Cpd	2-H	R^1	R^2	Ar ortho	Ar meta	Ar para
108a	8.89	2.46d J = 0.5 Hz	2.77	7.60-7.78	7.06-7.50	
108b	9.20	2.77t, 2.05m, 3.03t		7.51-7.69	7.01-7.50	
108c	9.09	2.56	2.83	7.73-7.90	8.19-8.38	
108d	9.36	2.83t, 2.11m, 3.06t		7.55-7.78	8.13-8.35	
108e	8.99	2.49	2.78	7.60-7.82	7.87-8.07	2.56
108f	9.29	2.80t, 2.08m, 3.03t		7.49-7.70	7.82-8.06	2.55

Table A10 : 6a-Thia-1,2,5,6-tetraazapentalenes

Cpd	R^1	R^2	Ar ortho	Ar meta	Ar para
113a	2.86		7.64-7.84	7.05-7.50	
113b	$3.17t^a$, 2.28qn, $3.17t^a$ J = 6.0 Hz		7.64-7.86	7.03-7.50	
113e	2.86		7.68-7.87	7.89-8.08	2.58
113f	$3.20t^a$, 2.32qn, $3.20t^a$ J = 5.9 Hz		7.74-7.92	7.94-8.12	2.59

a equivalent protons

APPENDIX B : ULTRAVIOLET AND VISIBLE SPECTRAL DATA

Solutions were in cyclohexane unless otherwise stated; sh = shoulder, infl = inflexion, br = very broad peak with no fine structure.

* qualitative spectrum

Table B1 : 1,6a-Dithia-5,6-diazapentalenes from the reaction of trithiapentalenes and related compounds with arenediazonium salts

Cpd	λ_{max} (nm)	log ε	Cpd	λ_{max} (nm)	log ε
20a	487	4.34	20d	474	4.13
	361	4.26		348	4.04
	315	4.10		319	3.95
	282	4.04		273	4.08
	246infl	4.19		235	4.40
	219	4.38		202	4.38
	200	4.47			
			20e	475	4.04
*20b	488			346	3.97
	357			312	4.02
	320br			243infl	4.33
	269infl			234	4.38
	244			201	4.36
	218				
	198		20f	492	4.24
				356	3.87
20c	506	4.36		315	4.30
	370	4.12		239	4.54
	328	4.33		205	4.52
	221infl	4.43			
	204	4.54	26e	498	4.36
				345infl	4.16
26a	499	4.32		335	4.19
	424	4.37		278	3.98
	328	4.21		254 infl	4.13
	245	4.31		221	4.43
	220	4.43		205	4.49
	202	4.48			

Table B1 (cont)

Cpd	λ_{max} (nm)	log ε
26b	511	4.33
	354	4.16
	323	4.14
	284br	4.15
	261	4.17
	220	4.49
	205	4.53
26c	491	4.16
	340 infl	3.78
	276	4.24
	259	4.26
	231	4.41
	206	4.48
26d	496	4.33
	366	4.24
	319	4.19
	250 infl	4.21
	219	4.39
	201	4.64
26f	478	4.16
	303	4.01
	273	4.06
	235	4.42
	205	4.47
*58	504	
	348sh	
	339	
	259	
	225	
	202	
59	506	4.40
	346sh	4.16
	338	4.19
	258	4.03
	225	4.49
	204	4.44

Table B2 : 1,6a-Dithia-5,6-diazapentalenes from the reaction of 3-methyl(ene)-1,2-dithiolium salts with arenediazonium salts

44a	483	4.23	44f	491	4.14
	285infl	3.98		299	4.11
	260infl	4.15		280	4.13
	234	4.39		257infl	4.21
	202	4.43		233	4.43
				205	4.44
44b	483	4.20			
	289	3.96	44g	507	4.29
	240sh	4.23		306	4.10
	234	4.42		264sh	4.41
	203	4.34		238	4.53
				204	4.57

Table B2 (cont)

Cpd	λ_{max} (nm)	log ε
44c	498	4.12
	293	4.00
	254infl	4.18
	235	4.41
	203	4.39
44d	504	4.17
	295	4.02
	254sh	4.21
	230	4.41
	203	4.34
44e	504	4.29
	302	4.13
	251sh	4.45
	237	4.57
	204	4.63
44k	513	4.31
	349sh	4.11
	339	4.19
	258	4.12
	228	4.45
	202	4.44
*44 l	525	
	350sh	
	342	
	260	
	225	
	203	
*44m	521	
	350sh	
	342	
	227	
	206	

Cpd	λ_{max} (nm)	log ε
44h	500	4.12
	323	3.97
	293	4.23
	250infl	4.37
	229	4.44
	206	4.54
44i	498	4.35
	343sh	4.10
	331	4.17
	255	4.07
	225	4.41
	205	4.33
44j	495	4.27
	339sh	4.13
	327	4.20
	251	4.10
	226	4.44
	205	4.38
44p	505	4.16
	335infl	3.49
	301	4.05
	256sh	4.23
	235	4.44
	207	4.27
44q	515	4.19
	338infl	3.45
	302	4.05
	253sh	4.22
	230	4.42
	205	4.36
44r	490	4.31
	307	4.37
	252	4.07
	227	4.32
	209	4.33

Table B2 (cont)

Cpd	λ_{max} (nm)	log ε	Cpd	λ_{max} (nm)	log ε
44n	488	4.22	44s	492	4.22
	296	3.94		305	4.36
	254infl	4.19		248infl	4.09
	233	4.39		227	4.38
	209	4.31		205	4.35
44o	486	4.14	44t	509	4.25
	329infl	3.52		314	4.38
	297	3.97		254	4.11
	248sh	4.27		229	4.38
	234	4.41		205	4.37
	216	4.22			
			44w	485	4.28
44u	519	4.29		289infl	4.05
	315	4.39		267	4.21
	257	4.10		231	4.32
	225	4.40		204	4.42
	205	4.41			
			44x	484	4.17
44v	481	4.21		292	4.07
	288infl	3.96		256	4.24
	257	4.18		231	4.38
	234	4.38		204	4.35
	206	4.38			

Table B3 : 1,6a-Diselena-5,6-diazapentalenes

64a	529	4.17	64d	561	4.24
	330br	3.54		361sh	4.11
	280	4.19		350	4.15
	250	4.47		286	4.01
	212	4.41		266infl	4.02
	202	4.42		248	4.27
				203	4.44
64b	542	4.14			
	340infl	4.39	64e	541	4.23
	286	4.22		348br	3.69
	251	4.46		289	4.15
	206sh	4.48		249	4.46
	202	4.48		216	3.36
64c	543	4.34	64c	220	4.36
	346br	4.20	(cont)	203	4.50
	277infl	4.00			
	244	4.35			

Table B4 : Products of the reaction of 1,6a-dithia-5,6-diaza-pentalenes with arenediazonium salts

Cpd	λ_{max} (nm)	log ε	Cpd	λ_{max} (nm)	log ε
62a	488	4.20	62d	444br	4.47
	424	4.34		288	4.42
	302 infl	4.05		251	4.26
	285	4.12		218 infl	4.35
	250	4.37		205	4.43
	238	4.38			
	224 infl	4.34	62e	487 infl	4.24
	201	4.52		426	4.39
				312	4.12
*62b	481			287	4.11
	251br			251	4.39
	222			242 infl	4.38
	200			224	4.38
				204	4.49
62c	489 infl	4.29			
	444 infl	4.39	62f	488 infl	4.29
	434	4.41		433	4.44
	332br	4.16		310br	4.13
	246	4.37		286 infl	4.17
	230br	4.41		260	4.41
	207	4.42		222	4.24
				201	4.55

Table B5 : Products of Electrophilic Substitution of 1,6a-dithia-5,6-diazapentalenes

83a	492	4.18	87a	418	3.87
	287 infl	3.90		346	4.24
	269 infl	4.09		280	4.11
	242	4.37		231	4.28
	205	4.41		205	4.18
83b	494	4.11	87b	422	3.80
	298	3.97		341	4.23
	241	4.43		273	4.00
	205	4.39		229	4.29
				200	4.25

Table B5 (cont)

Cpd	λ_{max} (nm)	log ε	Cpd	λ_{max} (nm)	log ε
84a	500	4.24	88a	476	4.15
	276	4.03		391	4.07
	264infl	4.23		310	3.81
	243	4.36		275infl	3.97
	206	4.42		234	4.39
				203	4.38
84b	502	4.17			
	301	4.07	88b	475	4.06
	251sh	4.34		384	3.97
	242	4.40		314	3.83
	205	4.41		231	4.39
				203	4.32

Table B6 : 5-(2-Methylthiovinyl)-2-phenyl-1,2,3-thiadiazolium fluorosulphonates

Solutions in methanol

99b	448	4.46	99d	475	4.30
	325 infl	3.49		339br	3.63
	261 infl	3.60		252 infl	3.86
	218 infl	3.98		226 infl	3.97
99c	460	4.45			
	323 infl	3.51			
	263 infl	3.68			
	226 infl	3.91			

Table B7 : 6a-Thia-1,2,6-triazapentalenes

48a	429	4.39	48d	458	4.33
	278	3.78		286	3.92
	248sh	4.11		243	4.05
	242	4.15		202	4.25
	201	4.31			
			48e	475	4.63
48b	430	4.33		355br	3.79
	277	3.79		285	3.64
	250sh	3.98		239	4.05
	239	4.10		201	4.34
	203	4.20			

Table B7 (cont)

Cpd	λ_{max} (nm)	log ε	Cpd	λ_{max} (nm)	log ε
48c	447	4.36	*48f	484	
	285	3.90		358br	
	242	4.12		288	
	202	4.24		238	
				201	

Table B8: 1,6a-Dithia-5,6-diazapentalenes in methanol and methanol/2% perchloric acid

	Methanol		Methanol/2% $HClO_4$	
Cpd	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε
44a	478	4.20	526br	4.53
	285 infl	3.94	292	4.00
	260 infl	4.14	259	4.12
	234	4.40		
44b	476	4.13	522br	4.37
	286	3.95	287	3.90
	249sh	4.21	269sh	3.95
	232	4.42	255	4.01
			232	4.13
44c	493	4.13	505	4.45
	289	4.00	296	3.95
	253 infl	4.18	269 infl	3.93
	234	4.43	262	3.95
			231	3.85
44n	486	4.23	570br	4.49
	292 infl	3.91	300 infl	4.06
	257 infl	4.16	286 infl	4.10
	232	4.40	263	4.18
			230	3.99
44o	486	4.16	570br	4.31
	295	3.95	289	3.92
	251sh	4.23	254 infl	4.05
	232	4.44	232	4.16
44p	502	4.16	538	4.43
	299	4.07	303br	3.92
	255 infl	4.19	288	3.92
	234	4.44	264	3.87
			233	3.93

Table B9 : 1-Oxa-6a-thia-5,6-diazapentalenes

Cpd	λ_{max} (nm)	log ε
108a	447	4.32
	275	3.83
	236	3.98
	201	4.26
108b	467sh	4.33
	456	4.36
	277	3.88
	238	3.94
	201	4.32
108c	460	4.53
	325br	3.75
	243infl	3.91
	199	4.38
108d	485	4.60
	459	4.53
	332br	3.77
	247infl	3.85
	200	4.44
108e	458	4.47
	299	4.15
	233	4.00
	201	4.37
108f	483	4.45
	475	4.44
	458	4.48
	306	4.16
	235	3.95
	204	4.36

Table B10 : 6a-Thia-1,2,5,6-tetraazapentalenes

113a	491	4.32
	300	4.20
	246	4.25
	204	4.39
113b	519	4.33
	306	4.15
	247	4.26
	204	4.40
*113c	524	
	343	
	254	
*113d	550	
	349	
	264	
*113e	517	
	322	
	273 infl	
	255	
	202	
*113f	542	
	327	
	280 infl	
	258	
	200	

APPENDIX C : MASS SPECTRAL DATA

* Metastable peak

a Calculated value for metastable peak

b Transition giving rise to metastable peak

Table C1 : 1,6a-Dithia-5,6-diazapentalenes

Cpd	m/e	R.I.(%)
44b	220	21
	147	6.8
	143	11
	115	28
	105	49
	92.5* (92.5[a]) (143-115[b])	
	78	7.9
	77	100
	71	22
	69	12
	64	6.8
	63	5.2
	58	5.0
	56.5* (56.5[a]) (105-77[b])	
	51	43
	50	10
	45	33
	39	12
	38	6.7
	33.8* (33.8[a]) (77-51[b])	
44e	296	22
	191	7.6
	190	12
	158	11
	147	23
	127	14
	121	39
	105	7.6
	78	8.6
	77	100
	69	6.6
	56.5* (56.5[a]) (105-77[b])	
	51	30
44c	249	7.0
	248	29
	156	18
	143	14
	117	5.9
	115	6.4
	106	6.8
	105	10
	99	7.1
	91	18
	78	11
	77	100
	71	13
	65	9.0
	64	7.0
	59	15
	56.5* (56.5[a]) (105-77[b])	
	51	21
	45	14
	44.5* (44.5[a]) (248-105[b])	
	41	6.9
	39	14
	33.8* (33.8[a]) (77-51[b])	
44f	296	6.1
	191	4.4
	190	12
	158	7.3
	147	12
	133	2.3
	105	18
	78	9.6
	77	100
	69	5.7

Table C1 (cont)

Cpd	m/e	R.I.(%)
44e (cont)	45	7.3
	39	6.6
	37.2^{*} (37.2^{a}) ($296-105^{b}$)	
	33.8^{*} (33.8^{a}) ($77-51^{b}$)	
44g	311	6.3
	310	23
	205	27
	139	6.3
	122	7.8
	121	84
	115	22
	106	12
	105	4.5
	101	5.9
	91	16
	78	8.9
	77	100
	71	7.8
	69	6.9
	64	7.5
	63	9.5
	59	9.3
	56.5^{*} (56.5^{a}) ($105-77^{b}$)	
	51	32
	47.2^{*} (47.2^{a}) ($310-121^{b}$)	
	45	10
	39	12
	33.8^{*} (33.8^{a}) ($77-51^{b}$)	

Cpd	m/e	R.I.(%)
44f (cont)	56.5^{*} (56.5^{a}) ($105-77^{b}$)	
	51	19
	45	16
	44	5.5
	39	5.1
	37.2^{*} (37.2^{a}) ($296-105^{b}$)	
	33.8^{*} (33.8^{a}) ($77-51^{b}$)	
44h	372	6.2
	371	40
	235	12
	222	4.4
	202	3.9
	121	7.4
	105	14
	91	8.4
	89	4.5
	78	11
	77	100
	64	5.2
	63	4.5
	56.5^{*} (56.5^{a}) ($105-77^{b}$)	
	51	23
	45	7.4
	39	6.1
	33.8^{*} (33.8^{a}) ($77-51^{b}$)	
	29.6^{*} (29.6^{a}) ($372-105^{b}$)	

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