ABSTRACT

Treatment of 3,4-disubstituted 6-oxa-6a-thia-1,2-diazapentalenes in dimethylformamide with phosphoryl chloride gave 5-(2-chlorovinyl)-1,2,3-thiadiazolium intermediates which reacted with amines and hydrazines to give 6a-thia-1,2,6-triazapentalenes. In three cases these thiadiazolium intermediates reacted with potassium selenosulphate to give the corresponding 6a-thia-6-selena-1,2-diazapentalenes, and with sodium sulphide or sodium hydrogen sulphide to give the corresponding 6,6a-dithia-1,2-diazapentalenes.

Methylation of the phenylhydrazone, the p-nitrophenylhydrazone and the methylhydrazone of 5-formylisothiazole with methyl fluorosulphonate gave the corresponding 2-methylisothiazolium fluorosulphonates which, when treated with aqueous sodium carbonate, gave 6-methyl-1-phenyl-, 6-methyl-1-p-nitrophenyl-, and 1,6-dimethyl-6a-thia-1,2,6-triazapentalene.

Treatment of methoxymethyl triphenylphosphonium chloride with phenyl lithium gave the corresponding phosphonium ylid, which reacted with 5-formylisothiazole to give 5-(2-methoxyvinyl)isothiazole. Methylation of this compound with methylfluorosulphonate gave 2-methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate which, when allowed to react with methylamine gave 1,6-dimethyl-6a-thia-1,6-diazapentalene. 2-Methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate also reacted with sodium hydroxide to give 6-methyl-1-oxa-6a-thia- 6- azapentalene, and with sodium hydrogen sulphide to give 6-methyl-1,6a-dithia-6-azapentalene. 1,6,6a-Trithiapentalene and 1-methylamino-5-methoxy-penta-1,4-diene-3-thione were also isolated as minor products from the reaction of 2-methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate

with sodium hydrogen sulphide.

5-Amino-1,2-dithiole-3-thiones reacted with carbon disulphide in the presence of triethylamine to give intermediates which when treated with methyl iodide afforded 2,5-dimethylmercapto-1,6,6a-trithia-3-azapentalenes. Also, the reaction of 5-amino-1,2-dithioles with phenyli sothi ocyanate in the presence of triethylamine, and subsequent methylation of the resulting intermediates with methyl iodide gave 2,5-dimethylmercapto-6,6a-dithia-1,3-diazapentalenes and 2-anilino-5-methylmercapto-1,6,6a-dithia-3-azapentalenes.

The protonation of 3,4-dimethyl-1,6,6a-trithiapentalene, in trifluoroacetic acid was reinvestigated using ^{1}H nmr spectroscopy. Protonation at S-1 occurred, forming the 4-methyl-3-(2-mercapto-1-methylvinyl)-1,2-dithiolium cation. Protonation at C-3 also occurred, resulting in the formation of an unstable thioformyl species. As the signal thought to originate from the thioformyl proton of this species was observed at δ7.18 it was concluded that the species which contained a free thioformyl group had polymerised, but the exact structure of the polymer remains uncertain. 3,4,5,6-Tetrahydrocyclohepta[c,d]- and 4,5,6,7-tetrahydro-3H-cycloocta-[c,d]-1,6,6a-trithiapentalene were synthesised from the corresponding 1,2-dithiolium salts as part of the study of the protonation of 1,6,6a-trithiapentalenes in trifluoroacetic acid.

The protonation of pyrrolo[2,1-b]thiazole-7-thioaldehydes in trifluoroacetic acid was studied using ^{1}H nmr spectroscopy. Protonation at the sulphur atom of the 7-thioformyl group resulted in 7- mercaptomethylenepyrrolo[2,1-b]thiazolium cations. Protonation at the C-5 position resulted in unstable thioformyl species

which polymerised to give α- and β -1, 3, 5-trithianes. The protonation of pyrrolo[2, 1-b]thiazole-7-thioaldehydes was observed as a function of time. The S-protonation products were gradually transformed into C-protonation products, and the α-1, 3, 5-trithianes were gradually converted into the β-1, 3, 5-trithianes.

The protonation of pyrrolo[2, 1-b]thiazole-5-thioaldehydes in trifluoroacetic acid was also studied. Protonation occurred at the sulphur atom of the 5-thioformyl group, and gave syn- and anti-5-mercaptomethylenepyrrolo[2, 1-b]thiazolium cations. H-D exchange at the 7-position indicated that C-7 protonation was also occurring simultaneously although at a concentration below the limits of detection by ^{1}H nmr spectroscopy.

To my mother and father

SYNTHESES OF AZA-ANALOGUES OF 1,6,6a-TRITHIAPENTALENES AND SOME RELATED STUDIES OF THIOALDEHYDES

being a Thesis

presented by

Jerzy Czyzewski, B.Sc.

to the

University of St. Andrews

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

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.

January 1977 Jerzy Czyzewski

CERTIFICATE

I hereby certify that Jerzy Czyzewski, B.Sc., has spent ten 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.

January 1977

Professor D.H. Reid
Director of Research

UNIVERSITY CAREER

I entered the University of St. Andrews in October 1969, and subsequently graduated B.Sc. with Upper Second Class Honours in Chemistry in July 1973.

In October 1973 I was awarded a Science Research Council CASE Studentship and from then until July 1976 I carried out the work which is embodied in this thesis. This work was carried out mainly in the Department of Chemistry, University of St. Andrews under the supervision of Professor D.H. Reid. Also, in accordance with the conditions of the Science Research Council CASE scheme, I spent three months (April 1975 to June 1975) working at the Esso Chemicals Research Centre, Abingdon under the supervision of Dr. R.W. Glyde.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professor D.H. Reid for his advice, guidance and continued interest in my work. I would also like to thank Dr. R.W. Glyde and Dr. S.J. Brois for their invaluable help and guidance during my stay at the Esso Chemicals Research Centre.

I would like to thank Professor Lord Tedder and Professor P.A.H. Wyatt for making available laboratory facilities in the Department of Chemistry, University of St. Andrews, and the Esso Chemicals Company for making available laboratory facilities at the Esso Research Centre, Abingdon.

I am extremely grateful to the technical staff of the Department of Chemistry, University of St. Andrews and to the technical staff of the Esso Research Centre, Abingdon for their invaluable assistance. Also, I am extremely grateful to Mrs. W. Pogorzelec, who prepared the typescript for this thesis.

Finally, I would like to thank the Science Research Council for the award of a CASE studentship, and to the Esso Chemicals Company for making this CASE award possible and for their assistance during my visits to Abingdon.

EXPLANATORY NOTE

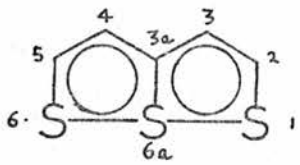
This thesis is divided into three sections, Parts 1, 2 and 3. Each part is divided into a number of principal sections, each prefixed by a capital letter.

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

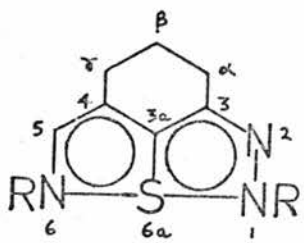
Part 2 consists of a discussion of the results obtained for this thesis.

Part 3 consists of the experimental details of the results discussed in Part 2 and is complementary to Part 2.

When 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 this thesis. The structural formulae reproduced here have been assigned Arabic numbers which correspond to the numbers which have been assigned to the relevant compounds in the text. The structural keys to Part 1 and 2 are distinct. The structural key to Part 3 is the same as that for Part 2.



I



II

NOTE ON NOMENCLATURE

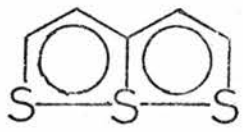
The system formulated (I) is commonly referred to in the literature as 6a-thiathiophthen and is numbered as shown. However, this nomenclature has the disadvantage that it cannot be extended to include oxygen, selenium or nitrogen analogues of (I). To overcome this difficulty Lozac'h has suggested a nomenclature based on pentalene[7]. This has been used extensively in the literature and will be used throughout this thesis. According to this nomenclature system (I) becomes 1, 6, 6a-trithiapentalene. It should be noted that this choice of name is based on practical nomenclature considerations and does not define the real electronic structure of the molecule, which will be discussed later. Chemical Abstracts indexes the system as [1, 2]-dithiolo-[1, 5-b][1, 2]-dithiole-7-S^{IV}.

When there is an alkyl bridging group across two positions (eg. II) the pentalene system of nomenclature is no longer used in the literature and a systematic nomenclature is used instead. However, in this thesis compounds possessing a trimethylene bridging group across the 3- and 4-positions (eg. II) are discussed as well as bicyclic compounds, and to maintain a uniform system of nomenclature throughout, the pentalene system of nomenclature will be used in all cases. System (II) will be referred to as 3, 4-trimethylene-6a-thia-1, 2, 6-triazapentane, with the bridging alkyl positions being numbered α, β and γ as shown. (According to systematic nomenclature system (II) should read 6, 7-dihydro-5H-2a, 3-thiaza-1, 2-diazacyclo-pent[c, d]-indene.)

CONTENTS

Part One

Part Two

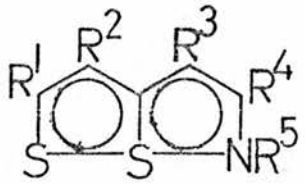


I

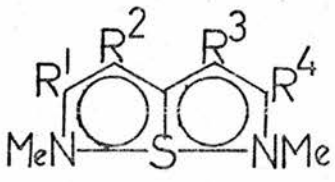
INTRODUCTION

Although the first 1, 6, 6a-trithiapentalene (I) was isolated in 1925, from the reaction of phosphorus pentasulphide with heptane-2, 4, 6-trione, the correct bicyclic structure was not established until 1958, when Bezzi and coworkers established the correct geometry of the molecule by X-ray crystallography. Since that time numerous other 1, 6, 6a-trithiapentalenes have been prepared by a wide variety of synthetic routes. The structures of trithiapentalenes have been examined by X-ray crystallography and the results have shown that these compounds are planar, that the three sulphur atoms are collinear, and that some degree of bonding exists between the sulphur atoms. Many theories of bonding have been proposed to account for the unique structural features of trithiapentalenes, but the theory proposed by Gleiter and Hoffmann is now most commonly accepted. According to this theory the three sulphur atoms are held together by four-electron three-centre bonding, with the central sulphur atom providing two electrons and the lateral sulphur atoms providing one electron each. The molecule also possesses a 10 π-electron system, with the carbon atoms and the central sulphur atom providing one electron each and the lateral sulphur atoms providing two electrons each.

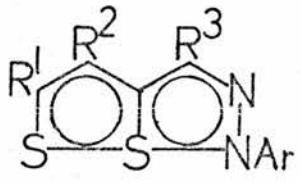
The replacement of a sulphur atom or a C-H (or C-R) unit in 1, 6, 6a-trithiapentalenes by nitrogen gives rise to structurally similar aza-analogues. The bonding in these analogues may be described by the same model as used for 1, 6, 6a-trithiapentalenes. Many examples



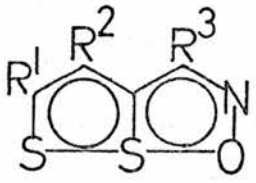
II



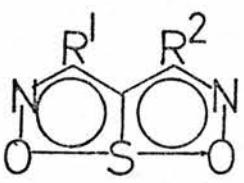
III



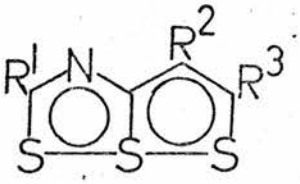
IV



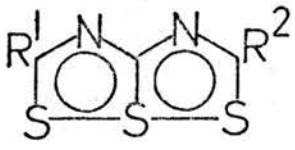
V



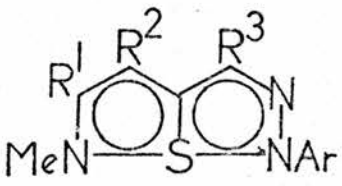
VI



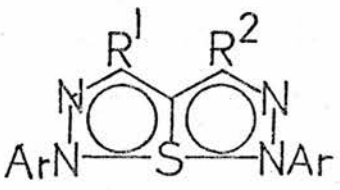
VII



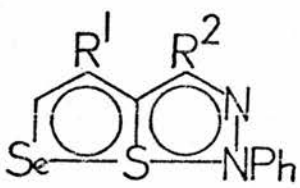
VIII



IX

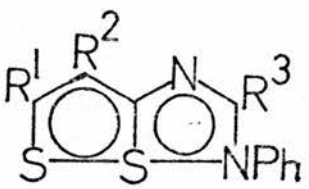


X



XI

XII



XIII

of the systems (II)-(X), containing up to four nitrogen atoms, have been synthesised. Much of the work described in this thesis includes the development of further syntheses of these classes of compounds. New synthetic routes to the previously known systems (II), (III), (VII) and (IX) and synthetic routes to members of the new systems (XI), (XII) and (XIII) are described.

The reactions of 1, 6, 6a-trithiapentalenes, including a study of their protonation, have previously been investigated. Since it was suspected that the protonation of 1, 6, 6a-trithiapentalenes and pyrrolo[2, 1-b]thiazole-thioaldehydes resulted in structurally related products, a study of the protonation of selected members of both these classes of compound was carried out, and the results are described in this thesis.

SUMMARY

Treatment of 3,4-disubstituted 6-oxa-6a-thia-1,2-diazapentalenes in dimethylformamide with phosphoryl chloride gave 5-(2-chlorovinyl)-1,2,3-thiadiazolium intermediates which reacted with amines and hydrazines to give 6a-thia-1,2,6-triazapentalenes. In three cases these thiadiazolium intermediates reacted with potassium selenosulphate to give the corresponding 6a-thia-6-selena-1,2-diazapentalenes, and with sodium sulphide or sodium hydrogen sulphide to give the corresponding 6,6a-dithia-1,2-diazapentalenes.

Methylation of the phenylhydrazone, the p-nitrophenylhydrazone and the methylhydrazone of 5-formylisothiazole with methyl fluorosulphonate gave the corresponding 2-methylisothiazolium fluorosulphonates which, when treated with aqueous sodium carbonate, gave 6-methyl-1-phenyl-, 6-methyl-1-p-nitrophenyl-, and 1,6-dimethyl-6a-thia-1,2,6-triazapentalene.

Treatment of methoxymethyl triphenylphosphonium chloride with phenyl lithium gave the corresponding phosphonium ylid, which reacted with 5-formylisothiazole to give 5-(2-methoxyvinyl)isothiazole. Methylation of this compound with methylfluorosulphonate gave 2-methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate which, when allowed to react with methylamine gave 1,6-dimethyl-6a-thia-1,6-diazapentalene. 2-Methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate also reacted with sodium hydroxide to give 6-methyl-1-oxa-6a-thia- 6- azapentalene, and with sodium hydrogen sulphide togive 6-methyl-1,6a-dithia-6-azapentalene. 1,6,6a-Trithiapentalene and 1-methylamino-5-methoxy-penta-1,4-diene-3-thione were also isolated as minor products from the reaction of 2-methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate

with sodium hydrogen sulphide.

5-Amino-1,2-dithiole-3-thiones reacted with carbon disulphide in the presence of triethylamine to give intermediates which when treated with methyl iodide afforded 2,5-dimethylmercapto-1,6,6a-trithia-3-azapentalenes. Also, the reaction of 5-amino-1,2-dithioles with phenyli sothi ocyanate in the presence of triethylamine, and subsequent methylation of the resulting intermediates with methyl iodide gave 2,5-dimethylmercapto-6,6a-dithia-1,3-diazapentalenes and 2-anilino-5-methylmercapto-1,6,6a-dithia-3-azapentalenes.

The protonation of 3,4-dimethyl-1,6,6a-trithiapentalene, in trifluoroacetic acid was reinvestigated using ^{1}H nmr spectroscopy. Protonation at S-1 occurred, forming the 4-methyl-3-(2-mercapto-1-methylvinyl)-1,2-dithiolium cation. Protonation at C-3 also occurred, resulting in the formation of an unstable thioformyl species. As the signal thought to originate from the thioformyl proton of this species was observed at δ7.18 it was concluded that the species which contained a free thioformyl group had polymerised, but the exact structure of the polymer remains uncertain. 3,4,5,6-Tetrahydrocyclohepta[c,d]- and 4,5,6,7-tetrahydro-3H-cycloocta-[c,d]-1,6,6a-trithiapentalene were synthesised from the corresponding 1,2-dithiolium salts as part of the study of the protonation of 1,6,6a-trithiapentalenes in trifluoroacetic acid.

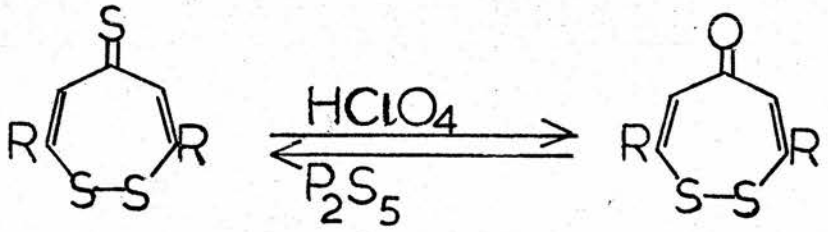
The protonation of pyrrolo[2,1-b]thiazole-7-thioaldehydes in trifluoroacetic acid was studied using ^{1}H nmr spectroscopy. Protonation at the sulphur atom of the 7-thioformyl group resulted in 7-mercaptomethylenepyrrolo[2,1-b]thiazolium cations. Protonation at the C-5 position resulted in unstable thioformyl species

which polymerised to give α- and β -1, 3, 5-trithianes. The protonation of pyrrolo[2, 1-b]thiazole-7-thioaldehydes was observed as a function of time. The S-protonation products were gradually transformed into C-protonation products, and the α-1, 3, 5-trithianes were gradually converted into the β -1, 3, 5-trithianes.

The protonation of pyrrolo[2, 1-b]thiazole-5-thioaldehydes in trifluoroacetic acid was also studied. Protonation occurred at the sulphur atom of the 5-thioformyl group, and gave syn- and anti-5-mercaptomethylenepyrrolo[2, 1-b]thiazolium cations. H-D exchange at the 7-position indicated that C-7 protonation was also occurring simultaneously although at a concentration below the limits of detection by ^{1}H nmr spectroscopy.

PART ONE

DISCUSSION OF BACKGROUND LITERATURE



1 2

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

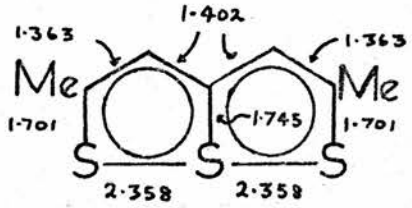
3

4

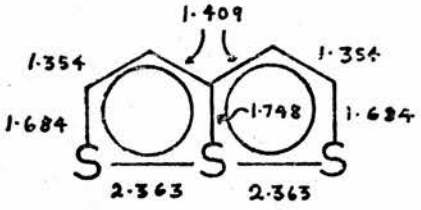
A. Structure and Bonding of 1, 6, 6a-Trithiapentalenes and Related Compounds

In 1925 Arndt, Nachtwey and Pusch[1] assigned the 1, 2-dithiepin-5-thione structure (1a) to the product from the reaction of phosphorus pentasulphide with heptane-2, 4, 6-trione. Arndt and coworkers[2] obtained results regarded as evidence for structure (1) by treating compound (1a) with 70% perchloric acid. The 1, 2-dithiepin-5-one structure (2a) was assigned to the product. The original compound (1a) was regenerated by treatment of the ketone (2a) with phosphorus pentasulphide. Also, Traverso and Sanesi[3], by treating 4-thiopyrones with potassium hydrogen sulphide, obtained two compounds for which they proposed formulae (2b) and (2c). Their reason for this choice was that these products, when treated with phosphorus pentasulphide, gave compounds (1b) and (1c), analogously to those already described by Arndt[1,2]. In 1958 Bezzi and coworkers[4,5] established the 1, 6, 6a-trithiapentalene structure (3) when they determined the correct geometry by X-ray crystallography. Independently Guillouzo[6] showed that the infrared carbonyl stretching frequency of compound (2a) indicated a high degree of polarisation inconsistent with the proposed structure (2a), and suggested as an alternative the 1-oxa-6, 6a-dithiapentalene structure (4).

Since that time a large number of 1, 6, 6a-trithiapentalenes and analogous systems containing selenium, oxygen and nitrogen have been synthesised and studies of these compounds have contributed towards a greater understanding of their structure, bonding and


1·402
1·363
1·363
Me
Me
1·701
1·701
1·745
S
S
S
2·358
2·358

5


1·409
1·354
1·354
1·684
1·684
1·748
S
S
S
2·363
2·363

6

reactivity. Reviews of the chemistry of 1, 6, 6a-trithiapentalenes and related systems have been written by Lozac'h[7], Klingsberg[8], Reid[9] and Beer[10, 11].

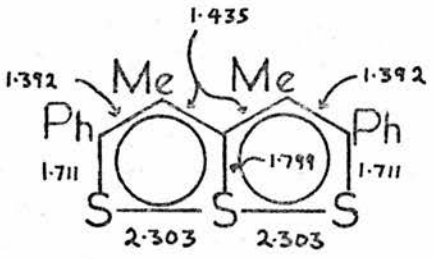
(a) Structural Studies of 1, 6, 6a-Trithiapentalenes and Related Compounds

(i) X-ray Crystallography

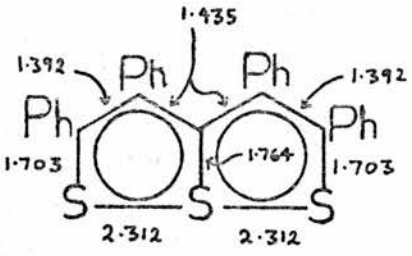
X-ray crystallography has been applied extensively to a study of the structure of 1, 6, 6a-trithiapentalenes and related compounds in the solid state. Comparison of interatomic distances found in these compounds with bond length data already in the literature has been useful in determining whether there is a bonding interaction between two given atoms, and also in determining the order of bonding between two given atoms.

The first X-ray crystal analysis, carried out on 2, 5-dimethyl-1, 6, 6a-trithiapentalene (5)[4, 5, 12], showed that the molecular was planar and possessed C_{2v} symmetry. In addition, the three sulphur atoms were found to be collinear.

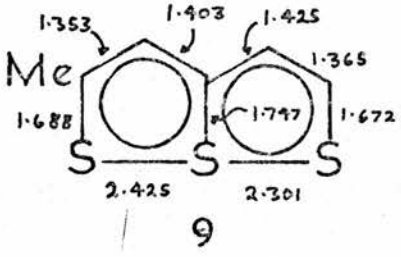
An analysis of the parent 1, 6, 6a-trithiapentalene (6) has been carried out by Hordvik[13]. The molecule possesses C_{2v} symmetry and has dimensions very similar to the dimensions found for the 2, 5-dimethyl derivative (5). The sulphur-sulphur bond distances (2.363 Å) are approximately 10% longer than the average distance found for an S-S bond[14] (2.10 Å), but shorter than the sum of the Van der Waal radii of two sulphur atoms[15] (3.70 Å). This indicates the presence of an equal bonding interaction between S(6a) and S(6), and S(6a) and S(1). The C(2)-S(1) (1.684 Å), C(5)-S(6) (1.684 Å)



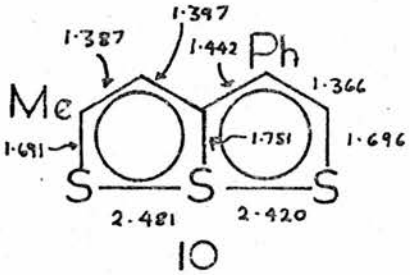
7



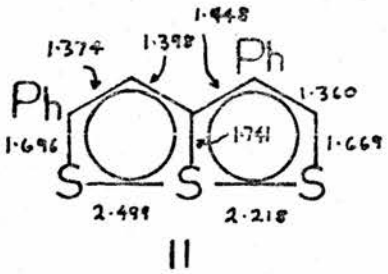
8



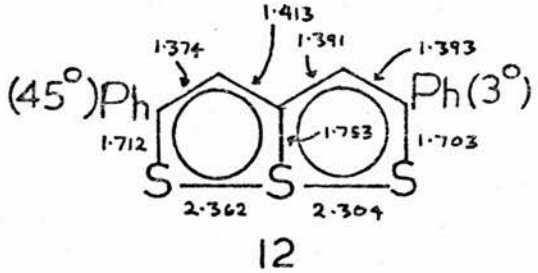
9



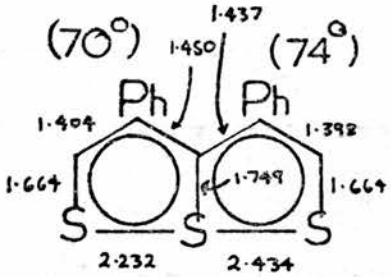
10



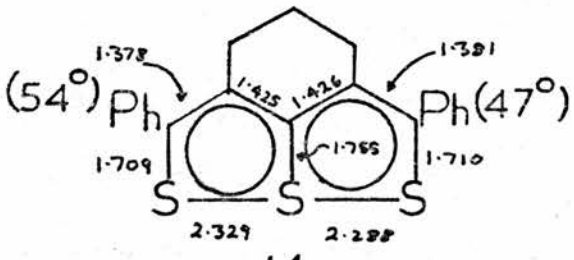
11



12



13



14

and C(3a)-S(6a) (1.784 Å) bond distances are less than the carbon-sulphur single bond distance[15] (1.81 Å), indicating bond orders greater than unity. The bonding of 1, 6, 6a-trithiapentalenes involves a delocalised 10 π-electron system (see page 11) and hence the C(2)-C(3) (1.354 Å) and C(3)-C(3a) (1.409 Å) bond distances are very similar to the C(1)-C(2) (1.358 Å) and C(1)-C(8a) (1.421 Å) bond distances in naphthalene, which possesses an analogous 10π-electron system[16]. Symmetrical structures were also found for the symmetrically substituted 1, 6, 6a-trithiapentalenes (7)[17] and (8)[18].

However, trithiapentalenes (9)[19], (10)[20] and (11)[21] have been shown to possess unequal S-S bond lengths, indicating that the individual S-S distances are extremely sensitive to intramolecular perturbation such as substitution. Symmetrically substituted trithiapentalenes (12)[22], (13)[23] and (14)[24] also have unequal S-S bond lengths due to intermolecular effects within the crystal lattice. In trithiapentalene (12) the phenyl groups are twisted at angles of 3° and 45° to the plane of the trithiapentalene system, presumably due to intermolecular interactions. In trithiapentalene (13) the inequality is due to a steric clash of the phenyl groups in the 3- and 4-positions, while in trithiapentalene (14) probably both inter and intramolecular forces bring about unequal S-S bond distances. Numerous other X-ray crystal structure determinations of trithiapentalenes have appeared in the literature and have been reviewed by Hordvik[25].

It is significant that although individual S-S bond distances may vary by as much as 0.4 Å the S(1)-S(6) bond distance remains fairly constant at 4.66-4.73 Å, unless there is a steric clash between substituents in the 3- and 4-positions. In all cases the individual S-S bond distances are very much less than the sum of the Van der Waal radii of two sulphur atoms[15], indicating bonding between S(1) and S(6a), and S(6a) and S(6), therefore supporting the bicyclic structure. Also the lengths of other bonds in the molecule do not vary by more than 0.05 Å.

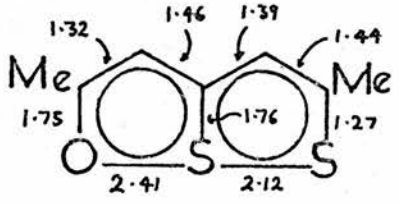
Hordvik[26] has rationalised the effect of phenyl and methyl substituents on individual S-S bond distances using CNDO/2 calculations, the results of which can be summarised as follows:-

(a) A 2-methyl substituent increases the S(1)-S(6a) bond distance, a 3-methyl substituent shortens it.

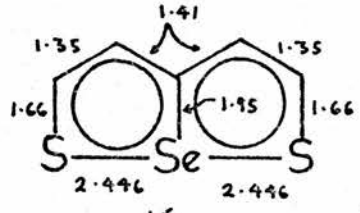
(b) A 2-phenyl substituent increases the S(1)-S(6a) bond distance, the effect being negligible for an angle of twist of 0° and maximum for 90°.

(c) A 3-phenyl group causes a slight shortening of the S(1)-S(6a) bond distance, irrespective of angle of twist. (It should be noted that the calculations do not take into account any intramolecular strain within the molecule.)

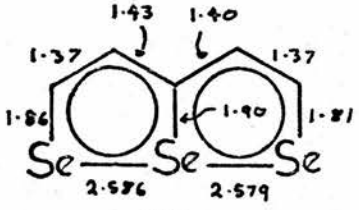
X-ray structure determinations have also been carried out on oxygen, selenium and nitrogen analogues of 1, 6, 6a-trithiapentalenes illustrating that the bicyclic structure may be extended to include these analogues. Compounds (15)-(22) will be discussed here.


1·32
1·46
1·39
1·44
Me
Me
1·75
1·76
1·27
O
S
S
2·41
2·12

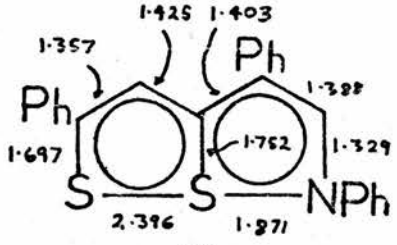
15


1·41
1·35
1·35
1·66
1·95
1·66
S
Se
S
2·446
2·446

16


1·43
1·40
1·37
1·37
1·86
1·90
1·81
Se
Se
Se
2·586
2·579

17

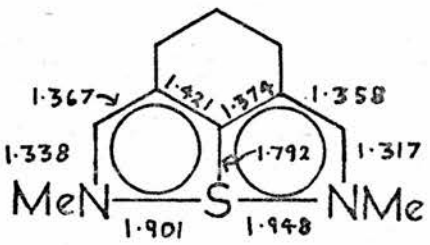

1·425
1·403
1·357
Ph
Ph
1·388
1·697
1·762
1·329
S
S
NPh
2·396
1·871

18

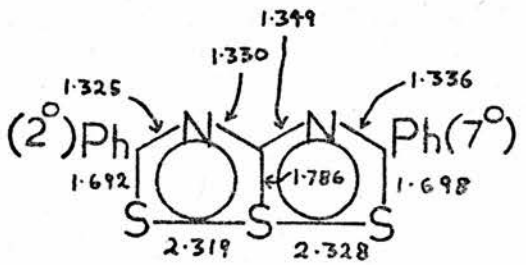
In the oxygen analogue (15)[27] the molecule was found to be nearly planar with the S-S-O sequence nearly linear. The S-O distance (2.41 Å) is considerably less than the sum of the Van der Waal radii of sulphur and oxygen[15] (3.25 Å) but well above the normal S-O covalent bond distance[15] (1.70 Å). The S-S distance (2.12 Å) is shorter than the S-S distance in the corresponding trithiapentalene (5) (cf. 2.358 Å). Thus the replacement of a sulphur atom by an oxygen atom in compound (5) results in a stronger S(6a)-S(6) interaction and a weaker S(6a)-O(1) interaction, but the molecule may still be regarded as bicyclic with some degree of bonding between O(1) and S(6).

In the selenium analogue (16)[28] the Se-S bonds (2.446 Å) are 10% longer than the normal Se-S covalent bond[15] (2.22 Å) indicating that the Se-S bond order is similar to the S-S bond order in 1, 6, 6a-trithiapentalenes. The molecule is planar and possesses C_{2v} symmetry. Although 1, 6, 6a-triselenapentalene (17)[29] shows a slight departure from C_{2v} symmetry it is structurally similar to 1, 6, 6a-trithiapentalene (6) with the average Se-Se bond length (2.583 Å) being approximately 11% longer than the normal Se-Se covalent bond distance[15] (2.34 Å).

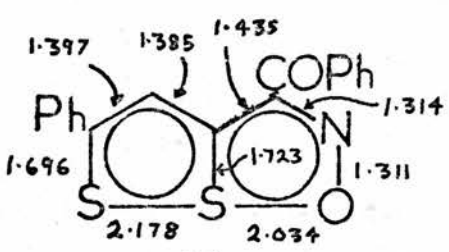
Data on the aza analogue (18)[30] shows that the molecule is planar and that the S-S-N sequence is almost collinear. The S-N bond distance (1.871 Å) is closer to the normal S-N covalent bond distance[15] (1.74 Å) than to the sum of the Van der Waal radii of a sulphur and a nitrogen atom[15] (3.35 Å), indicating that a


1·367
1·421
1·379
1·358
1·338
1·792
1·317
MeN
S
NMe
1·901
1·948

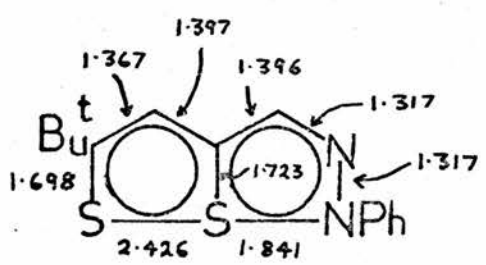
19


1·349
1·330
1·325
1·336
(2°)Ph
N
N
Ph(7°)
1·692
1·786
1·698
S
S
S
2·319
2·328

20


1·397
1·385
1·435
COPh
Ph
1·314
N
1·696
1·723
1·311
S
S
O
2·178
2·034

21


1·397
1·367
1·396
1·317
t
Bu
N
1·317
1·698
1·723
S
S
NPh
2·426
1·841

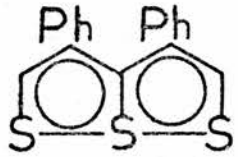
22

significant bonding interaction exists between sulphur and nitrogen. The S-S bond distance (2.396 Å) is shorter than the S-S bond distance in the corresponding trithiapentalene (11)[21] (cf. 2.499 Å). In the 6a-thia-1, 6-diazapentalene(19)[31] there is some departure from C_{2v} symmetry, probably due to strain caused by the trimethylene bridge. The average N-S bond length (1.925 Å) is approximately 10% longer than the distance found for a normal S-N covalent bond[15] (1.74 Å) which indicates that the N-S bond order is similar to the S-S bond order found for trithiapentalenes.

In compound (20)[32] the departure from C_{2v} symmetry is probably due to the phenyl groups being twisted at different angles to the plane of the heterocyclic system, due to intermolecular interactions. The average S-S bond distance (2.323 Å) is similar to the average S-S bond distance found in the corresponding trithiapentalene (12)[22] (cf. 2.333 Å), and the C-N bond distances (1.325, 1.330, 1.349 and 1.336 Å) are similar to the C-N bond distances (1.340 Å) found in pyridine[33]. These results indicate a structure analogous to the trithiapentalene system.

Compound (21)[34] has a shorter S-O bond length (2.034 Å) and a longer S-S bond length (2.178 Å) than the oxadithiapentalene (15) and therefore this molecule may also be regarded as bicyclic. Hordvik[35] has recently carried out a study on the 6, 6a-dithia-1, 2-diazapentalene (22) and the S-S bond distance (2.426 Å) and the S-N bond distance (1.841 Å) have been found to be similar to the

12



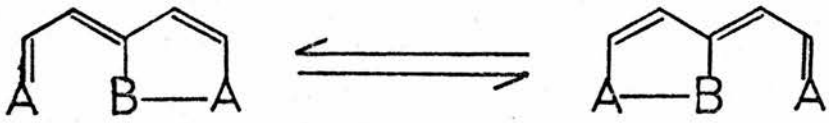
13

23

24

25

26



27a 27b

corresponding bond distances in compound (18).

These results indicate that the aza analogues are structurally related to 1, 6, 6a-trithiapentalenes with similar bond orders between atoms in the 1- and 6a-, and the 6- and 6a-positions.

(ii) ^{1}H Nuclear Magnetic Resonance Spectroscopy

The nmr spectra of symmetrically substituted 1, 6, 6a-trithiapentalenes[36, 37] show in all cases magnetic equivalence of ring protons or substituents at the C(2)-and C(5)-positions, and the C(3)- and C(4)-positions, indicating that these compounds possess real or time averaged C_{2v} symmetry in solution. 2, 5-Diphenyl-1, 6, 6a-trithiapentalene (12)[36] and 3, 4-diphenyl-1, 6, 6a-trithiapentalene (13)[38] show this symmetry even though they have unequal S-S bonds in the solid state. This observed C_{2v} symmetry occurs as a result of intermolecular forces being averaged in solution. Compounds (23)-(26)[39-42], analogous to 1, 6, 6a-trithiapentalenes, also show real or time averaged C_{2v} symmetry in solution.

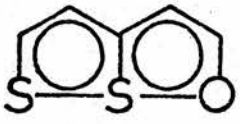
However the equivalence observed could be due to two rapidly interconverting valence tautomers (27a) and (27b) resulting in time averaged C_{2v} symmetry in solution. The nmr spectra of a number of compounds were studied at temperatures down to -60°C[39, 43, 44] and no departure from C_{2v} symmetry was detected. Therefore it seems most likely that the equivalence observed is due to a symmetrical bonding pattern in the molecule, rather than due to two rapidly interconverting valence tautomers.

28a

28b

6

29



30

5

Reid and coworkers[37] have compared the chemical shift of the 2-H protons in 1, 6, 6a-trithiapentalenes with the chemical shift of the thioformyl proton in stable heterocyclic thioaldehydes[45,46]. The chemical shift of the thioformyl proton does not fall below δ10.2 even when the thioaldehyde is highly polarised in the sense $\overset{+}{R}=CH-\bar{S}$. The chemical shifts of the 2-H protons in trithiapentalenes occur in the region δ8.5-9.4 and are therefore consistent with H-2 being in environment (28a) rather than environment (28b). The ring proton chemical shifts for 1, 6, 6a-trithiapentalene (6)[37], 6-methyl-1, 6a-dithia-6-azapentalene (29)[47] and 1-oxa-6, 6a-dithia-pentalene (30)[48] are respectively, 2-H [≡5-H in (30)] δ9.18, 8.86 and 7.98; 3-H [≡4-H in (30)] δ7.96, 7.45 and 7.23; 4-H [≡3-H in (30)] δ7.96, 7.05 and 6.98. These values indicate the presence of a ring current due to π-electron delocalisation, with deshielding of protons increasing from oxadithiapentalene to dithiaazapentalene to trithiapentalene. From nmr data Lozac'h[49] has estimated that the ring current in 2, 5-dimethyl-1, 6, 6a-trithiapentalene (5) is 65% of that in naphthalene.

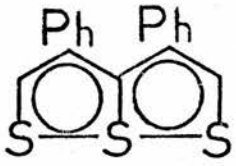
(iii) X-ray Photoelectron Spectroscopy

Clark and coworkers[50,51] have applied X-ray photoelectron spectroscopy to a study of the structure of 1, 6, 6a-trithiapentalenes in the solid state, by measuring the sulphur (2s and 2p) molecular core binding energies. The sulphur molecular core binding energies for 2, 5-dimethyl-1, 6, 6a-trithiapentalene (5) indicate that there are two types of sulphur present in a 2:1 ratio and therefore

5

6

9

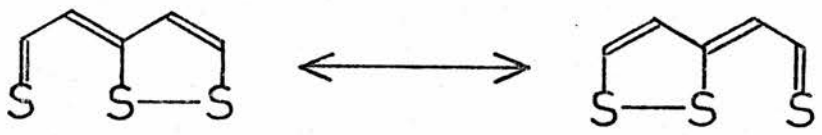


13

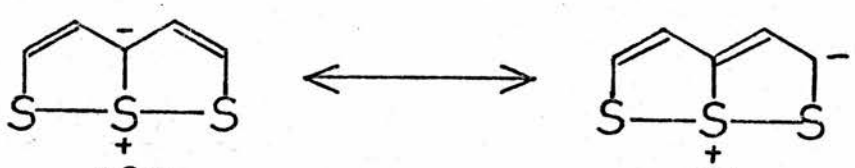
that this compound possesses a symmetrical structure. A similar result was obtained for 1, 6, 6a-trithiapentalene (6) which also indicated a symmetrical structure. By contrast the sulphur molecular core binding energies for trithiapentalenes (9) and (13) indicate three types of sulphur present in the molecule and thus unsymmetrical structures for these compounds. These results are in agreement with X-ray crystallographic data which suggests symmetrical structures for compounds (5)[12] and (6)[13] and unsymmetrical structures for compounds (9)[19] and (13)[23]. However Lindberg and coworkers[52] have carried out a similar study on 2, 5-dimethyl-1, 6, 6a-trithiapentalene (5) and on the basis of their results suggest an unsymmetrical structure.

(iv) Visible and Ultraviolet Spectroscopy

Visible and ultraviolet spectra of trithiapentalenes in solution have been measured for numerous compounds and have been reviewed by Lozac'h[7]. The spectra of trithiapentalenes are characterised by strong absorption bands near 500 nm in the visible region and near 260 nm in the ultraviolet region. An SCF-MO calculation[53] carried through for the 1, 6, 6a-trithiapentalene system has given a satisfactory explanation for the band occurring near 500 nm, assigned to a $\pi \longrightarrow \pi^*$ transition. The electronic spectra of selenium[37], oxygen[54] and nitrogen[55, 56] analogues have been used as proof of the structural similarity of these analogues to trithiapentalenes.



31a 31b



32a 32b

(v) Miscellaneous Spectroscopic Techniques

The electron spin resonance spectra of radical ions generated from several symmetrically substituted 1, 6, 6a-trithiapentalenes, either by electrolytic reduction or by reaction with metallic potassium, suggest that these species have symmetrical structures[57]. An electron diffraction study of 1, 6, 6a-trithiapentalene in the gaseous state also supports the view that the molecule possesses C_{2v} symmetry[58].

(b) Theories of Bonding in 1, 6, 6a-Trithiapentalenes

Various theories have been proposed to account for the unique features of the structure of the 1, 6, 6a-trithiapentalene system, such as the collinear sequence of the three sulphur atoms, the planarity of the molecule and the S-S interatomic distances.

The first explanation given was the existence of a "single-bond no-bond resonance" between structures (31a) and (31b)[4, 5] and calculations based on this concept were later carried out according to the Hückel MO method[59]. This hypothesis requires bonds between S(1) and S(6a), and S(6a) and S(6). The involvement of d-orbitals of the central sulphur atom in bonding is not required for this theory.

Lozac'h suggested the sulphonium ylid structure (32a)[60], but delocalisation of negative charge as in structure (32b) implies that electrophilic attack should occur at the 2-position, which is in direct conflict with the experimental evidence (see page 16).

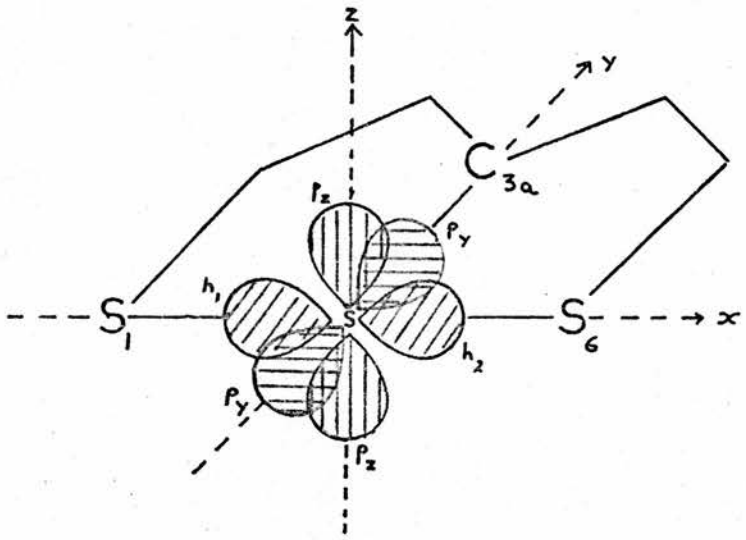


FIGURE 1

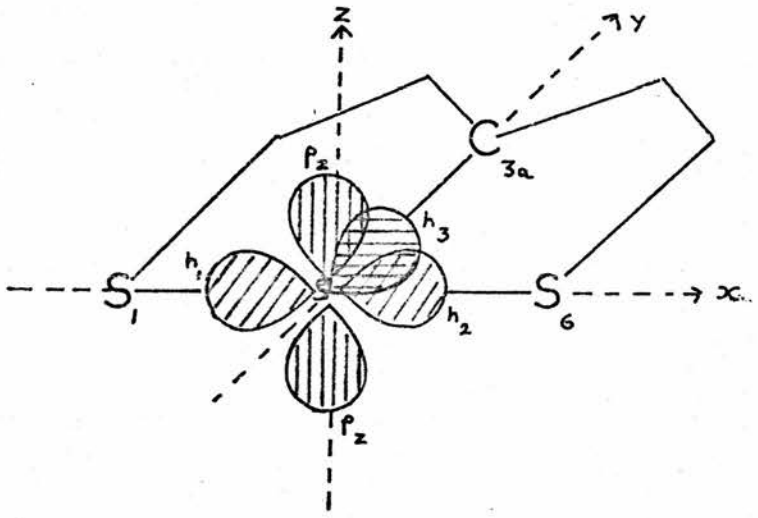


FIGURE 2

33a

33b

The use of a double bond between the central carbon atom and the central sulphur atom introduces valence shell expansion of sulphur involving d-orbitals. Maeda[61,62,63] has proposed a structure (figure 1) with σ-bonding between the sulphur atoms utilising two pd hybrid orbitals (h_1 and h_2) from the central sulphur atom and a p-orbital from each of the lateral sulphur atoms. σ-Bonding between the carbon atoms and between the carbon and sulphur atoms is completed using sp^2 hybrid orbitals from each of the carbon atoms and p-orbitals from each of the sulphur atoms. A 10-π electron system (consisting of one 2p electron from each carbon atom, one 3p electron from the central sulphur atom and two 3p electrons from each of the lateral sulphur atoms) is superimposed on the σ-framework. The 1, 6, 6a-trithiapentalene system may now be represented by formulae (33a) or (33b).

Johnstone and Ward[64] have proposed a similar model (figure 2) where the central sulphur atom is σ-bonded to the lateral sulphur atoms and to the central carbon atom by three p^2d hybrid orbitals (h_1, h_2 and h_3) with the remaining p-orbital on S(6a) used for π-bonding. There appears to be support from ultraviolet spectroscopic data for this theory.

Gleiter and Hoffmann[65] have made a notable contribution to the theory of bonding in 1, 6, 6a-trithiapentalenes by postulating that the three sulphur atoms are held as a unit by using four-electron three-centre bonding with superimposed π-bonding. In this model three atomic orbitals, one from each of the three collinear

heteroatoms are used to construct three molecular orbitals. One of these is a doubly occupied bonding-orbital with the charge spread over all three centres. The second is a doubly occupied non-bonding orbital with the charge localised on the lateral atoms. The third is a vacant anti-bonding orbital. The stabilisation from superimposed π-bonding of the sulphur atoms is not expected to be large as the equilibrium distance for the three-centre bond is reached at a stage where $p\pi$-$p\pi$ overlap is small.

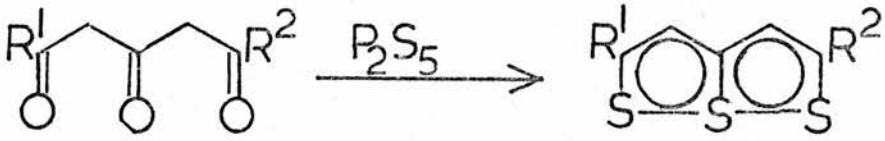
Gleiter and Hoffmann[65], using the four-electron three-centre model, have also calculated the potential energy of the S-S-S sequence as a function of the displacement of the central sulphur atom in relation to the fixed lateral sulphur atoms. When d-orbitals are not involved in the central sulphur atom the energy curve shows a minimum for an unsymmetrical structure. However when d-orbitals are involved the energy curve shows a flat minimum of ± 0.2 Å favouring a nearly symmetrical structure. The latter case is in good agreement with X-ray crystallographic data where the S(1)-S(6) distance remains fairly constant but individual S-S distances may vary by as much as 0.4 Å, thus verifying d-orbital participation.

The concept of electron-rich three-centre bonds is familiar in the chemistry of trihalide ions[66,67], and the four-electron three-centre model has been used to describe the transition state for S_N2 displacement at a saturated carbon atom[68]. In the triiodide ion the I-I distances (2.90-2.93 Å)[69,70,71] are approximately 9% longer than the I-I distance found in molecular iodine. In

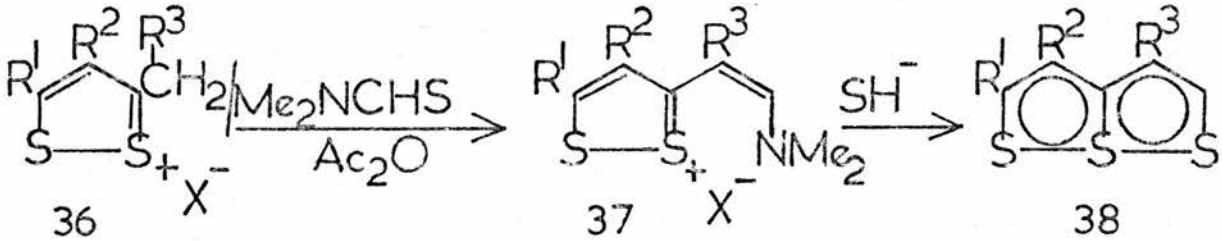
1, 6, 6a-trithiapentalenes the S-S distances are approximately 10% longer than the normal S-S distance, thus demonstrating the similarity in the bonding of triiodide ions and trithiapentalenes.

Oxygen, selenium and nitrogen analogues have been shown to be structurally similar to 1, 6, 6a-trithiapentalenes and the bonding in these compounds may also be described by the four-electron three-centre model. Nitrogen, oxygen or selenium may be substituted for sulphur in the lateral positions, and they provide one electron to the 10π-system and one electron to the three-centre bond as before. Selenium, which is capable of valence shell expansion, may replace sulphur in the central position. Also nitrogen may replace a C-H (or C-R) unit in the 2, 3, 4 or 5 positions donating one electron to the 10π-system like carbon.

3



34 35



36 37 38

R^1 R^2 R^3

(X = $HClO_4$)

(a) Me H H

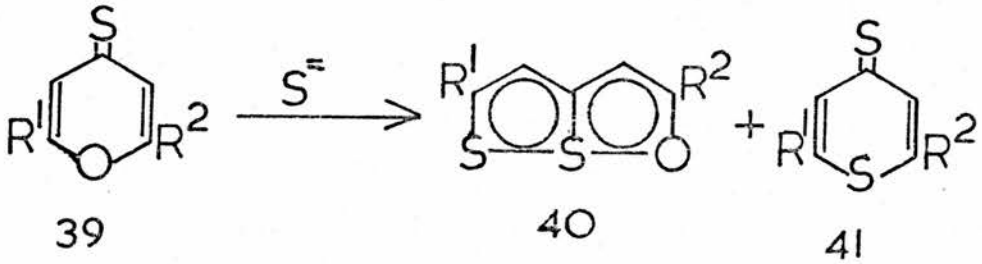
(b) Ph H H

(c) Ph H Ph

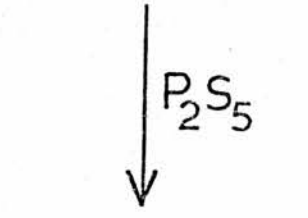
(d) H Me Me

(e) H $-(CH_2)_3-$

(f) H H H



39 40 41



42

B. Synthesis and Reactivity of 1, 6, 6a-Trithiapentalenes

(a) Synthesis of 1, 6, 6a-Trithiapentalenes

The first trithiapentalene (3) was prepared, from the reaction of phosphorus pentasulphide with heptane-2, 4, 6-trione, in 1925[1]. Since that time numerous other trithiapentalenes have been synthesised by a variety of different methods. Only the most convenient methods resulting in simple derivatives will be discussed here.

(i) From 1, 3, 5-Triones

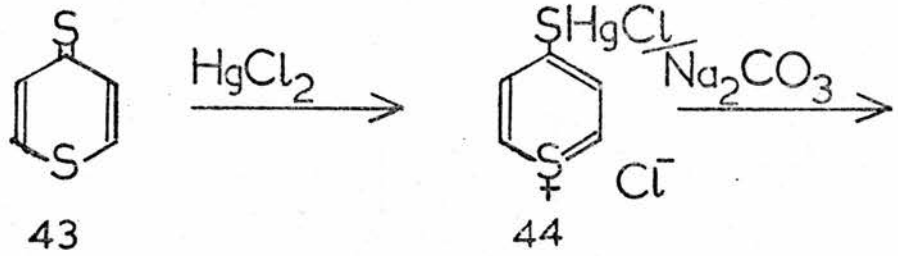
The reaction of phosphorus pentasulphide with 1, 3, 5-triones (34) gives rise to trithiapentalenes (35). Numerous compounds have been prepared by this method[1, 72-75] in varying yields.

(ii) From 1, 2-Dithiolium Salts

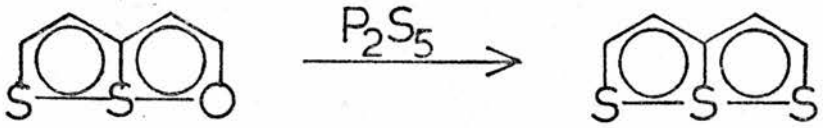
The 3-methyl(ene) group in 1, 2-dithiolium salts (36) is acidic[76] and condenses readily with dimethylthioformamide in boiling acetic anhydride resulting in the Vilsmeier salts (37). These salts react smoothly with sodium hydrogen sulphide to give trithiapentalenes (38).[37]

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

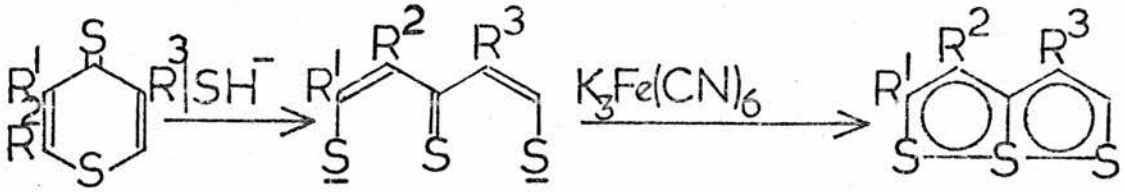
Traverso[3, 73, 74, 77] found that 4H-pyran-4-thiones (39) react with sodium sulphide or sodium hydrogen sulphide to give the 1-oxa-6, 6a-dithiapentalenes (40) as well as the 4H-thiopyran-4-thiones (41). The trithiapentalenes (42) were obtained by treating compounds (40) with phosphorous pentasulphide.



43 44

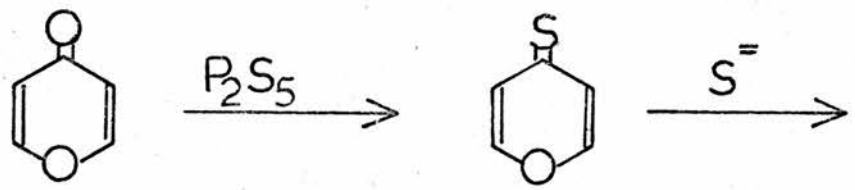


45 46

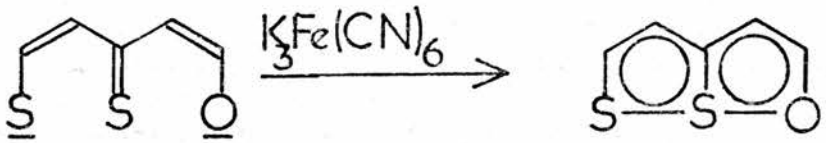


47 48 49

	R^1	R^2	R^3
(a)	H	Me	Me
(b)	Ph	H	H
(c)	Bu^t	H	H
(d)	Ph	H	Ph
(e)	Ph	H	Me



50 51



52 45

(iv) From 4H-thiopyran-4-thiones

The reaction of 4H-thiopyran-4-thione (43) with mercury(II) chloride gave the salt (44) which was converted into the parent oxadithiapentalene (45) by alkaline hydrolysis. Thionation of this compound gave the parent trithiapentalene (46)[78]. Reid and coworkers[79] have developed a more convenient synthesis from 4H-thiopyran-4-thiones. The thiones (47) are ring-opened by sodium hydrogen sulphide in dimethylformamide or dimethylsulphoxide, forming anions (48) which undergo intramolecular oxidative coupling with potassium ferricyanide to give trithiapentalenes (49).

(v) From γ-Pyrone

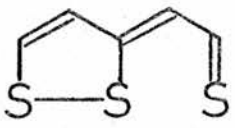
Reid[48] has developed a synthesis of the parent trithiapentalene (46), in 12% overall yield, from readily accessible γ-pyrone (50). Thionation of γ-pyrone with phosphorous pentasulphide gave 4H-pyran-4-thione (51)[80] which was ring opened by sodium sulphide to give the anion (52). Intramolecular oxidative coupling of this anion with potassium ferricyanide gave the parent oxadithiapentalene (45) which was thionated with phosphorous pentasulphide to give trithiapentalene (46).

(b) Reactivity of 1, 6, 6a-Trithiapentalenes

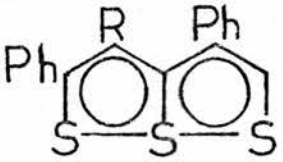
(i) Thiocarbonyl Reactions

Although structural studies have shown that 1, 6, 6a-trithiapentalenes exist in the bicyclic form (53), they may undergo carbonyl reactions, and reaction may be regarded as taking place via the

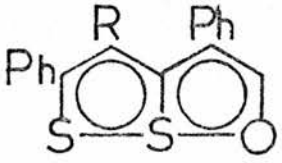
53



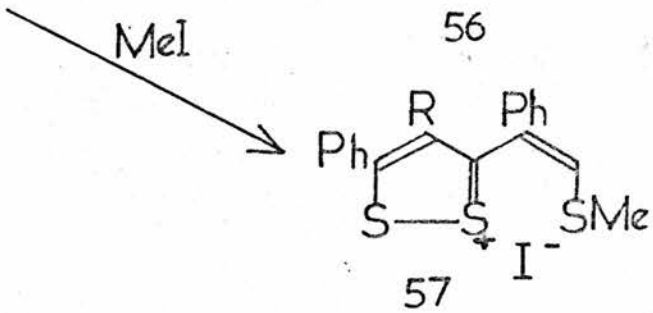
54



55



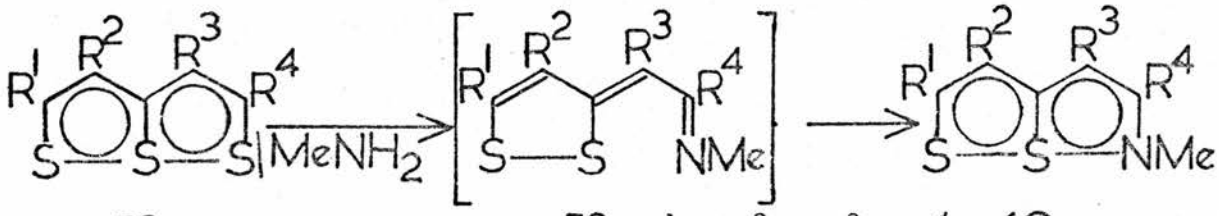
56



(a) R=H

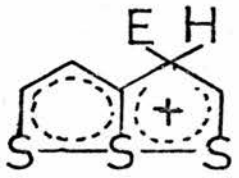
(b) R=Ph

57

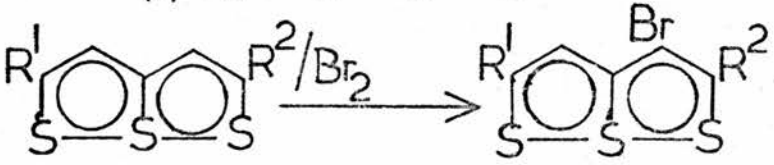


58 59 60

	R^1	R^2	R^3	R^4
(a)	Me	H	H	Me
(b)	Bu^t	H	H	H
(c)	H	Me	Me	H
(d)	H	$-(CH_2)_3-$		H
(e)	Ph	H	H	H
(f)	H	H	H	H

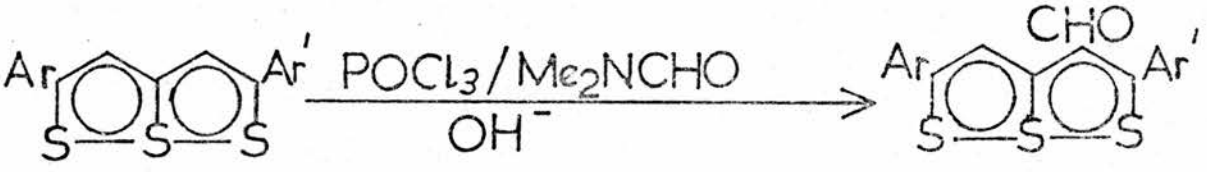


61



62 63

	R^1	R^2
(a)	Me	Me
(b)	Ph	Ph
(c)	Ph	Me
(d)	Ph	MeS



64 65

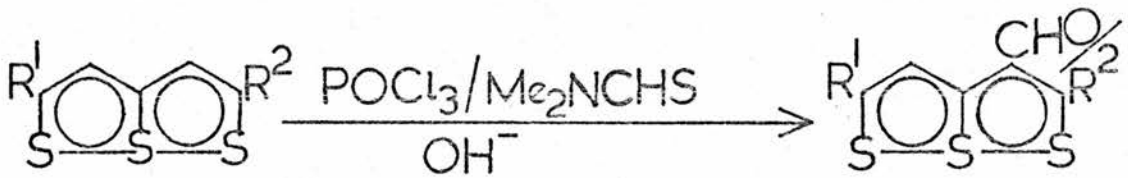
masked thioaldehyde form (54). For example trithiapentalenes react with mercury(II) compounds forming salts with mercury(II) chloride[3], and are desulphurised by mercury(II) acetate. Trithiapentalenes (55) are selectively desulphurised to give the oxadithiapentalenes (56)[81]. The action of acid also causes hydrolytic desulphurisation resulting in 1-oxa-6, 6a-dithiapentalenes[2, 82, 83]. Trithiapentalenes are methylated at sulphur using methyl iodide[56, 82] [eg. (55)⟶(57)[56]] or ethylated using triethyloxonium fluoroborate[43]. Potential thiocarbonyl activity is also demonstrated by treating trithiapentalenes (58) with methylamine resulting in imine derivatives (59), better represented as the bicyclic 1, 6a, -dithia-6-azapentalenes (60)[47].

(ii) Electrophilic Substitution

Electrophilic substitution takes place at the 3(4)-position in accordance with the results of calculations of electrophilic localisation energies, using conventional Wheland-type intermediates (61)[84]. These calculations also indicate that attack at sulphur [S(1)] may occur as a competing reaction.

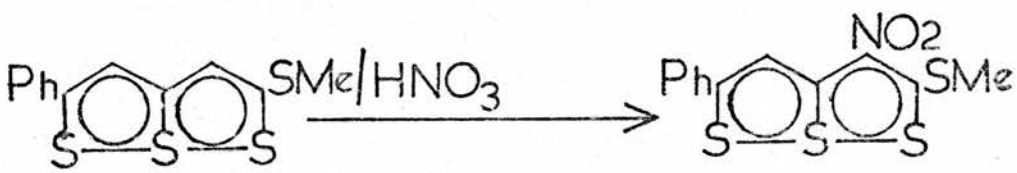
Bromination of trithiapentalenes (62)[85, 86, 87] gives the monobromo compounds (63), the nmr spectra of the products being used to assign the correct structure.

Formylation of 2, 5-diaryl-1, 6, 6a-trithiapentalenes (64)[88, 89, 90] using phosphoryl chloride and dimethylformamide gives the 3-formyl compounds (65). Reid and coworkers[91] have modified the Vilsmeier reaction by replacing dimethylformamide with dimethylthioformamide. This resulted in improved yields. The parent compound and several

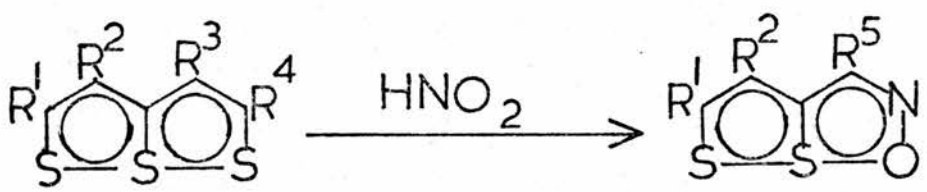


66 67

	R^1	R^2
(a)	H	H
(b)	D	D
(c)	Ph	H
(d)	Bu^t	H
(e)	Bu^t	D



62d 68



69 70

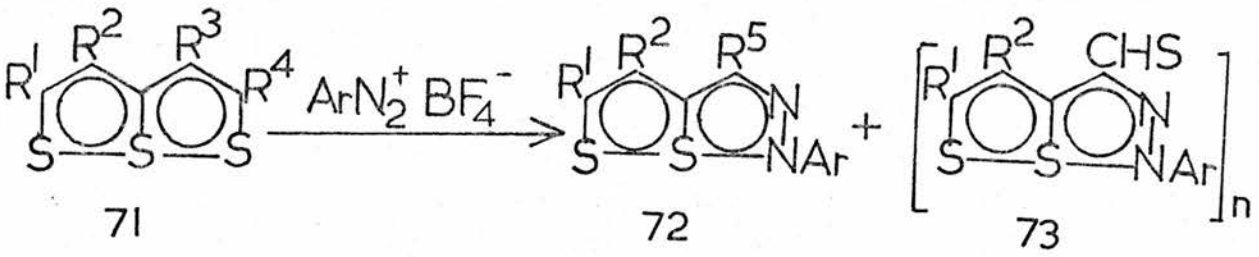
	R^1	R^2	R^3	R^4
(a)	Ph	H	H	Ph
(b)	Ph	H	H	SMe
(c)	Ph	H	H	Me_2N
(d)	H	Me	Me	H
(e)	H	$-(CH_2)_3-$		H

	R^1	R^2	R^5
(a)	Ph	H	COPh
(b)	Ph	H	CS_2Me
(c)	Ph	H	$CSNMe_2$
(d)	H	Me	Me
(e)	H	$-(CH_2)_3-$	
(f)	Ph	H	CSPh

derivatives have been formylated by this method[92] [eg. (66) ⟶ (67)]. The position of formylation was determined unambiguously by formylating the deuterio compounds (66b) and (66e), and comparing the nmr spectra of the products (67b) and (67e) with the products (67a) and (67d).

Beer and coworkers[86,87] have successfully nitrated trithiapentalene (62d) using nitric acid in hot acetic acid. The structure (68) was confirmed unambiguously by synthesis. However attempted nitration of trithiapentalene (69a)[87] gave a product identical with that obtained by nitrosation, namely the 1-oxa-6, 6a-dithia-2-azapentalene (70a). Similar results were obtained from attempted nitration with tetranitromethane in pyridine[93].

Nitrosation of trithiapentalenes (69) gave the oxadithiaazapentalenes (70)[87,94]. It is though that nitrosation proceeds by electrophilic attack at the 3(4)-position as before, followed by a rearrangement to give the 1-oxa-6, 6a-dithia-2-azapentalene (See page 18 for an explanation of the mechanism). Nitrosation of compound (69a) followed by rearrangement gives compound (70f) which possesses an unstable thiocarbonyl group, and replacement of sulphur by oxygen takes place giving the more stable ketone (70a). In compounds (70b) and (70c) the resulting thiocarbonyl group is stabilised (by being polarised in the sense $\overset{+}{X}$=CR-$\bar{S}$) by the adjacent SMe and NMe_2 groups, and hence sulphur is not replaced by oxygen as in the previous case. (Stable thiocarbonyl compounds are discussed in greater detail on page 29). From the

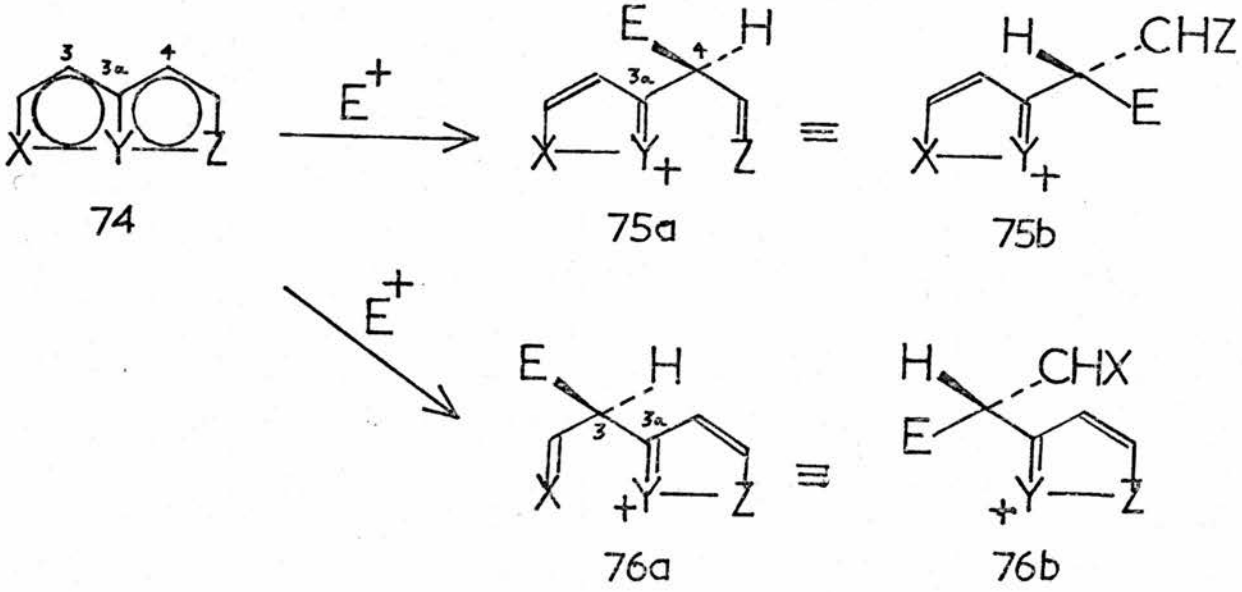


71 72 73

	R^2	R^2	R^3	R^4
(a)	Bu^t	H	H	H
(b)	Ph	H	H	H
(c)	H	H	H	H
(d)	MeS	H	H	H
(e)	Me_2N	H	H	H
(f)	H	Me	Me	H
(g)	H	$-(CH_2)_3-$		H

	R^1	R^2	R^5
(a)	Bu^t	H	CHO
(b)	Ph	H	CHO
[(c)	H	H	CHO]
(d)	H	H	CS_2Me
(e)	H	H	$CSNMe_2$
(f)	H	Me	Me
(g)	H	$-(CH_2)_3-$	
(h)	Bu^t	H	CHS
(i)	Ph	H	CHS
(j)	H	H	CHS

	R^1	R^2
(a)	Bu^t	H
(b)	Ph	H
(c)	H	H



74 75a 75b

76a 76b

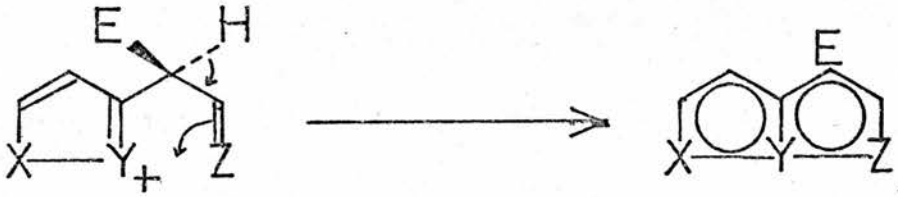
trithiapentalenes (69d) and (69e), substituted in both the 3- and 4-positions, the oxadithiaazapentalenes (70d) and (70e) were obtained, the CHS group being eliminated in the reaction[95]. (For an explanation of the mechanism see page 19).

As in nitrosation, the reaction of arenediazonium salts with trithiapentalenes (71)[41,96] involved electrophilic attack at the 3(4)-position, with subsequent rearrangement giving 6, 6a-dithia-1, 2.-diazapentalenes. Trithiapentalenes (71a-c) gave the unstable intermediates (72h-j) which were hydrolysed to the more stable aldehydes (72a) and (72b), and in this case the polymers (73a-c) were also isolated. Trithiapentalene (71c) gave only the polymer (73c). In dithiadiazapentalenes (72d) and (72e) the thiocarbonyl substituents are stabilised by the adjacent SMe and NMe_2 groups. Compounds (72f) and (72g) were formed, from trithiapentalenes (71f) and (71g), by the elimination of a CHS group, as in nitrosation.

(iii) Mechanism of Electrophilic Substitution

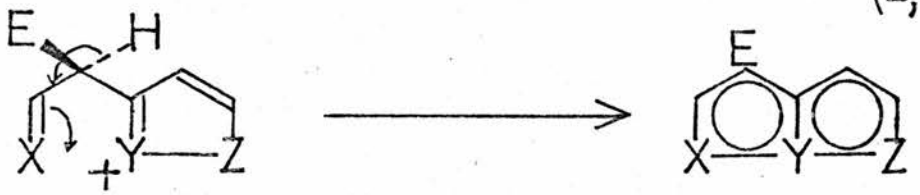
Reid and coworkers[95] have proposed a mechanism which accounts for the various features of electrophilic substitution of 1, 6, 6a-trithiapentalenes and analogous systems.

The electrophile E^+ adds at the 3- or 4-position of the substrate (74) with accompanying breaking of the Y-Z or X-Y bond and formation of a stable 6 π-electron monocyclic intermediate (75) or (76). Free rotation about the C(3a)-C(3) or C(3a)-C(4) bond allows the group E to come into proximity to Y [ie. (75b) and (76b)]. In the case where E is an atom (eg. Br) or group (eg.

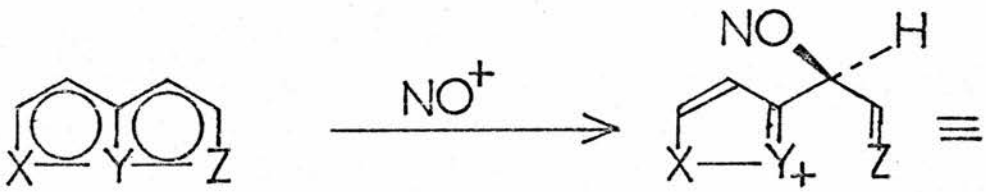


75a 77

(Y = S, Se)
(Z, X = S, Se, O, NR)

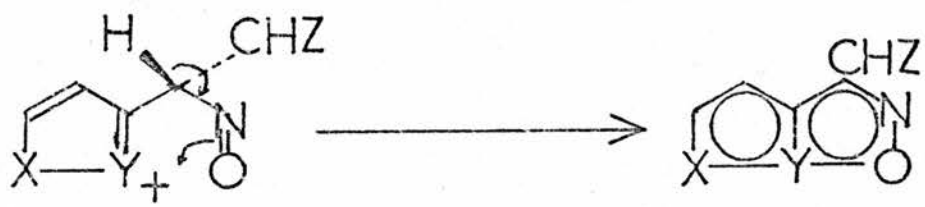


76a 78

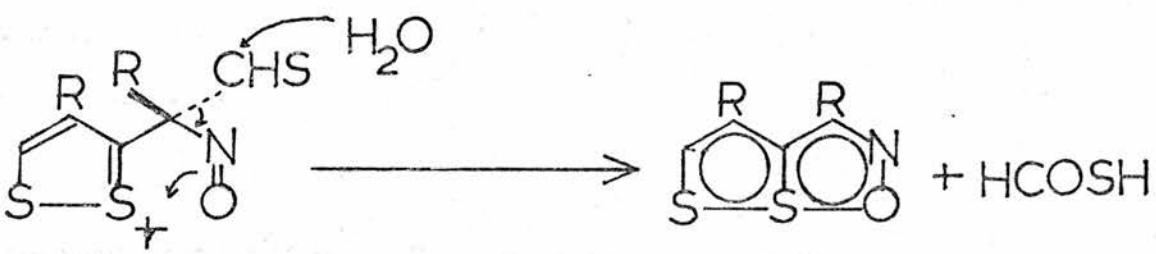


74 79a ≡

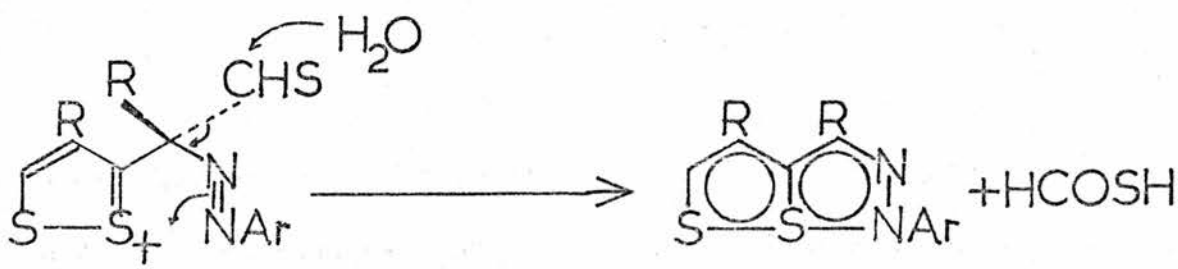
(X, Y, Z = S)

≡ 

79b 80



81 83



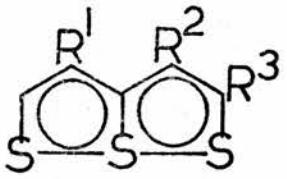
82 84

$CH{=}\overset{+}{N}Me_2$) which cannot interact with Y to form a new three-centre heteroatom sequence, loss of a proton from the intermediate (75a) or (76a) gives the normal substitution product (77) or (78) with reformation of the original X-Y-Z three-centre heteroatom sequence. However if E is a group (eg. NO) containing a heteroatom (eg. O) which can bond with Y, two routes are open to intermediates (75) and (76), depending on the relative strengths of the original X-Y-Z interaction and the new interaction with E (eg. XYO). If the original interaction is stronger the substitution product (77) or (78) will occur again. Alternatively if the new interaction with E is stronger a rearrangement product is formed via conformations (75b) or (76b). For example in nitrosation electrophilic attack takes place at the 3(4)-position to give intermediate (79a). Free rotation about the C(3)-C(3a) bond gives conformation (79b), and subsequent elimination of a proton and ring closure gives rise to product (80).

In the nitrosation and diazo coupling reactions of trithiapentalenes, substituted in the 3- and 4-positions, elimination of the CHS group is though to occur by nucleophilic attack of water on intermediates (81) and (82) giving products (83) and (84). These reactions were carried out in ethanol or acetonitrile and it is thought that these solvents, even after drying, contain traces of water which may attack the intermediates (81) and (82).

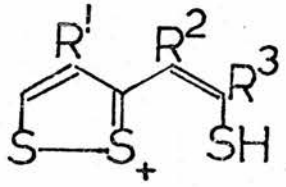
(iv) Protonation

The protonation of trithiapentalenes (85a-e), in trifluoroacetic acid solution, has been studied by ^1H nmr spectroscopy[110]. The



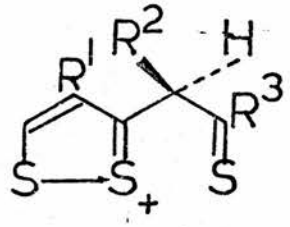
85

	R^1	R^2	R^3
(a)	H	H	H
(b)	Me	Me	H
(c)	$-(CH_2)_3-$		H
(d)	H	H	SMe
(e)	H	H	NMe_2



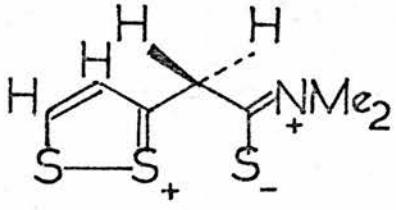
86

	R^1	R^2	R^3
(b)	Me	Me	H
(c)	$-(CH_2)_3-$		H

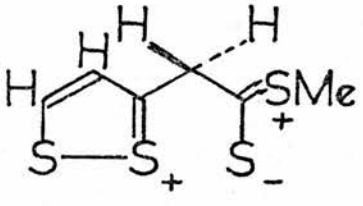


87

	R^1	R^2	R^3
(a)	H	H	H
(d)	H	H	SMe
(e)	H	H	NMe_2

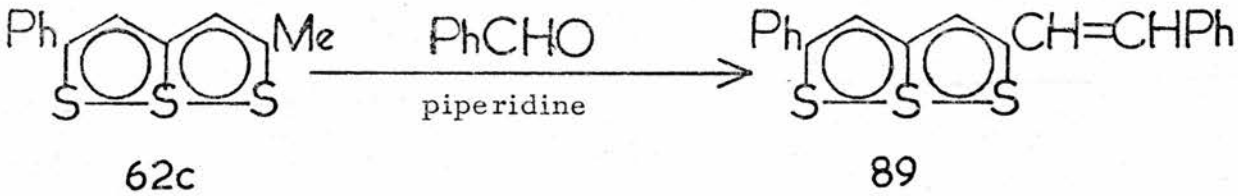


88e



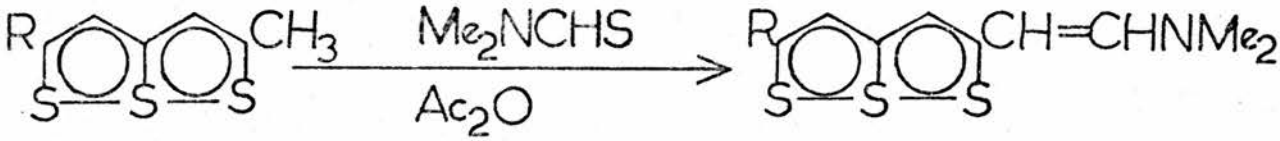
88d

spectra of compounds (85b) and (85c) showed that S-protonation had taken place resulting in the dithiolium ions (86b) and (86c). The spectrum of compound (85a) was too complex to analyse. To determine whether C(3)-protonation of compound (85a) had taken place a sample of trithiapentalene (85a) was taken up in deuteriotrifluoroacetic acid. After a period of time the trithiapentalene was recovered, by treating the acid solution with aqueous sodium carbonate and extracting the aqueous phase with benzene. The nmr spectrum of the recovered trithiapentalene in $CDCl_3$ showed that partial exchange of D for H had taken place at the 3- and 4-positions, thus confirming the existence of the C-protonated species (87a). This species is of particular interest in that it contains an unconjugated thioformyl group. Compounds containing unconjugated thioformyl groups have never been isolated owing to their instability and they generally tend to polymerise. In an attempt to observe C-protonated species (87) directly and to determine the fate of the resulting unstable thioformyl group further protonation studies of trithiapentalenes have been carried out and are discussed in part 2. Trithiapentalenes (85d) and (85e) contain electron-releasing groups in the 2-position and are protonated exclusively at the 3-position resulting in the dithiolium ions (87d) and (87e). The resulting thiocarbonyl groups are stabilised by the adjacent electron-releasing group, by being polarised in the sense $\bar{S}-CR=\overset{+}{X}$ [eg. (88d) and (88e)].



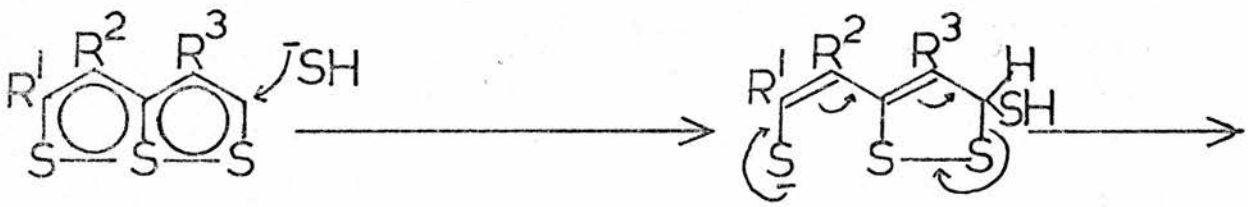
62c 89

69b

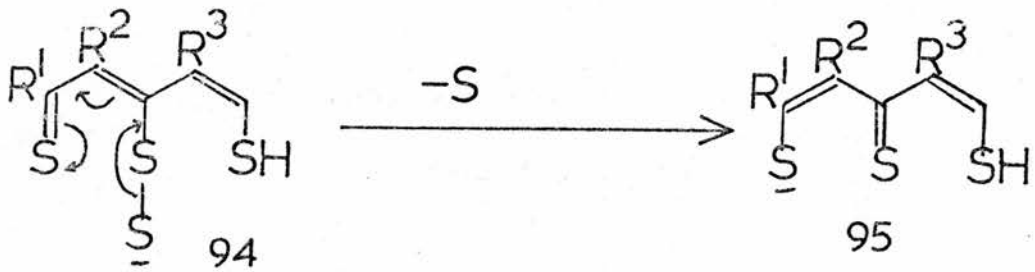


90 91

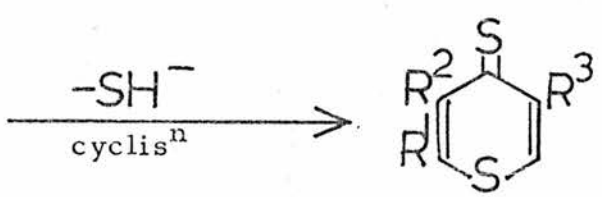
(a) R=H (b) R=Me



92 93



94 95



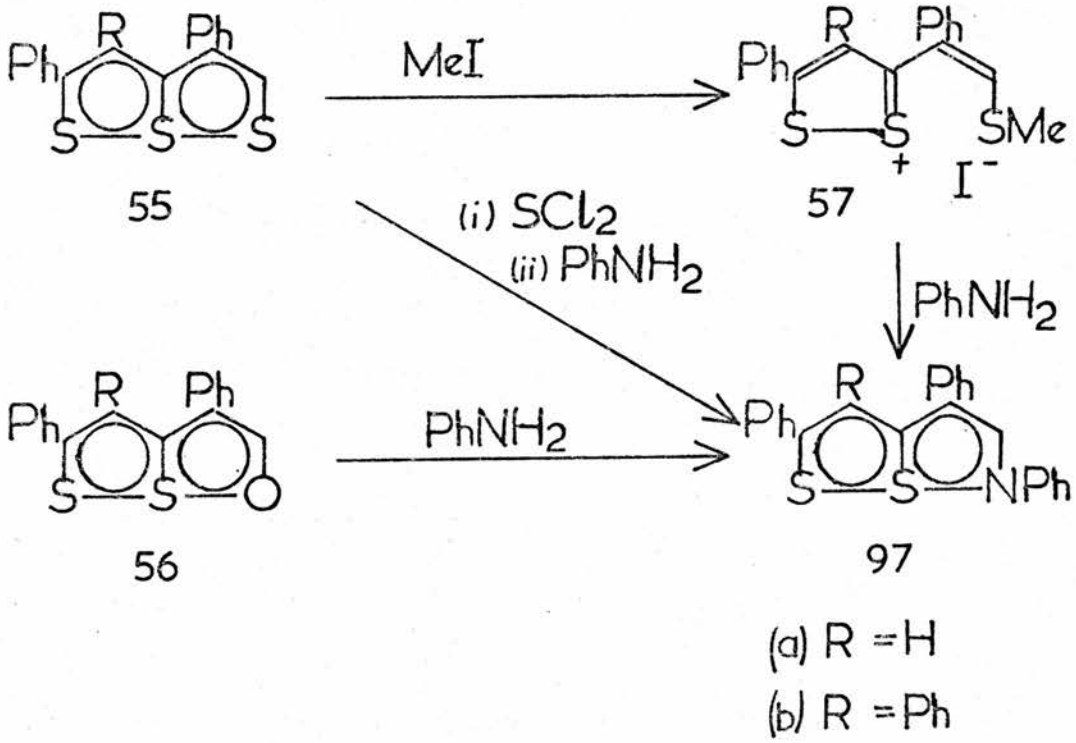
96

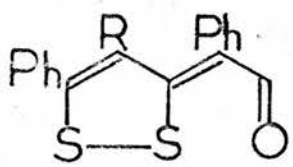
(v) Other Reactions

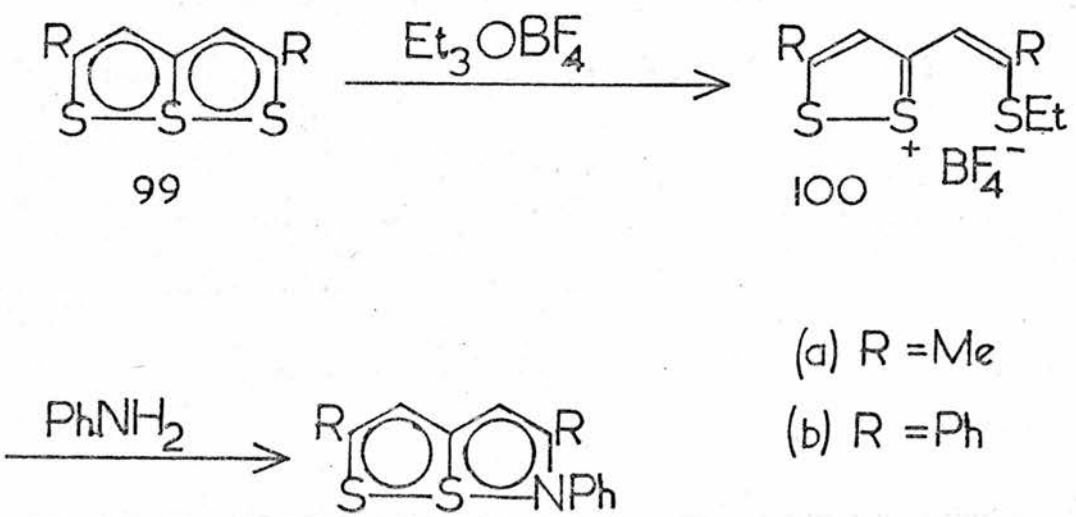
A few examples of nucleophilic substitution in the 2(5)-position of 1, 6, 6a-trithiapentalenes are known. In trithiapentalene (69b) the methylmercapto group is replaced by the ethoxide group, by means of a prolonged reaction with sodium ethoxide in ethanol under reflux[86, 97]. The methylmercapto group in trithiapentalene (69b) is also replaced by alkylamino groups, by the reaction with amines[86, 87].

A methyl(ene) group in the 2(5)-position of trithiapentalenes is relatively acidic. An example of the acidity of this group is the condensation of benzaldehyde with trithiapentalene (62c), in the presence of a weak base such as piperidine, to give the styryl derivative (89)[98]. Also attempted formylation of trithiapentalenes (90a) and (90b) gave enamines (91) by condensation of dimethylthioformamide with the reactive 2-methyl substituents[92].

Trithiapentalenes (92) react with sodium hydrogen sulphide or sodium sulphide to give 4H-thiopyran-4-thiones (96), providing at least one of the positions 2 and 5 is unsubstituted[99]. The mechanism (92) $\longrightarrow$ (96) is outlined.


MeI
(i) SCl2
(ii) PhNH2
PhNH2
PhNH2
55
56
57
97
(a) R =H
(b) R =Ph


98


Et3OBF4
99
100
(a) R =Me
(b) R =Ph
PhNH2
101

C. Synthesis and Reactivity of Aza Analogues of 1, 6, 6a-Trithiapentalenes

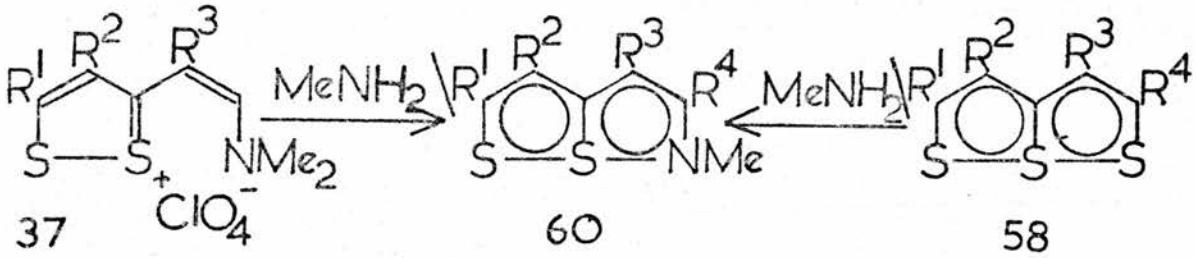
(a) Synthesis of Aza-Analogues of 1, 6, 6a-Trithiapentalenes

Replacement of sulphur or a CH(CR) unit by nitrogen in 1, 6, 6a-trithiapentalenes gives rise to aza-analogues which have been shown to be structurally similar to trithiapentalenes. Analogues containing up to four nitrogen atoms are known and the synthetic routes to these compounds are outlined here.

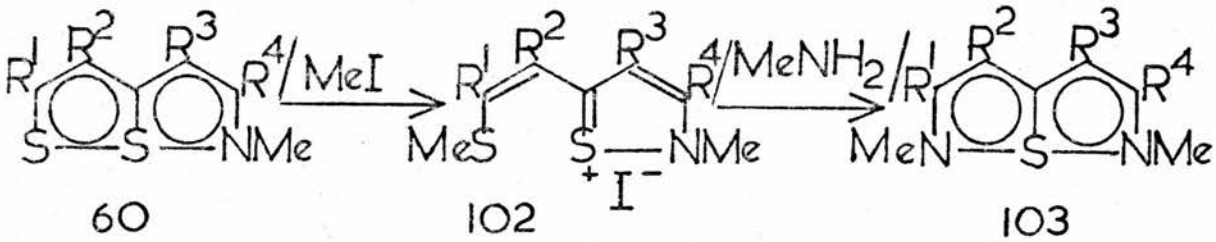
(i) 1, 6a-Dithia-6-azapentalenes

Addition of methyl iodide to trithiapentalenes (55) gave the iodide salts (57), which on treatment with aniline gave the 1, 6a-dithia-6-azapentalenes (97)[56]. Reaction of trithiapentalenes (55) with sulphur dichloride gave intermediates which were not characterised, but on treatment with aniline they gave compounds (97)[56]. Reaction of oxadithiapentalenes (56) with aniline also gave the dithiaaza-pentalenes (97)[56]. This reaction, taking place via the masked aldehyde form (98), demonstrates the potential carbonyl reactivity of oxadithiapentalenes (56). Trithiapentalenes (99) react less readily with methyl iodide than trithiapentalenes (55) and are ethylated by the more powerful alkylating agent triethyloxonium fluoroborate[43]. The resulting salts (100) react with aniline to give the 1, 6a-dithia-6-azapentalenes (101).

Reid and coworkers[47] have developed two routes to structurally simple dithiaazapentalenes (60). The first route involves the

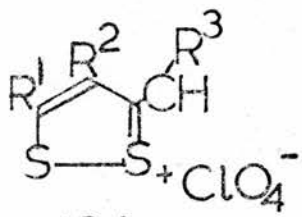


37 60 58

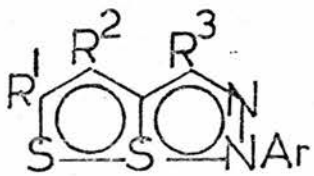


60 102 103

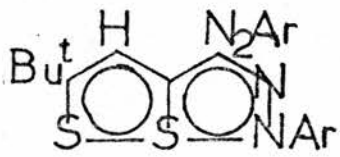
	R^1	R^2	R^3	R^4
(a)	H	H	H	H
(b)	H	Me	Me	H
(c)	H	$-(CH_2)_3-$		H
(d)	Me	H	H	Me



104

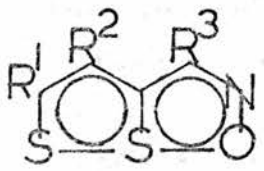


105



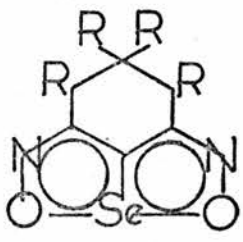
106

	R^1	R^2	R^3
(a)	H	H	H
(b)	Bu^t	H	H
(c)	H	Me	Me
(d)	H	$-(CH_2)_3-$	
(e)	Ph	H	Me
(f)	Ph	H	H
(g)	H	Ph	H
(h)	H	Ph	Ph



107

	R^1	R^2	R^3
(a)	H	H	H
(b)	Bu^t	H	H
(c)	Ph	H	H
(d)	H	Me	Me
(e)	H	$-(CH_2)_3-$	



108

reaction of trithiapentalenes (58) with methylamine, and the second route involves the treatment of the Vilsmeier salts (37) (see page 14) with methylamine.

(ii) 6a-Thia-1,6-diazapentalenes

Treatment of 1,6a-dithia-6-azapentalenes (60) with methyl iodide gave the isothiazolium salts (102) which then reacted with methylamine to give the thiadiazapentalenes (103)[39]. In part 2 of this thesis a new synthetic route to dithiaazapentalene (60a) and thiadiazapentalene (103a) will be described.

(iii) 6,6a-Dithia-1,2-diazapentalenes

1,2-Dithiolium salts (104) react with arenediazonium fluoroborates to give the dithiadiazapentalenes (105)[100]. It should be noted that in some cases ($R'=Bu^t$) an excess of the diazonium salt reacts with the dithiadiazapentalene to give the electrophilic substitution product (106).

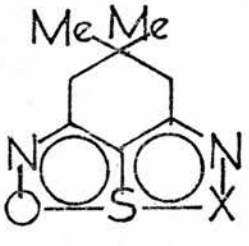
(iv) 1-Oxa-6,6a-dithia-2-azapentalenes

Several members of this class of compound have been obtained from attempts to nitrate or nitrosate trithiapentalenes[87,93,94,95]. The oxadithiaazapentalenes (107) are obtained in good yield from the reaction of 1,2-dithiolium salts (104) with sodium nitrite in acetic acid[93].

(v) 1,6-Dioxa-6a-thia-2,5-diazapentalenes

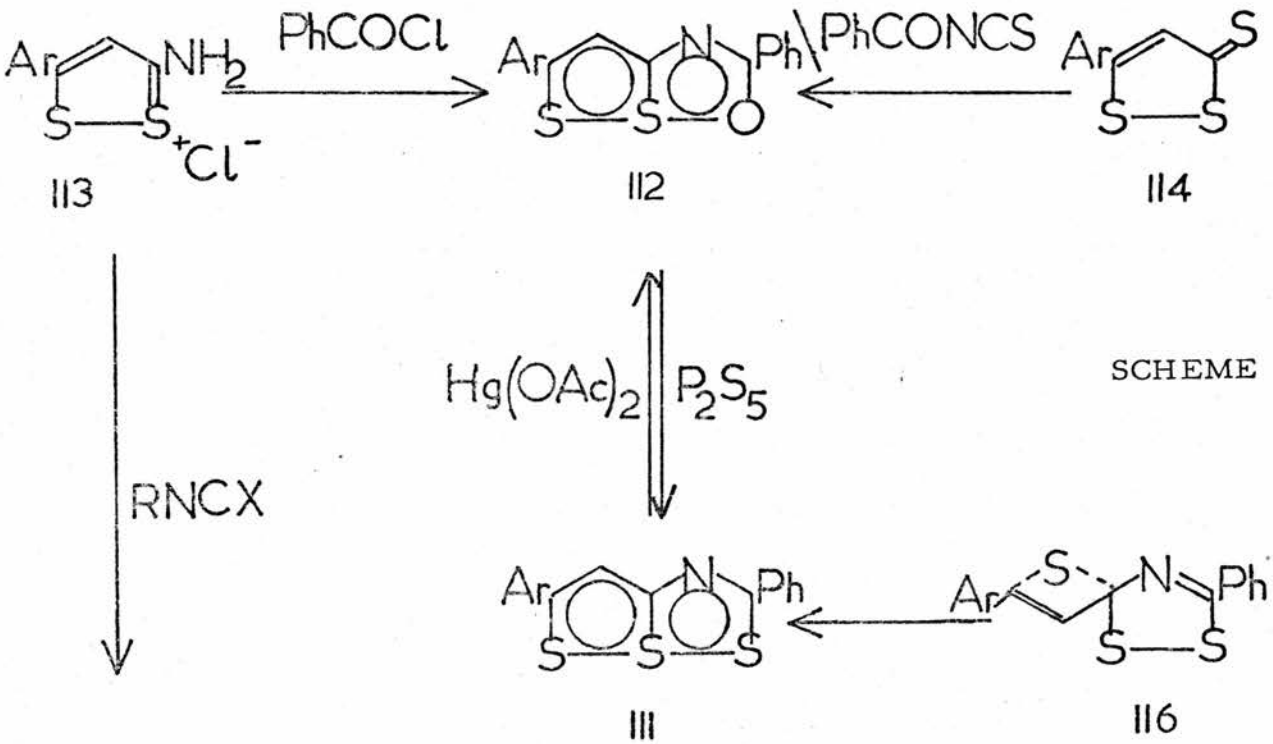
The selenium analogues (108) were first isolated by King and Felton in 1949[101], by the reaction of oximes of 1,3-diketones

109



(a) X=O
(b) X=S

110



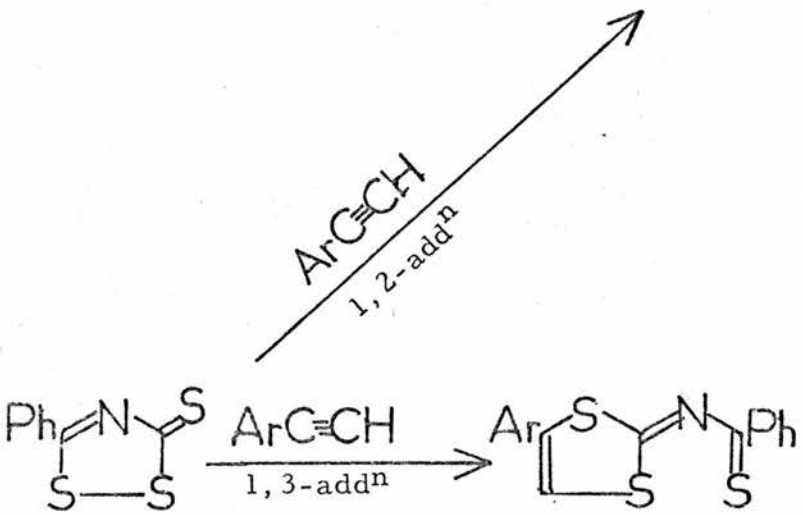
113 112 114

SCHEME 1

111 116

118

(a) X=S
(b) X=O



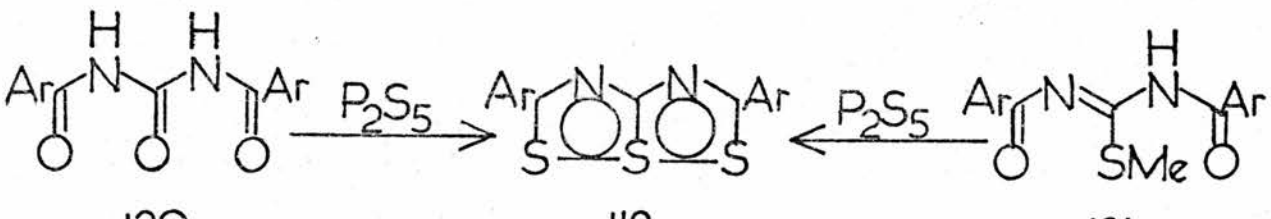
115 117

with selenium dioxide. Vialle and coworkers[44,102] extended this synthesis and isolated the parent compound (109). The sulphur compound (110a) has been prepared more recently by the action of sulphur dichloride on dimedone dioxime[42]. A minor product isolated from the same reaction appears to be the structurally related compound (110b).

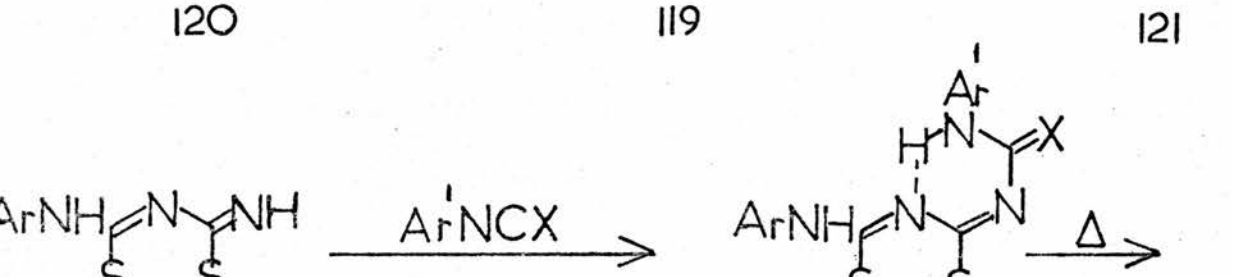
(vi) 1, 6, 6a-Trithia-3-azapentalenes

Trithiaazapentalenes (111) and their 1-oxa analogues (112) have been prepared by the methods outlined in scheme 1. In part 2 of this thesis further syntheses of trithiaazapentalenes are described.

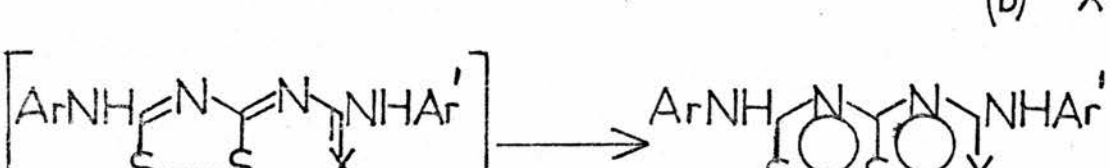
Reaction of the 1, 2-dithiolium salts (113) with benzoyl chloride gave the 1-oxa-6, 6a-dithia-3-azapentalenes (112), which were also prepared by treatment of 1, 2-dithiole-3-thiones (114) with benzoyl isothiocyanate[103,104]. Compound (112) reacted with phosphorus pentasulphide to give the 1, 6, 6a-trithia-3-azapentalene (111), and treatment of compound (111) with mercury(II) acetate regenerated the oxygen compound (112). Trithiaazapentalene (111) was also obtained by the 1, 2-dipolar addition of acetylenes to 1, 2, 4-dithiazole-3-thione (115) and rearrangement of the resulting intermediate (116). The thione (117) resulted from the 1, 3-dipolar addition of acetylenes to 1, 2, 4-dithiazole-3-thione (115)[103]. 1, 2-Dithiolium salts (113) react with aromatic and aliphatic isothiocyanates or isocyanates to give the trithiaazapentalenes (118a) and oxadithiaazapentalenes (118b), respectively[105].



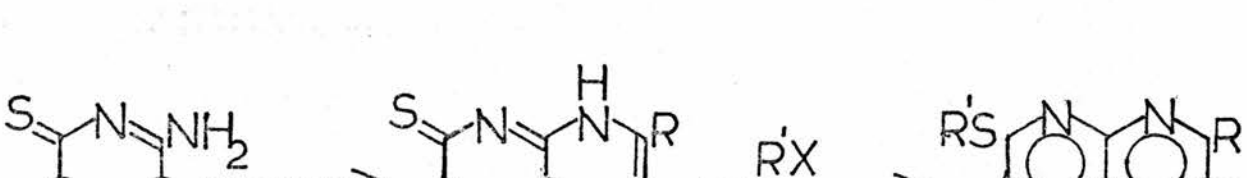
120 119 121



122 123 (a) X=S (b) X=O



124 125



127 128 126

129 130 131

	R^1	R^2	R^3	Ar
(a)	H	H	H	Ph
(b)	H	Me	Me	Ph
(c)	H	$-(CH_2)_3-$		Ph
(d)	Bu^t	H	H	Ph
(e)	H	Me	Me	$p\text{-}NO_2C_6H_4$
(f)	H	$-(CH_2)_3-$		$p\text{-}NO_2C_6H_4$

	R^1	R^2	R^3	Ar
(a)	H	H	H	Ph
(b)	H	Me	Me	Ph
(c)	H	$-(CH_2)_3-$		Ph

	R^1	R^2	R^3	Ar
(a)	H	H	H	Ph
(b)	H	Me	Me	Ph
(c)	H	$-(CH_2)_3-$		Ph
(d)	Bu^t	H	H	Ph
(e)	H	Me	Me	$p\text{-}NO_2$
(f)	H	$-(CH_2)_3-$		$p\text{-}NO_2$

(vii) 3,4-Diaza-1,6,6a-trithiapentalenes

3,4-Diaza-1,6,6a-trithiapentalenes (119) were obtained in low yield, from the reaction of N,N'-diaroylureas (120) with phosphorous pentasulphide. Improved yields were obtained by using N,N'-diaroyl-S-methylisothioureas (121)[106,107].

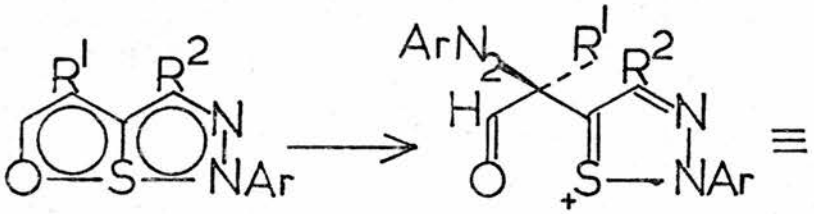
Arylisothiocyanates and arylisocyanates react with 3-arylamino-1,2,4-dithiazole-5-imines (122) to give the trans compounds (123a) and (123b) which are thought to be stabilised by hydrogen bonding. On heating compounds (123a) and (123b) rearrangement takes place to the cis isomers (124a) and (124b), which are better represented as the bicyclic structures (125a) and (125b)[55].

Wobig[108] has synthesised the 1-oxa-6,6a-dithia-3,4-diaza-pentalenes (126) from 5-amino-1,2,4-dithiazole-3-thione (127) by S-alkylating the acyl derivatives (128) in sodium ethoxide in ethanol.

(viii) 6a-Thia-1,2,6-triazapentalenes

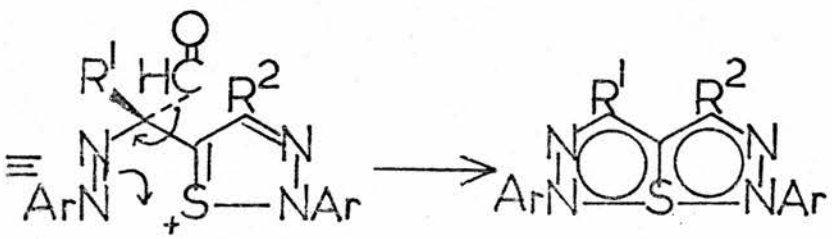
Methylation of 6,6a-dithia-1,2-diazapentalenes (129a-c) with methyl fluorosulphonate gave the thiadiazolium salts (130a-c) which reacted with methylamine to give the thiatriazapentalenes (131a-c)[41]. Small amounts of compounds (129a-c) were reformed in the second step due to a demethylation reaction. Compounds (131a-f) were also formed by the direct reaction of dithiadiazapentalenes (129a-f) with methylamine[41]. In part 2 of this thesis the synthesis of 6a-thia-1,2,6-triazapentalenes, with alkyl, phenyl and other substituents in the 6-position, will be discussed.

132

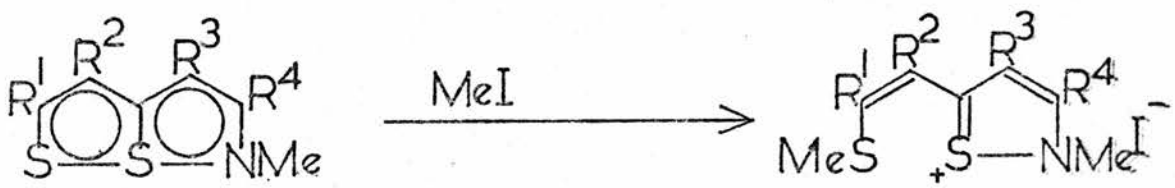


134 135a

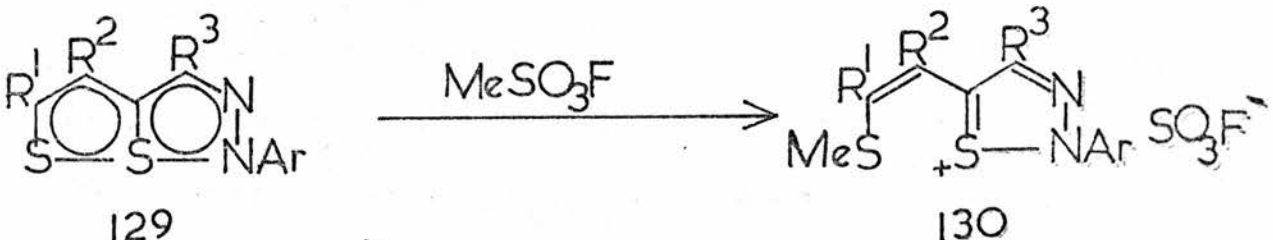
	R^1	R^2	Ar
(a)	Me	Me	Ph
(b)	$-(CH_2)_3-$		Ph
(c)	Me	Me	p-NO_2C
(d)	$-(CH_2)_3-$		p-NO_2C
(e)	Me	Me	p-MeOC
(f)	$-(CH_2)_3-$		p-MeOC



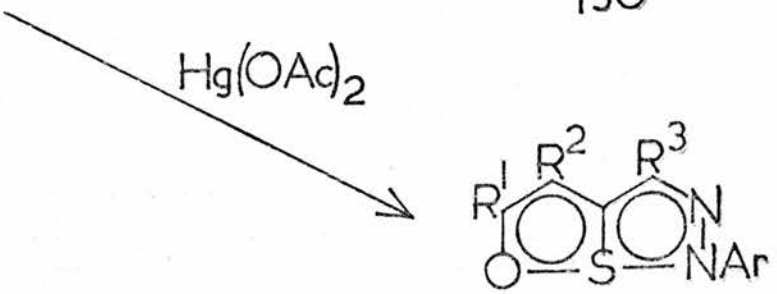
135b 133



60 102



129 130



134

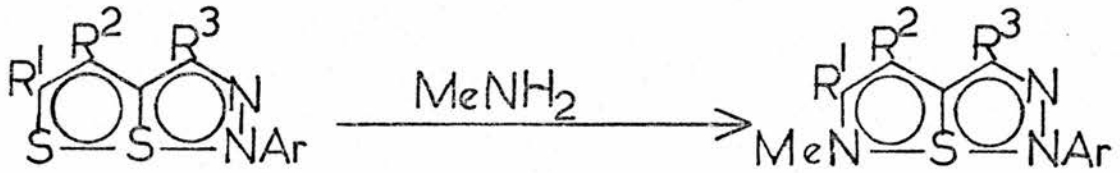
(ix) 6a-Thia-1, 2, 5, 6-tetraazapentalenes

The selenium analogue (132), the first example of this class of compound, was isolated from the reaction of the bis(2, 4-dinitrophenyl hydrazone) of pentane-2, 4-dione with selenium dioxide[102]. 6a-Thia-1, 2, 5, 6-tetraazapentalenes (133) have been synthesised from the reaction of 6-oxa-6a-thia-1, 2-diazapentalenes (134) with arenediazonium fluoroborates[41]. The required oxathiadiazapentalenes were prepared by reaction of the corresponding dithiadiazapentalenes with mercury(II) acetate[41]. Electrophilic attack by the diazonium salt is thought to take place at the 3-position, giving rise to intermediates (135a). Free rotation about the C(3a)-C(4) bond in intermediates (135a), with elimination of a formyl group from the resulting intermediates (135b), gave the thiatetraazapentalenes (133).

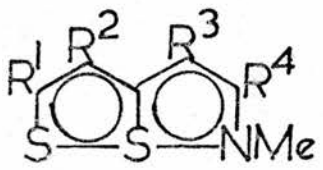
(b) Reactivity of Aza Analogues of 1, 6, 6a-Trithiapentalenes

(i) Thiocarbonyl Reactions

Although structural studies have shown that aza analogues of trithiapentalenes exist in the bicyclic form, they may undergo carbonyl reactions in a similar manner to trithiapentalenes. For example, compounds (60) and (129) undergo S-methylation by methyl iodide or methyl fluorosulphonate to give the corresponding salts (102) and (130), respectively[39,41]. Dithiadiazapentalenes (129) are desulphurised by mercury(II) acetate to give the corresponding oxathiadiazapentalenes[41] (134). This reaction is limited to dithiadiazapentalenes substituted in the 3- and 4-positions in order to

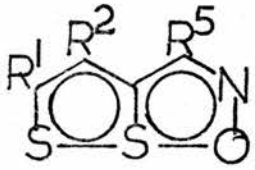


129 131



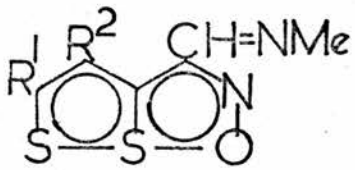
136

	R^1	R^2	R^3	R^4
(a)	Ph	H	H	H
(b)	Bu^t	H	H	H
(c)	Ph	H	Me	H



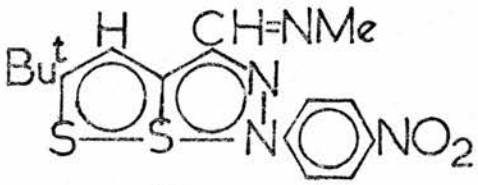
137

	R^1	R^2	R^5
(a)	Ph	H	CHO
(b)	Bu^t	H	CHO
(c)	Ph	H	Me

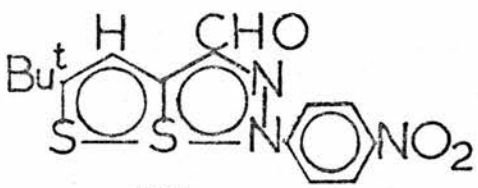


138

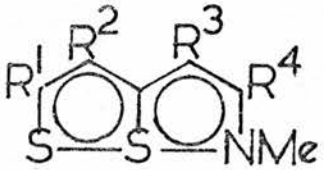
	R^1	R^2
(a)	Ph	H
(b)	Bu^t	H



140

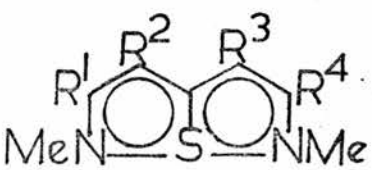


139



60

	R^1	R^2	R^3	R^4
(a)	Me	H	H	Me
(b)	Bu^t	H	H	H
(c)	H	Me	Me	H
(d)	H	$-(CH_2)_3-$		H
(f)	H	H	H	H



103

	R^1	R^2	R^3	R^4
(a)	H	H	H	H
(b)	H	Me	Me	H
(c)	H	$-(CH_2)_3-$		H
(d)	Me	H	H	Me

prevent electrophilic attack by mercury(II) acetate in these positions. The potential thiocarbonyl activity of dithiadiazapentalenes (129) is also demonstrated by their reaction with methylamine, resulting in thiatriazapentalenes (131)[41].

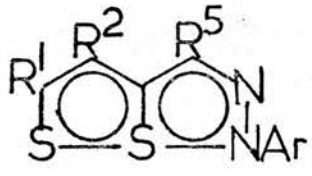
(ii) Electrophilic Substitution

The mechanism of electrophilic substitution of 1, 6, 6a-trithiapentalenes already discussed (see page 18) also applies to the electrophilic substitution of aza-analogues of trithiapentalenes. Nitrosation of dithiaazapentalenes (136) gave the oxadithiaazapentalenes (137)[95]. It is thought that electrophilic attack of compounds (136a) and (136b) at the 4-position, followed by a rearrangement, gave the imines (138a) and (138b). The imines were then acid hydrolysed to the corresponding aldehydes (137a) and (137b). The dithiaazapentalene (136c) gave the oxadithiaazapentalene (137c) by loss of an N-methyliminomethyl group. Similarly the reaction of dithiaazapentalene (136b) with p-nitrobenzenediazonium fluoroborate gave the dithiadiazapentalene (139)[96]. Electrophilic attack at the 4-position, followed by a rearrangement, gave the imine intermediate (140) which was hydrolysed to the corresponding aldehyde (139).

(iii) Trinitrobenzene Charge-Transfer Complexes

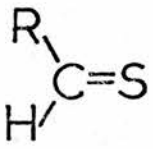
1, 6a-Dithia-6-azapentalenes form stable charge transfer complexes with 1, 3, 5-trinitrobenzene, indicating the electron rich character of this class of compound[47]. The stoicheiometry was found to be 1:1 for the complexes of compounds (60a), (60b) and (60f), whereas the 3,4-disubstituted dithiaazapentalenes (60c) and (60d)

gave the 2:1 and 3:2 complexes, respectively. 6a-Thia-1, 6-diaza-pentalenes (103a-d) also form stable 1:1 complexes with trinitro-benzene[39]. In part 2 of this thesis the trinitrobenzene complexes of 6a-thia-1, 2, 6-triazapentalenes will be discussed.

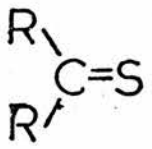


72

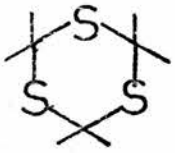
	R^1	R^2	R^5
(d)	H	H	CS_2Me
(e)	H	H	$CSNMe_2$
(j)	H	H	CHS



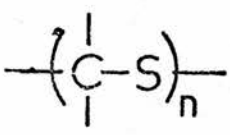
141



142

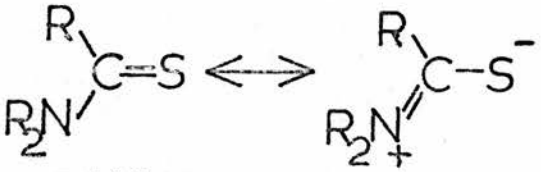


143

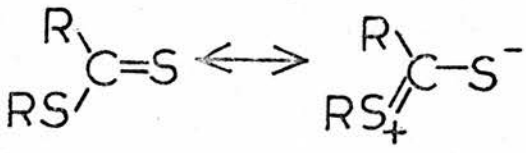


144

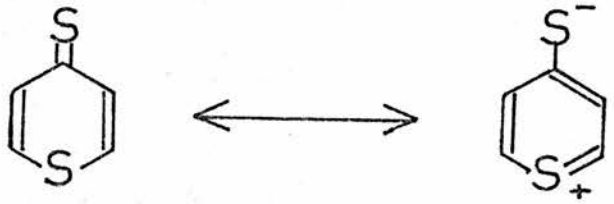
145



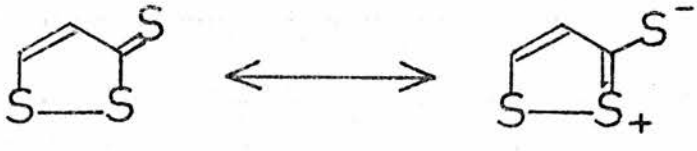
146a 146b



147a 147b



148a 148b

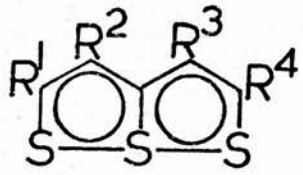


149a 149b

D. Thiocarbonyl Compounds and 1, 3, 5-Trithianes

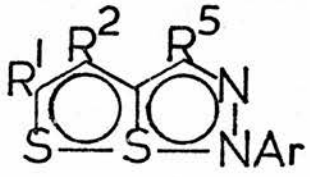
Various aspects of thiocarbonyl chemistry have been encountered in the preceding discussion of the chemistry of 1, 6, 6a-trithiapentalenes and analogous systems. For example trithiapentalenes and their aza-analogues undergo thiocarbonyl reactions (see pages 15 and 26). Also in certain cases the reactions of trithiapentalenes with electrophiles resulted in thiocarbonyl compounds (eg. compounds (72d), (72e) and (72j), see page 18). In part 2 of this thesis the protonation of heterocyclic thioaldehydes will be discussed along with the protonation of trithiapentalenes, as both classes of compound undergo C-protonation and S-protonation in trifluoroacetic acid solution. Thiocarbonyl compounds and their related systems are therefore briefly discussed here.

Thioaldehydes (141) and thioketones (142) are much less stable than their oxygen analogues and the carbon-sulphur double bond tends to open out to the carbon-sulphur single bond resulting in 1, 3, 5-trithianes (143) and other less well defined polymeric species (144). However the thiocarbonyl group is readily polarised in the sense of (145) and when thus polarised has enhanced stability. If the C=S bond is adjacent to a group which can delocalise the resulting positive charge on the thiocarbonyl carbon, then stable thiocarbonyl compounds will occur. For example, thioamides (146a)[109, 111] and dithioesters (147a)[112] are stable thiocarbonyl compounds. 4H-Thiopyran-4-thiones (148a) and 1, 2-dithiole-3-thiones (149a), which have already been encountered as starting compounds in the syntheses



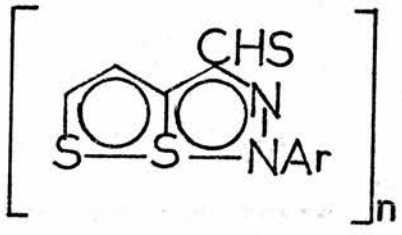
71

	R^1	R^2	R^3	R^4
(c)	H	H	H	H
(d)	MeS	H	H	H
(e)	Me_2N	H	H	H



72

	R^1	R^2	R^5
(d)	H	H	CS_2Me
(e)	H	H	$CSNMe_2$
(j)	H	H	CHS



73c

of trithiapentalenes and their aza-analogues (see pages 15 and 24), are also stable thiocarbonyl compounds. The stability of these compounds is no doubt due to a considerable contribution from structures (146b-149b) to the ground state of the molecules.

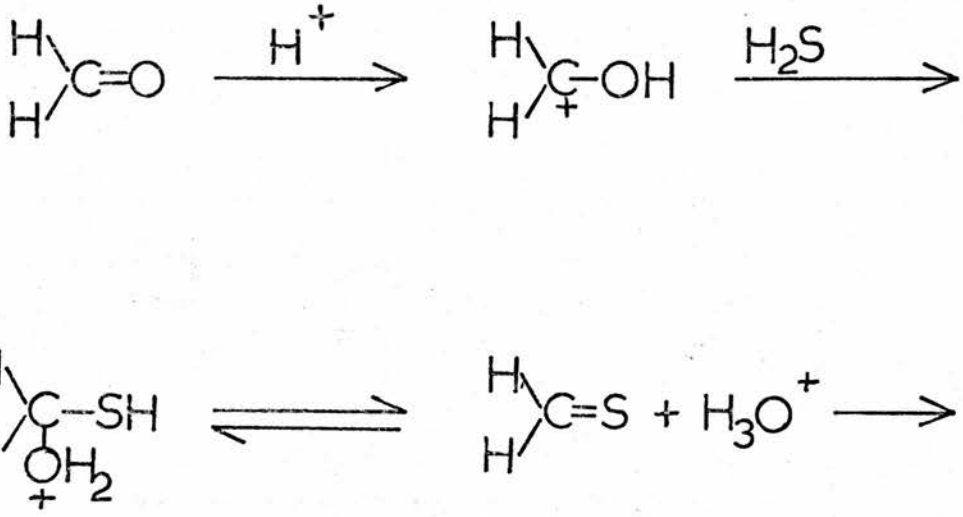
The reaction of trithiapentalenes (71c), (71d) and (71e) with arenediazonium fluoroborates resulted in the products (72j), (72d) and (72e), respectively. The dithioester derivative (72d) and the thioamide derivative (72e) were stable compounds whereas the thioaldehyde derivative (72j) was not isolated as it formed the polymer (73c). These reactions demonstrate the relative stabilities of dithioesters, thioamides and thioaldehydes.

Stable thioaldehydes have also been isolated where the thiocarbonyl group is conjugated with a heterocyclic base, with the positive charge on the thiocarbonyl carbon being delocalised throughout the heterocyclic system. Further discussion in this section will be restricted to stable heterocyclic thioaldehydes, and to 1, 3, 5-trithianes resulting from the attempted syntheses of simple alkyl and aryl thioaldehydes.

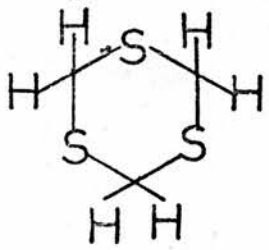
(a) 1, 3, 5-Trithianes

(i) Attempted Synthesis of Simple Thioaldehydes resulting in 1, 3, 5-Trithianes

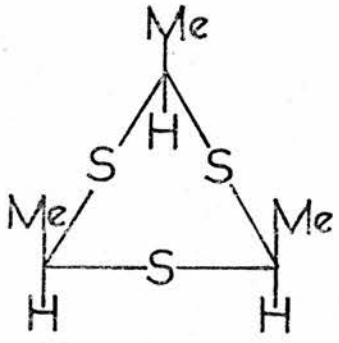
The first attempted synthesis of a thioaldehyde was carried out by Hofmann in 1868[113], by the reaction of formaldehyde with



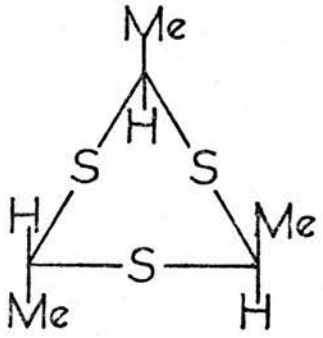
SCHEME 2



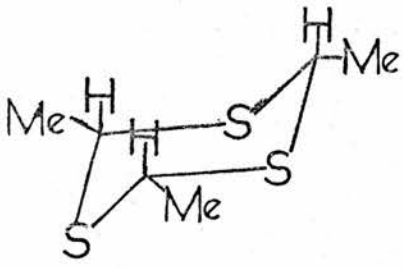
150



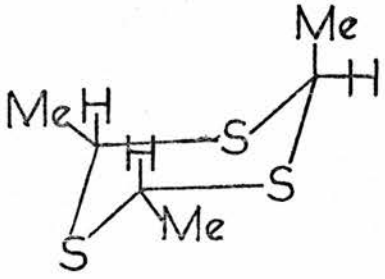
151a–cis



151b–trans



152a – β

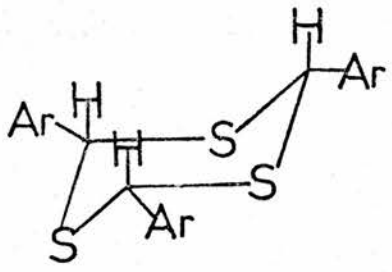


152b – α

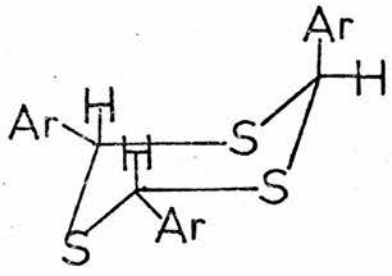
hydrogen sulphide in the presence of hydrogen chloride (scheme 2). The trimer (150) was isolated. Using this method, cyclic trimers have been obtained from acetaldehyde, benzaldehyde, and other aryl aldehydes.

(ii) Structure of 1, 3, 5-Trithianes

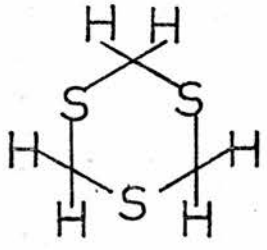
The structures of the products from the reaction of aldehydes with hydrogen sulphide, in the presence of hydrogen chloride, have aroused much interest. Klinger[114] first proposed the 1, 3, 5-trithiane structures (151a) and (151b) for the products obtained from acetaldehyde. Two products were isolated from the reaction mixture by repeated crystallisation, and as both were shown to have the same molecular formula $(CH_3CHS)_3$, they were assumed to be the cis (151a) and trans (151b) isomers. The higher melting compound (mp 126°C) was designated the β-isomer, and the lower melting compound was designated the α-isomer (mp 101°C). A third isomer, designated the γ-isomer was subsequently obtained[115], but was later shown to be a eutectic mixture of the α-isomer and the β-isomer[116]. On the basis of chemical evidence[117] the higher melting β-isomer was assigned the cis-structure (151a). An electron diffraction study[118] also identified the higher melting β-isomer as the cis-compound which was shown to exist in the puckered chair form (152a), with all the methyl groups in equatorial positions. The α-isomer was identified as the trans-compound, which was also shown to exist in the puckered chair form (152b), with two methyl groups in an equatorial position and one methyl group in an axial position. X-ray diffraction[119] and



153a-β



153b — α



150

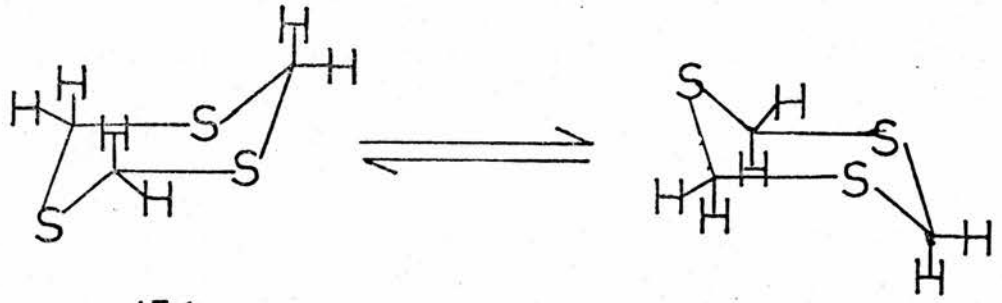
dipole moment studies[120, 121, 122] of 2, 4, 6-trimethyl-1, 3, 5-trithiane confirmed the puckered chair structures and the existence of α- and β-isomers.

2, 4, 6-Triaryl-1, 3, 5-trithianes were assumed to exist in the puckered chair form, with all the aryl groups in equatorial positions in the β-isomer (153a), and with two aryl groups in equatorial positions and one aryl group in an axial position in the α-isomer (153b), by analogy with 2, 4, 6-trimethyl-1, 3, 5-trithiane. 2, 4, 6-Triphenyl-1, 3, 5-trithiane was first isolated by Baumann and Fromm[123] who obtained three products, namely, the higher melting β-isomer (mp 226°C), the lower melting α-isomer (mp 85°C), and the so-called γ-isomer which was later shown to be a eutectic mixture of the α-isomer and the β-isomer[116]. Over forty different aromatic aldehydes have since been converted into 1, 3, 5-trithianes, with never more than two isomers being isolated[124, 125].

(iii) ^{1}H NMR Spectra of 1, 3, 5-Trithianes

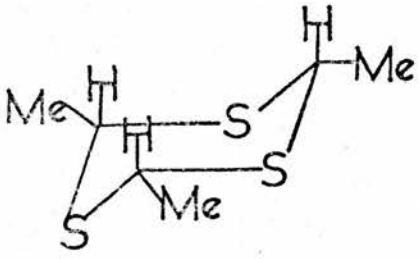
^{1}H nmr offers a convenient method for differentiating between the α- and β-isomers of 1, 3, 5-trithianes, as it has been shown[126] that axial and equatorial hydrogen atoms in a puckered six-membered ring resonate at different field strengths. Therefore 1, 3, 5-trithianes, with all the substituents in equatorial positions, should exhibit only one ring hydrogen peak, while 1, 3, 5-trithianes, with two substituents in equatorial positions and one substituent in the axial position, should exhibit two peaks for ring hydrogens in a 2:1 ratio.

The nmr spectrum of 1, 3, 5-trithiane (150) showed only one

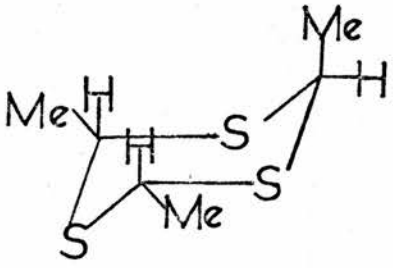


154a

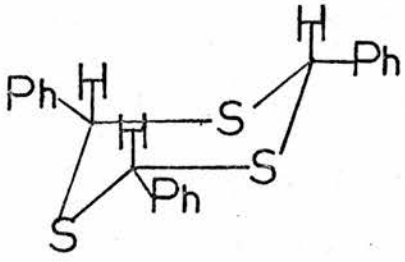
154b



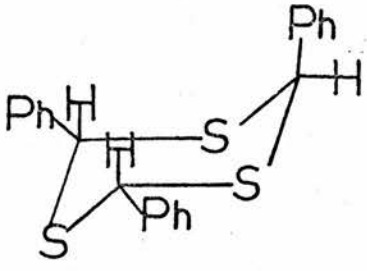
152a – β



152b – α



155a – β



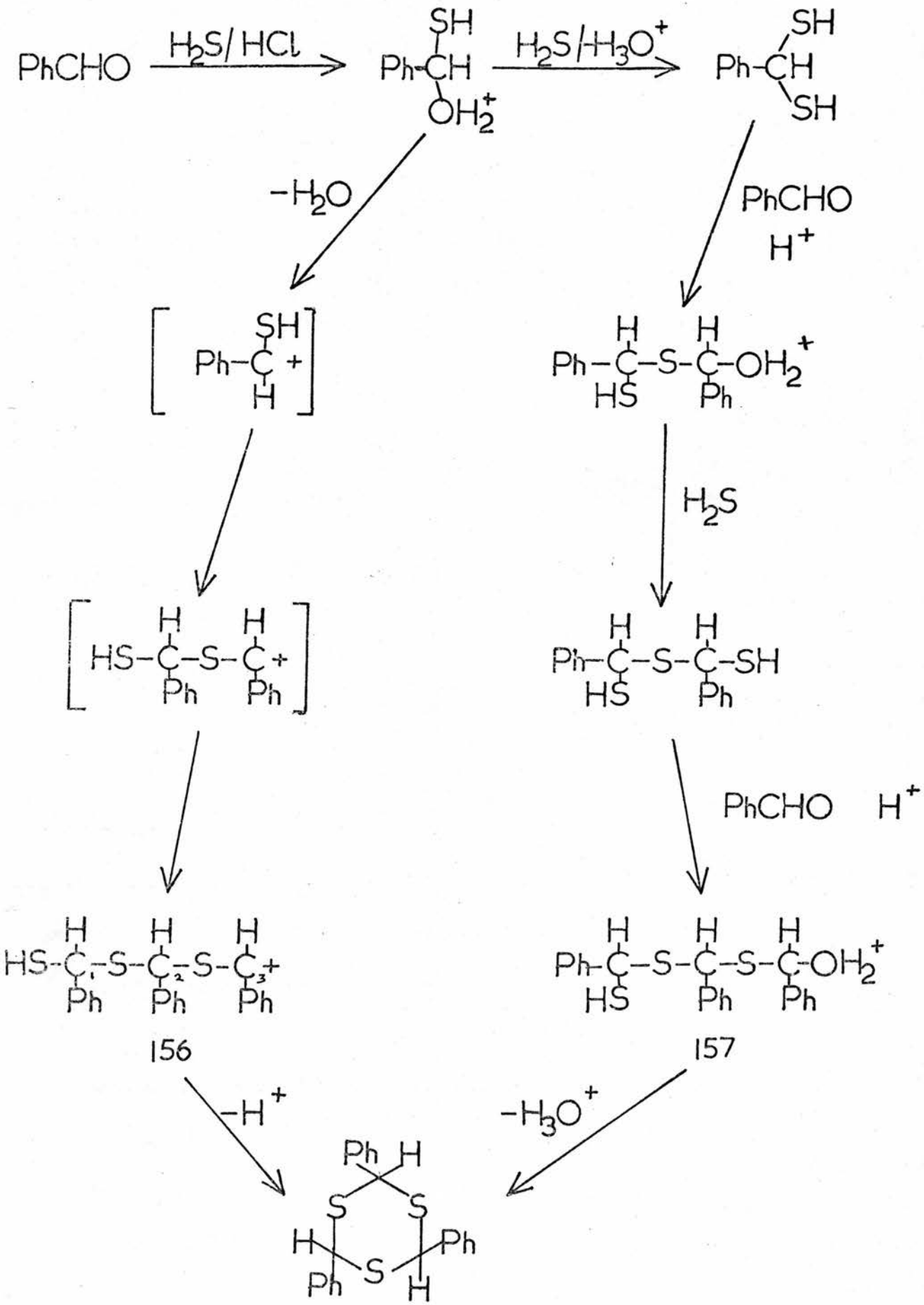
155b – α

peak indicating that all six ring protons were magnetically equivalent[127]. This was in contradiction to the results of dipole moment[120], X-ray diffraction[119] and electron diffraction[118] studies, all of which indicated that 1, 3, 5-trithiane existed in the puckered chair form. Campaigne[127] proposed two rapidly interchanging chair structures [(154a)⇌(154b)], in which each hydrogen atom of the trithiane ring interchanges rapidly between the axial and equatorial positions, with ^{1}H nmr detecting the average of the two structures.

The nmr spectra of 2, 4, 6-triphenyl-1, 3, 5-trithiane (155) and 2, 4, 6-trimethyl-1, 3, 5-trithiane (152) were also described in the same paper[127]. The α-isomers of compounds (155) and (152) showed two signals in a 2:1 ratio for the trithiane ring protons. This confirmed that the α-isomers were in fact structures (155b) and (152b), with two substituents in the equatorial positions and one substituent in an axial position. The β-isomers showed only one signal for the trithiane ring protons confirming that the β-isomers possessed the structures (155a) and (152a), with all the substituents in equatorial positions.

Although the technique of repeated crystallisation was successfully applied in isolating samples of α- and β-isomers from a crude reaction mixture, the relative amounts of the two isomers formed could not be estimated. However nmr spectroscopy has provided a useful guide to the relative amounts of the α- and β-isomers present in a reaction mixture. Campaigne and coworkers[128, 129]

SCHEME 3



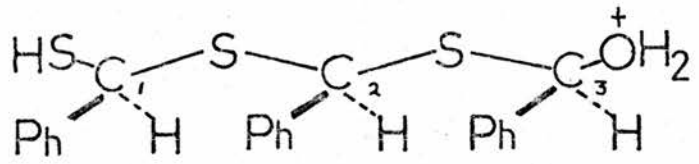
have studied a number of 2,4,6-tris(halophenyl)-1,3,5-trithianes and contrary to a previous claim[125], found that the α-isomer is always formed to a greater extent than the β-isomer.

Data on 2,4,6-triaryl-1,3,5-trithianes[127,128,129] shows that the ring proton signals occur in the region δ5.1-6.3, with equatorial protons being more deshielded than axial protons, and with the α-axial protons being more deshielded than the β-axial protons. In part 2 of this thesis the C-protonation products of heterocyclic thioaldehydes will be assigned 1,3,5-trithiane structures on the basis of nmr evidence.

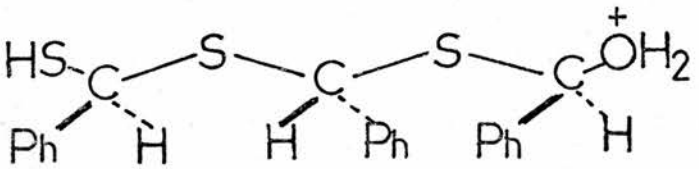
(iv) Mechanism of Formation of 1,3,5-Trithianes

Although the β-isomer of 1,3,5-trithianes is thermodynamically more stable with all the substituents in the less hindered equatorial posititions, the sterically more hindered α-isomer generally predominates and Campaigne[128] has proposed a mechanism (scheme 3) to account for this fact. It is thought that the formation of the trithiane ring is most likely to take place after linear intermediates (156) or (157) have been formed, as it is unlikely that three molecules would collide simultaneously to give a trimer.

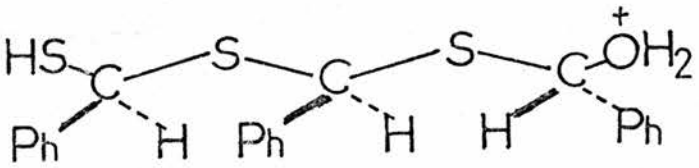
Two alternate pathways are given for trimerisation. If the reaction takes place via intermediate (156) then at the moment of ring closure the substituents at C(1) and C(2) may either be in a cis or trans conformation. At the moment of ring-closure the C(3) phenyl substituents may either be in an equatorial or axial position and so if C(1) and C(2) are in the cis conformation either the α- or



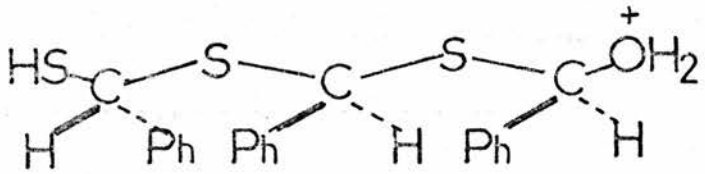
157a cis-cis



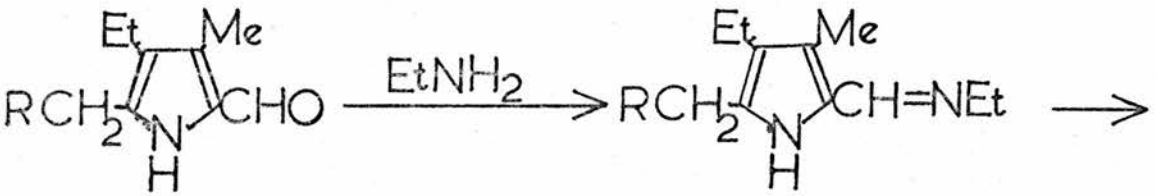
157b trans-trans



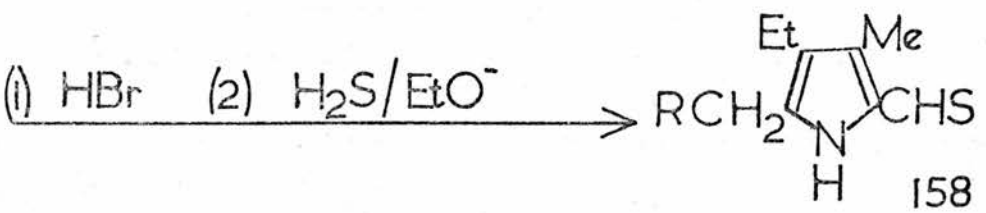
157c cis-trans



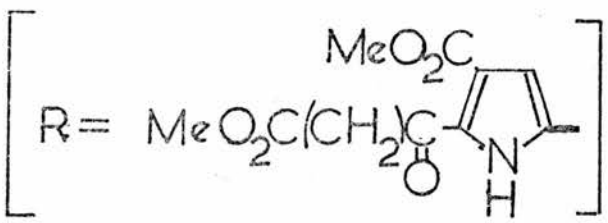
157d trans-cis

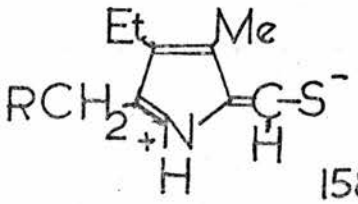


SCHEME 4



158





158a

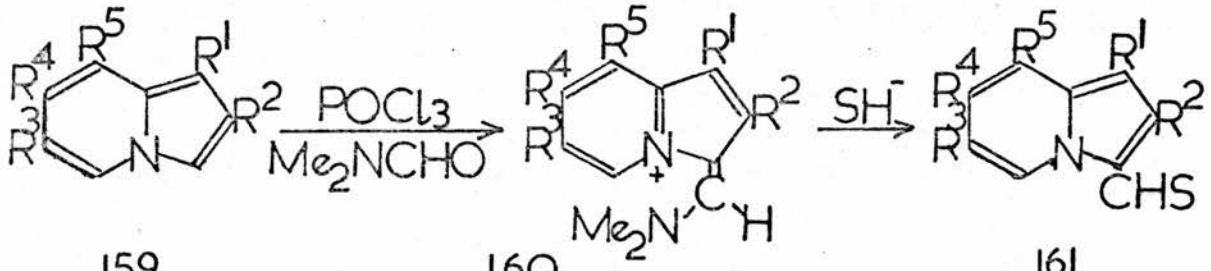
the β-isomer may be formed depending on the conformation of C(3). If C(1) and C(2) are in the trans conformation then ring-closure may only take place with the C(3) phenyl group entering the ring in an equatorial position giving only the α-isomer. As it is equally probable that the substituents on C(1) and C(2) are either in the cis or trans conformation it follows that the α-isomer will be the major product by this mechanism.

Alternatively ring-closure may take place via intermediate (157) which may have the conformations (157a-d). Ring closure of conformation (157a) leads to the α-isomer, since inversion at C(3) gives the cis-trans configuration to the ring. Conformation (157b) likewise forms the α-isomer, since inversion at C(3) gives the trans-cis configuration. Conformation (157c) will therefore yield the β-isomer (cis-cis) while conformation (157d) must again form the α-isomer (trans-cis). Thus three of the four possible linear intermediates will form the α-isomer on ring closure, and therefore the α-isomer will also be the major isomer by this mechanism.

(b) Stable Heterocyclic Thioaldehydes

(i) Synthesis of Stable Heterocyclic Thioaldehydes

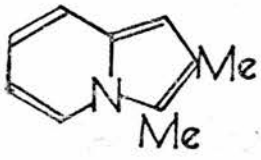
The first authentic stable thioaldehyde to be reported was the dipyrrylmethane (158), a key intermediate in Woodward's synthesis of chlorophyll-a[130]. Compound (158) was prepared from the corresponding aldehyde (scheme 4) and its stability is no doubt due to the polarised form (158a).



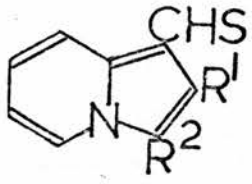
159 160 161

160

	R^1	R^2	R^3	R^4	R^5
(a)	H	H	H	H	H
(b)	H	Me	H	H	H
(c)	H	Bu^t	H	H	H
(d)	Me	Me	H	H	H
(e)	H	Me	Me	H	H
(f)	H	Me	H	Me	H
(g)	H	Me	H	H	Me

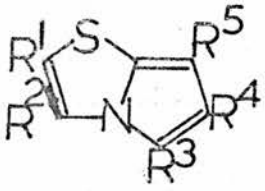


162



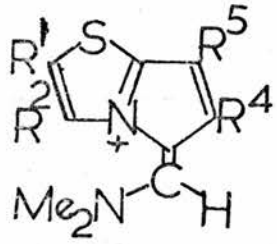
163

	R^1	R^2
(a)	Me	Me
(b)	Bu^t	H



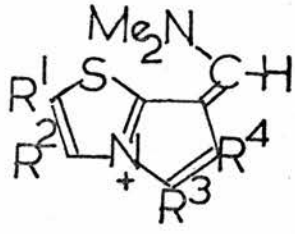
164

	R^1	R^2	R^3	R^4	R^5
(a)	H	H	H	Me	H
(b)	Me	H	H	Me	H
(c)	H	H	H	Me	Me
(d)	H	Me	H	Bu^t	H
(e)	H	Me	H	Me	H
(f)	Me	Me	H	Me	H
(g)	H	H	Me	Me	H
(h)	H	Me	Me	Me	H
(i)	Me	Me	Me	Me	H



165

	R^1	R^2	R^4	R^5
(a)	H	H	Me	H
(b)	Me	H	Me	H
(c)	H	H	Me	Me
(d)	H	Me	Bu^t	H
(e)	H	Me	Me	H
(f)	Me	Me	Me	H

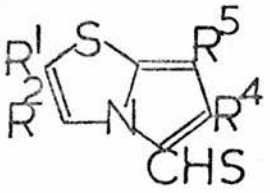


166

	R^1	R^2	R^3	R^4
(a)	H	Me	H	Bu^t
(b)	H	Me	H	Me
(c)	H	H	Me	Me
(d)	H	Me	Me	Me
(e)	Me	Me	Me	Me

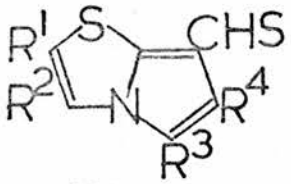
Reid and coworkers have adapted the Vilsmeier reaction to prepare stable thioaldehydes from indolizines[45] and pyrrolo[2,1-b]-thiazoles[46]. Indolizines undergo electrophilic substitution preferentially at the 3-position and treatment of compounds (159a-g) in dimethylformamide with phosphoryl chloride gave the corresponding Vilsmeier salts (160a-g), which when solvolysed with aqueous sodium hydrogen sulphide gave the thioaldehydes (161a-g) in good yield. The indolizine (162), which is blocked in the 3-position, gave the 1-thioaldehyde (163a), while indolizine (159c) gave an appreciable amount of the 1-thioaldehyde (163b) in addition to the major product (161c).

Pyrrolo[2,1-b]thiazoles undergo electrophilic substitution preferentially at the 5-position or, if it is blocked, at the 7-position[131]. Treatment of pyrrolo[2,1-b]thiazoles (164a-i) in dimethylformamide with phosphoryl chloride gave the corresponding Vilsmeier salts (165) and (166) which were converted to the corresponding thioaldehydes (167) and (168), in good yield, by the reaction with sodium hydrogen sulphide. Compounds (164a-c) and (164f) gave only the 5-thioformyl products (167a-c) and (167f), while compounds (164d) and (164e) reacted at both the 5- and 7-positions to give the minor products (168a) and (168b) resulting from attack at the 7-position, in addition to the major products (167d) and (167e). Pyrrolo[2,1-b]thiazoles (164g-i), which were blocked in the 5-position, gave only the 7-thioaldehydes (168c-e). In addition deuterated thioaldehydes (169a) and (169b) were prepared by replacing dimethylformamide with



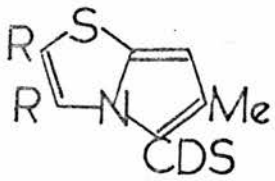
167

	R^1	R^2	R^4	R^5
(a)	H	H	Me	H
(b)	Me	H	Me	H
(c)	H	H	Me	Me
(d)	H	Me	Bu^t	H
(e)	H	Me	Me	H
(f)	Me	Me	Me	H



168

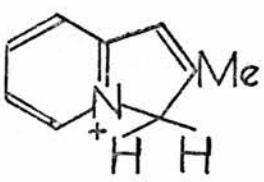
	R^1	R^2	R^3	R^4
(a)	H	Me	H	Bu^t
(b)	H	Me	H	Me
(c)	H	H	Me	Me
(d)	H	Me	Me	Me
(e)	Me	Me	Me	Me



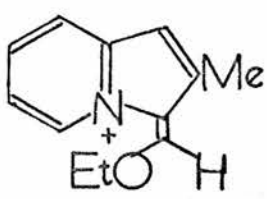
169

(a) R=H

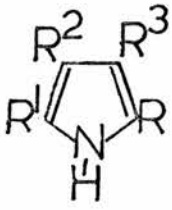
(b) R=Me



170

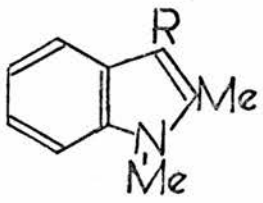


171



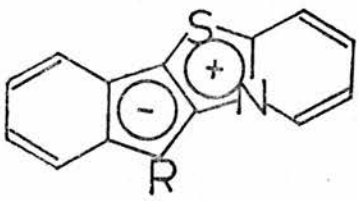
172 (a) R=CHS

(b) R=H



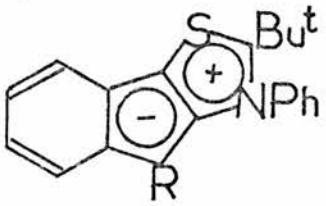
173 (a) R=CHS

(b) R=H



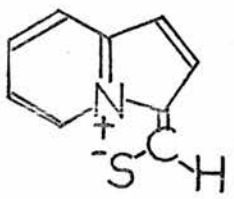
174 (a) R=CHS

(b) R=H

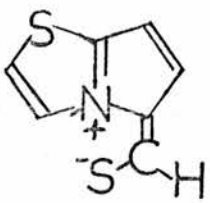


175 (a) R=CHS

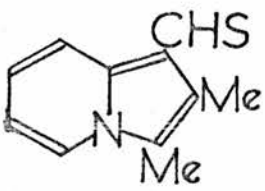
(b) R=H



176



177



163a

[$^{2}H_{7}$]dimethylformamide in 1, 2-dichloroethane, in the Vilsmeier synthesis.

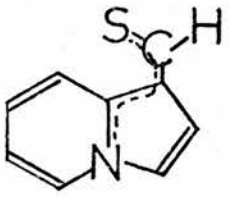
Two further routes to thioformylindolizines have been investigated[45]. The first involved thionation of the corresponding aldehydes with phosphorous pentasulphide. The thioformylindolizines were obtained in low yield by this method. The second route involved the condensation of 3H-indolizinium perchlorates[132] (170) with triethyl orthoformate and treatment of the resulting 3-ethoxymethylene-3H-indolizinium perchlorates (171) with sodium hydrogen sulphide. The thioformyl indolizines were also obtained in low yield by this method.

Thioaldehydes (172a-175a)[91, 133] were also prepared from the corresponding bases (172b-175b) by a similar application of the Vilsmeier reaction. The stability of compounds (172a-175a) is no doubt due to the conjugation of the thioformyl groups with the heterocyclic systems.

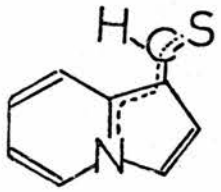
(ii) ^{1}H NMR Spectra and Geometry of Indolizine and Pyrrolo[2,1-b]-thiazole Thioaldehydes

The stability of indolizine and pyrrolo[2,1-b]thiazole thioaldehydes undoubtedly arises from a considerable contribution of the polarised forms (176) and (177) to the ground state of the molecules. This polarisation also sets up a barrier to free rotation about the CHS-ring bond which may be detected by ^{1}H nmr spectroscopy.

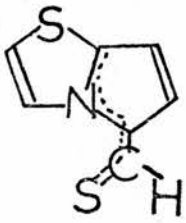
Restricted rotation about the CHS-ring bond was detected in compound (163a)[45]. At low temperatures ($< 0^{o}C$) the 8-H signal



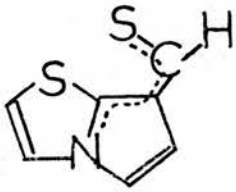
178-syn



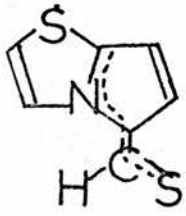
179-anti



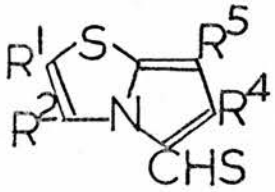
180-syn



181-syn

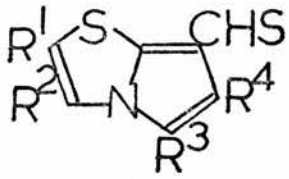


182-anti



167

	R^1	R^2	R^4	R^5
(a)	H	H	Me	H
(b)	Me	H	Me	H
(c)	H	H	Me	Me
(d)	H	Me	Bu^t	H
(e)	H	Me	Me	H
(f)	Me	Me	Me	H



168

	R^1	R^2	R^3	R^4
(a)	H	Me	H	Bu^t
(b)	H	Me	H	Me
(c)	H	H	Me	Me
(d)	H	Me	Me	Me
(e)	Me	Me	Me	Me

consisted of a doublet which collapsed to a broad singlet (coalescence temperature 22 ± 3°C) and subsequently reappeared (< 40°C). The thioformyl proton signal remained a singlet and broadened in the temperature range over which the 8-H signal was broad. The large deshielding of the 8-H signal and the occurrence of the thioformyl proton signal as a singlet indicated that compound (163a) existed exclusively in the syn-form (178), below the coalescence temperature. It was thought that the syn-structure (178) was more stable than the anti-structure (179) due to an electrostatic attraction between the fractional charges on the sulphur atom and the pyridine ring.

Restricted rotation about the CHS-ring bond was also detected in pyrrolo[2,1-b]thiazole thioaldehydes (167a-c)[46], by using the change in shape of the 3-H and CHS signals with temperature as a probe. ^{1}H nmr spectral data also indicated that compounds (167a-d) and compounds (168a-e) existed in the syn-configurations (180) and (181) respectively. Compounds (167e) and (167f) were shown to exist in the anti-configuration (182).

It was suggested that the greater stability of the syn-structures (180) and (181) was due to the electrostatic attraction between the fractional charges on the thioformyl sulphur atom and on the thiazole ring. In the exceptional cases of compounds (167e) and (167f) the preference for the anti-structure (182) was attributed to the steric effect of the 3-methyl substituent which directed the thioformyl sulphur atom away from the thiazole ring. In the case of compound (167d) the bulky t-butyl group adjacent to the thioformyl group caused a steric effect greater than that of the 3-methyl group, and caused the thioformyl group to revert to the syn-configuration (180).

E. Lubricating Oil Additives

Part of the work embodied in this thesis involves the synthesis of aza analogues of 1, 6, 6a-trithiapentalenes for testing as potential antioxidants in lubricating oil additives. This section therefore gives a brief background to the field of lubricating oil additives, and in particular to the use of 1, 6, 6a-trithiapentalenes and analogous systems.

Lubricating oil additives are chemicals added as minor components to lubricating oils to enhance desirable properties, modify undesirable properties or to provide completely new properties. Over the last 25 years their use has become widespread, the growth being mainly due to their increasing use in oils for the internal combustion engine. The benefits in terms of performance of the internal combustion engine have been so large that few lubricating oils used today are devoid of additives. The main functions of additives can be summarised as follows:-

(a) To reduce engine deposits and sludge -detergents, antioxidants and dispersants.

(b) To reduce corrosive wear - basic detergents and antioxidants.

(c) To reduce mechanical wear - antiwear and extreme pressure agents.

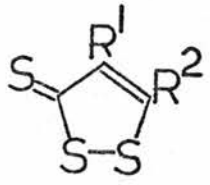
(d) To modify oil properties - viscosity index improvers and pour point depressants.

Additives listed under (a) and (b) are used to combat adverse engine conditions arising from chemical change. For example,

antioxidants help to control oxidative attack on the oil and dispersants keep insoluble products suspended in the oil, thus preventing deposits occurring on critical parts of the engine. Additives listed under (c) are used to help reduce mechanical wear on heavily loaded parts of the enginge and those under (d) help to modify physical properties of the oil such as variation of viscosity with temperature. It should be noted that many additives used today fulfil simultaneously more than one of the functions mentioned. Subsequent discussion will be limited to antioxidants.

(a) Antioxidants

During its circulation around the engine the oil is subject to severe oxidative attack giving rise to a number of products which have an adverse effect on engine condition and lubricating oil performance. The final products of oxidation include acids which corrode metal parts of the engine, and polymers which deposit on metal surfaces. Therefore, good stability of an oil towards oxidative attack is of vital importance and is generally achieved by the use of antioxidant additives. The oxidation of a mineral oil is a free radical chain reaction[134] and if the chain sequence can be stopped by a chain inhibitor, then the rate of oxidation should be reduced considerably. The primary product of the chain reaction is a peroxide which decomposes rapidly at elevated temperatures giving initiators which catalyse the chain reaction, and so the use of peroxide decomposers should also reduce the rate of oxidation. In theory it should be



183

	R^1	R^2
(a)	H	Ar
(b)	alkyl	alkyl

possible to stop oxidation by either the use of a chain inhibitor or a peroxide decomposer, but in practice a combination of a chain inhibitor and a peroxide decomposer is most effective. Oxidation cannot be prevented indefinitely by antioxidants, as the antioxidants themselves are slowly destroyed. The most important types of oxidation inhibitors can be classified into four broad chemical groups, namely:

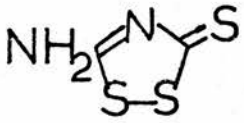
(i) Phenols
(ii) Aromatic amines — Chain inhibitors

(iii) Phosphasulphurised terpenes
(iv) Zinc dialkyldithiophosphates — Peroxide destroyers

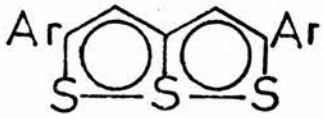
An important function of antioxidants is to prevent the formation of acidic and peroxidic products of oxidation which help corrode sensitive bearings. The use of basic additives will clearly neutralise acidic products of oxidation.

(b) Use of Sulphur-Containing Heterocyclic Systems as Antioxidants

Due to increasing concern regarding environmental considerations, attention is now turning from additives containing phosphorous and metals to organic structures based on sulphur, nitrogen and oxygen. The use of 1,2-dithiole structures as lubricating oil additives is well known in the patent literature.[135,136] For example, early patents claimed aryl derivatives of 1,2-dithiole-3-thiones (183a), prepared by the action of sulphur on olefins, as lubricating oil additives. Alkyl 1,2-dithiole-3-thiones (183b) have been claimed as antioxidants[137]



184



185

186

and in addition much interest has centred on derivatives of the related ring system (184), with a 5-amino substituent. The reaction products of compound (184) with mercaptans, aldehydes[138], isocyanates and isothiocyanates[139] have been claimed as antioxidants and the acyl derivative has also been claimed as a peroxide decomposer[140].

Interest has also been shown in 1, 6, 6a-trithiapentalenes and analogous systems as potential lubricating oil additives. 2, 5-Diaryl-1, 6, 6a-trithiapentalenes (185), prepared from the reaction of phosphorous pentasulphide and 1, 3, 5-triketones, have been claimed as antioxidant lubricating oil additives[141] and more recently the aza analogues (186) have been claimed, also as antioxidants[142].

The interest of compounds of the type (183) and (184) as lubricating oil additives is relevant to this thesis as trithiapentalene analogues can readily be prepared from these systems. As interest has also been shown in 1, 6, 6a-trithiapentalene type systems as antioxidants further examples of aza analogues of trithiapentalenes were synthesised from 1, 2-dithiole-thiones, for testing as potential lubricating oil additives, and this work will be discussed in Part 2 of this thesis.

PART TWO

DISCUSSION OF THE RESULTS OBTAINED

A. Synthesis of 6a-Thia-1,2,6-triazapentalenes and Related Compounds from 6-Oxa-6a-thia-1,2-diazapentalenes

6a-Thia-1,2,6-triazapentalenes (1) have previously been prepared from 6,6a-dithia-1,2-diazapentalenes (2) by two different routes. The first method involved the methylation of the dithiadiazapentalenes (2) with methyl fluorosulphonate. The resulting salts (3), on reaction with methylamine, gave the thiatriazapentalenes (1)[41]. The second method gave the thiatriazapentalenes (1) by direct reaction of the dithiadiazapentalenes (2) with methylamine. These two methods give only the 6-methyl thiatriazapentalenes and we have therefore developed a more versatile synthesis of thiatriazapentalenes (1) from 6-oxa-6a-thia-1,2-diazapentalenes (4a) and (4b). The required compounds (4a) and (4b) were prepared from the corresponding dithiadiazapentalenes (2a) and (2b) by a method recently developed in this laboratory[41].

(a) Mechanism of Formation of 6a-Thia-1,2,6-triazapentalenes from 6-Oxa-6a-thia-1,2-diazapentalenes

Treatment of the oxathiadiazapentalenes (4a) and (4b), in dimethylformamide, with phosphoryl chloride gave the intermediates (5a) and (5b), which on reaction with amines or hydrazines gave the 6a-thia-1,2,6-triazapentalenes (1). The chlorovinyl intermediates (5a) and (5b) separated from the reaction solution, as red oils, on the addition of ether and were not characterised. However, treatment of these oils, in acetic acid solution, with perchloric acid gave the

corresponding perchlorate salts (6a) and (6b), which were isolated as crystalline solids and characterised.

Phosphoryl chloride, on being added to the solution of the oxathiadiazapentalenes (4) in dimethylformamide, may react either with the substrates (4) directly or with dimethylformamide, and the resulting Vilsmeier adduct (7) would then attack the substrates (4). The latter possibility is thought to be the most likely one, although the former cannot be completely ruled out. Reaction of the oxathiadiazapentalenes (4a) and (4b) with phosphoryl chloride or with the Vilsmeier adduct (7) gave the same intermediates (5a) and (5b), which were formed by the reaction routes (4) ⟶ (8) ⟶ (5) or (4) ⟶ (9) ⟶ (5), respectively. However, if dimethylformamide is replaced by an inert solvent, such as 1,2-dichloroethane, then only the reaction route (4) ⟶ (8) ⟶ (5) is possible. The feasibility of this route was demonstrated by preparing the perchlorate salts (6a) and (6b) from compounds (4a) and (4b) in 1,2-dichloroethane.

The correct geometry of the perchlorate salts (6a) and (6b) could not be deduced from their nmr spectra. Attack on the cations (8) and (9) by chloride ion results in intermediates possessing tetrahedral 2'-carbon atoms. Free rotation about the C(2')-C(1') bond is possible in these intermediates and subsequent elimination of a $PO_2Cl_2^-$ group or a $(CH_3)_2\dot{N}CHO$ group may result in either the E- or the Z-isomers of the intermediates (5) being formed. The nmr spectrum of compound (6a) showed signals due to the major isomer and relatively weak signals due to the presence of a trace of a minor isomer. The coupling between the 1'-Me group and 2'-H

proton (J=1.6 Hz) was identical for both isomers; hence E- and Z-structures could not be assigned. The nmr spectrum of compound (6b) showed signals due to one isomer only. The chlorovinyl compounds (5) and (6) are represented here and henceforth as the Z-isomers for convenience only.

The intermediates (5a) and (5b) may react with compounds containing primary amino groups (eg. amines and hydrazines) to give thiatriazapentalenes (1). Attack takes place at the 2'-position of the chlorovinyl intermediates (5), with displacement of the chloride ion. The reaction route (5)$\longrightarrow$ (10)$\longrightarrow$ (11) $\longrightarrow$ (1) is proposed. The chlorovinyl intermediates (5) may also react similarly with other nucleophiles (eg. $S^{=}$, $Se^{=}$ and SH^{-}).

(b) Synthesis of 1,6-Diaryl-6a-thia-1,2,6-triazapentalenes

The reaction of the oxathiadiazapentalenes (4a) and (4b), in dimethylformamide, with phosphoryl chloride, and treatment of the resulting intermediates (5) with anililine or p-anisidine gave the thiatriazapentalenes (1a-d) in excellent yields. Small amounts of the starting materials (4a) and (4b) were isolated along with the major products (1a-d). As aniline and p-anisidine are relatively weak nucleophiles it is thought that they do not react completely with the chlorovinyl intermediates (5a) and (5b). During the work-up procedure water is added to the reaction mixture and any unreacted chlorovinyl intermediate (5) present at that stage will react with water, to give the oxathiadiazapentalenes (4). It is thought unlikely that the

small amounts of starting material (4) recovered result from incomplete reaction of the oxathiadiazapentalenes (4) with the Vilsmeier adduct (7).

Prolonged reaction of the intermediates (5a) and (5b) with the less nucleophilic p-nitroaniline was required, and resulted in formation of the thiatriazapentalenes (1e) and (1f) in yields of 72% and 86% respectively. The oxathiadiazapentalenes (4a) and (4b) were also isolated in yields of 17% and 11%, respectively, and were probably formed by the same mechanism as described for the formation of compounds (4a) and (4b) isolated along with major products (1a-d).

The reaction of o-phenylene diamine with intermediates (5a) and (5b) gave the thiatriazapentalenes (1g) and (1h) and, in each case, two other products. Compounds (1g) and (1h), which possessed a primary amino group, also reacted with the intermediates (5) and gave the bis-(thiatriazapentalenes) (12a) and (12b). Also, the primary amino groups of compounds (1g) and (1h) condensed with the Vilsmeier adduct (7) to form the imines (13a) and (13b). A trace of compound (13b) was isolated and only its mass spectrum was recorded. The molecular ion peak (m/e = 389) was consistent with the imine structure (13b), which was assumed to be correct by analogy with that of the fully characterised compound (13a).

The nmr spectra of thiatriazapentalenes (1a-h), (12a-b) and (13a) (in $CDCl_3$) showed that the chemical shifts of the 5-H protons occurred in the region δ7.90-8.42. (The nmr spectra of compounds (1e) and (1f) were not obtainable owing to the insufficient solubility

of these compounds in all available solvents.) These chemical shift values indicate that the 5-H protons are considerably deshielded, presumably due to the presence of a ring-current arising from a delocalised 10 π-electron system. The chemical shifts of the 5-H protons of the corresponding 3,4-disubstituted dithiaazapentalenes (14a) and (14b) and thiadiazapentalenes (15a) and (15b) are, respectively, δ7.67, 7.75, 7.48 and 7.67. These values suggest that the thiatriazapentalenes discussed here possess a greater ring-current than do the corresponding dithiaazapentalenes and thiadiazapentalenes.

The thiatriazapentalenes (1a-d) formed stable charge transfer complexes (16a-d) with 1,3,5-trinitrobenzene. The formation of these complexes indicates that the thiatriazapentalenes (1a-d) are electron rich and that they may behave as π-electron donors. 1,6a-Dithia-6-azapentalenes[47] and 6a-thia-1,6-diazapentalenes[39] also form charge-transfer complexes with 1,3,5-trinitrobenzene. The 3:2 stoicheiometry of complex (16a) and the 1:1 stoicheiometry of complexes (16b-d) was deduced from their nmr spectra and elemental (C,H and N) analyses. Complexes (16c-d) were prepared by adding boiling solutions of trinitriobenzene in ethanol to boiling solutions of the bases (1c) and (1d) in ethanol. The complexes separated from solution on cooling and were filtered. The same procedure was used for the bases (1a) and (1b) but on filtering the cold reaction solution only the uncomplexed bases were recovered. Evaporation of the filtrates gave complexes (16a) and (16b) in low yield.

The electronic spectra of the thiatriazapentalenes (1a-h), (12a-b) and (13a) showed strong absorption in the visible region in the

range 475-530 nm, which is responsible for the red colour of these compounds. The spectra of compounds (1a-d), (1g-h), (12a-b) and (13) also show strong absorption in the ultraviolet region in the ranges 202-210 nm, 220-253 nm and 288-295 nm. The 6-p-nitrophenyl derivatives (1e) and (1f) both showed strong absorption in the ultraviolet region at 203, 284 and 361 nm.

(c) Synthesis of 1-Aryl-6-alkyl-6a-thia-1, 2, 6-triazapentalenes

Reaction of the oxathiadiazapentalenes (4), in dimethylformamide, with phosphoryl chloride, and treatment of the resulting chlorovinyl intermediates (5) with aqueous methylamine gave the thiatriaza-pentalenes (1i) and (1j) in yields of 23% and 44%, respectively. Compound (1i) was isolated along with small amounts of the corresponding dithiadiazapentalene (2a) and the corresponding oxathiadiazapentalene (4a), and compound (1j) was isolated along with a small amount of the dithiadiazapentalene (2b).

It is thought that these minor products arise from a competing reaction of the chlorovinyl intermediates (5a) and (5b) with hydroxide ions. The hydroxide ions may attack the 2'-position of the chlorovinyl intermediates (5) with displacement of a chloride ion, and this reaction accounts for the isolation of the minor product (4a) along with the major product (1i). It is also thought that the hydroxide ions may degrade the thiadiazolium rings of intermediates (5), generating sulphide ions in the process. These sulphide ions may then attack the 2'-position of the intermediates (5), and this process

results in the minor products (2a) and (2b). To determine whether the mechanism proposed here to account for the formation of the minor products (4a), (2a) and (2b) is in fact feasible, the reactions of the chlorovinyl intermediates (5a) and (5b) with sodium hydroxide and sodium sulphide were investigated and are described later (see page 56).

Thiatriazapentalenes (1i) and (1j) have been prepared by an earlier synthesis[41], and the products (1i) and (1j) prepared here were identical (nmr spectrum, mass spectrum and melting point) with the compounds prepared previously. The minor product (2a) was also shown to be identical (nmr spectrum and mass spectrum) with the previously prepared dithiadiazapentalene (2a)[100]. Only a trace of the minor product was isolated along with the thiatriazapentalene (1j), and was assumed to be the dithiadiazapentalene (2b) since it ran concurrently with an authentic sample of compound (2b)[100] on tlc.

The attempted synthesis of the thiatriazapentalene (1k) by the reaction of the chlorovinyl intermediate (5b) with t-butylamine was unsuccessful, and only a dark intractable tar was isolated.

(d) Synthesis of 6a-Thia-1, 2, 6-triazapentalenes with 6-Substituents Other than Alkyl and Aryl

6a-Thia-1, 2, 6-triazapentalenes, 6a-thia-1, 6-diazapentalenes, 1, 6a-dithia-6-azapentalenes and 6, 6a-dithia-1, 2-diazapentalenes have hitherto been prepared with alkyl or aryl substituents at N-1 and N-6. However, the chlorovinyl intermediates (5a) and (5b) may react with hydroxylamine, methoxyamine and hydrazines to give

6a-thia-1,2,6-triazapentalenes with non-alkyl and non-aryl substituents in the 6-position. These compounds were of interest as it was thought that the substituents at position-6 might cause a departure from the three-centre bonded bicyclic structure (1).

Reaction of the oxathiadiazapentalenes (4a) and (4b), in dimethylformamide, with phosphoryl chloride, and treatment of the resulting intermediates (5) with hydroxylamine hydrochloride in aqueous sodium carbonate gave the thiatriazapentalenes (1l) and (1m) in yields of 28% and 51%, respectively. Starting materials (4a) and (4b) were also isolated in yields of 28% and 34%, respectively, along with small amounts of the corresponding dithiadiazapentalenes (2a) and (2b). It is thought that the minor products (4a), (4b), (2a) and (2b) isolated here are formed by the same mechanism as was proposed for the formation of the minor products isolated along with thiatriazapentalenes (1i) and (1j) (see page 48). The dithiadiazapentalene (2a) isolated here was identified by its nmr spectrum and mass spectrum, and the dithiadiazapentalene (2b) was identified by tlc as only a trace quantity of this compound was obtained.

In structures (1l) and (1m) there is localisation of charge at the N(1)- and N(6)-positions from the non-bonding orbital of the three-centre bond which links the nitrogen atoms with the central sulphur atom. It was thought that there would be a repulsion between the lone pairs of electrons of the 6-substituent and the charge on the N(6)-atom, which would destabilise compounds (1l) and (1n), and thus the alternative structures (17a) and (17b) were thought to be

possible. However, the infrared spectra of compounds (11) and (1m) showed broad absorptions at 3340 and 3290 cm^{-1}, respectively (figure 1). These absorptions are more characteristic of the O-H stretching frequency of structures (11) and (1m) rather than N-H stretching frequency of structures (17a) and (17b). The infrared spectra of compounds (11) and (1m) may be compared with the infrared spectrum of the hydrazone (25a), which will be discussed later. The hydrazone has an NHPh group in a similar environment to the NHPh groups of structures (17) and the infrared spectrum of compound (25a) showed a narrow band at 3220 cm^{-1} (figure 1), due to the N-H stretching frequency. This band at 3220 cm^{-1} was not similar to the broad bands observed at 3340 and 3290 cm^{-1}, in the spectra of compounds (11) and (1m), respectively. Also the nmr spectra of compounds (11) and (1m) [in $(CD_3)_2SO$] show sharp singlets at δ11.70 and 11.60 which are assigned to the 6-OH protons. These spectra may be compared to the nmr spectrum of the hydrazone (25a) [in $(CD_3)_2SO$] which shows a broad singlet at δ10.78, due to the NHPh proton. We therefore believe that compounds (11) and (1m) exist as bicyclic compounds with similar structures to the thiatriazapentalenes already discussed. It is thought that the localised charge on the N(6)-atoms is drawn towards the electronegative oxygen atom of the 6-substituents of compounds (11) and (1m), thus reducing the repulsion between the lone pairs of electrons on the oxygen atom and the localised charge on the N(6)-atom.

Thiatriazapentalenes (1n) and (1o) were synthesised with a view to comparing their spectra data with the spectral data of the 6-hydroxy

derivatives (1l) and (1m). Compounds (1n) and (1o) are similar to the 6-hydroxy derivatives (1l) and (1m) as they also have oxygen atoms bonded directly to the N(6)-positions. However alternative dipolar structures, similar to the dipolar structures (17) envisaged for compounds (1l) and (1m), are not possible for compounds (1n) and (1o). Thiatriazapentalenes (1n) and (1o) were prepared in almost quantitative yield from the reaction of the chlorovinyl intermediates (5a) and (5b) with methoxyamine hydrochloride in aqueous sodium carbonate. The electronic spectra of the pairs of compounds (1l) and (1n), and (1m) and (1o) were almost identical. The nmr spectra [$(CD_3)_2SO$] of these pairs of compounds were also very similar. Therefore it seems most likely that the 6-hydroxy thiatriazapentalenes (1l) and (1m) and the 6-methoxy thiatriazapentalenes (1n) and (1o) are structurally similar.

The electronic spectra of compounds (1l-o) were similar to the electronic spectra of the 1,6-diaryl derivatives (1a-d), indicating that the 6-methoxy and 6-hydroxy substituents do not cause any departure from the bicyclic three-centre bonded structure. Compounds (1l-o) show three absorptions in the ultraviolet region in the ranges 201-205 nm, 221-227 nm and 277-280 nm. The spectra of these compounds also show absorptions in the visible region accounting for their red or orange colours. The 3,4-dimethyl derivatives (1l) and (1n) show one band in this region and the 3,4-trimethylene derivatives (1m) and (1o) show two close bands of equal intensity in this region. The chemical shifts of the 5-H protons of compounds (1n) and (1o) (in $CDCl_3$) were δ7.85 and δ7.88. These values indicate

that these compounds possess a ring-current of a similar magnitude to the ring-currents of the 1, 6-diaryl thiatriazapentalenes described earlier.

The attempted synthesis of compounds (1p) and (1q) by the reaction of intermediates (5a) and (5b) with N, N-dimethylhydrazine and phenylhydrazine were unsuccessful, and only dark intractable tars were isolated from these reactions. We believe that the charge localised on the N(6)-atom, from the non-bonding orbital of the three-centre bond, causes a repulsion with the lone pair of electrons on the 6-dimethylamino and 6-anilino substituents of compounds (1p) and (1q). It is thought that as a result of this repulsion compounds (1p) and (1q) are unstable and decompose on formation.

However, we thought that if the lone pairs of electrons of the nitrogen atoms in the 6-substituents could be delocalised by adjacent electron-withdrawing groups, then thiatriazapentalenes with nitrogen atoms bonded directly to the N(6)-positions should be sufficiently stable to allow their isolation. With this in mind, thiatriazapentalenes (1r-u) were successfully synthesised by the reaction of the chlorovinyl intermediates (5) with p-nitrophenylhydrazine and acethydrazine. Compounds (1t) and (1u) were isolated along with small amounts of the corresponding oxathiadiazapentalenes (4a) and (4b). It is thought that these minor products were formed by a similar mechanism to that proposed for the formation of the minor products isolated along with compounds (1a-d) (see page 45). The fact that compounds (1r-u) are stable, whereas compounds (1p) and (1q) could not be isolated, is regarded as proof that these compounds exist as the three-centre

bonded bicyclic structures as opposed to the monocyclic structures (18a-d). The formation of the unstable compounds (1p) and (1q), which subsequently decompose, in preference to the more stable monocyclic compounds (18e) and (18f) indicates that there is a strong tendency to form a three-centre N-S-N bond in these reactions, even when the resulting compounds are unstable.

The nmr spectra of the thiatriazapentalenes (1r) and (1s) were determined in [$^2D_6$]dimethylsulphoxide at 100°C since these compounds were insufficiently soluble at lower temperatures. The chemical shifts of the 5-H protons of compounds (1r) and (1s) were δ7.90 and 7.92, respectively. These values may be compared with the shifts of the 5-H protons of thiatriazapentalenes (1l-o) [in $(CD_3)_2SO$], which occur in the range δ8.01-8.08. They indicate that compounds (1r-s) have a slightly smaller ring-current than do compounds (1l-o), probably due to the effect of the electron-withdrawing 6-substituents.

(e) Synthesis of 6a-Thia-6-selena-1,2-diazapentalenes

The reactivity of the chlorovinyl intermediates (5a) and (5b) with nucleophiles other than primary amines and hydrazines was successfully utilised in the preparation of the 6a-thia-6-selena-1,2-diazapentalenes (19a) and (19b). These compounds are the first two examples of a new class of heterocyclic system. The reaction of the oxathiadiazapentalenes (4a) and (4b), in dimethylformamide, with phosphoryl chloride and treatment of the resulting intermediates (5) with aqueous potassium selenosulphate at 65°C gave the

thiaselenadiazapentalenes (19a) and (19b) in yields of 52% and 56%, respectively. The starting materials (4a) and (4b) were also recovered in low yield.

It should be noted that an aqueous solution of potassium selenosulphate at room temperature contains precipitated selenium due to hydrolysis:-

$$SeSO_3^{=} + H_2O \rightleftharpoons Se + HSO_3^{-} + OH^{-}.$$

Raising the temperature causes the equilibrium to move to the left. The selenosulphate ion may be regarded as a selenide ion co-ordinated to sulphur trioxide, but with the reducing properties of the selenide ion absent. We believe that the minor products (4a) and (4b) isolated along with the major products (19a) and (19b) were formed from the reaction of the intermediates (5) with hydroxide ion, present in the above equilibrium.

There is little doubt that compounds (19a) and (19b) exist in the bicyclic form. The nmr spectra of these compounds (in $CDCl_3$) were recorded, and the chemical shifts of the 5-H protons were δ10.18 and 10.02, respectively. Data available for stable selenoformyl compounds[143] shows that the chemical shifts of selenoformyl protons occur in the range δ11.97-12.77. Therefore it seems most likely that these compounds exist in the bicyclic form (19) and not as the selenoformyl structures (20). The electronic spectra of thiaselenadiazapentalenes (19a) and (19b) show absorptions in the visible region at 514 and 525 nm and in the ultraviolet region at 204 and 204 nm, 254 and 250 nm, and 281 and 279 nm.

(f) Reaction of Intermediates (5) with Sodium Hydroxide, Sodium Sulphide and Sodium Hydrogen Sulphide

The reaction of the intermediates (5) with methylamine and hydroxylamine gave the oxathiadiazapentalenes (4a) and (4b) and the dithiadiazapentalenes (2a) and (2b), as minor products, in addition to the expected thiatriazapentalenes (1i-j) and (1l-m). We have proposed that the minor products were formed by the reaction of hydroxide ions, present in the aqueous amine solutions, with the chlorovinyl intermediates (5). Reaction of the oxathiadiazapentalenes (4a) and (4b) with phosphoryl chloride, and treatment of the resulting intermediates (5) with sodium hydroxide gave compounds (4a) and (4b) in yields of 12% and 25%, respectively. The dithiadiazapentalenes (2a) and (2b) were also isolated in low yield together with large amounts of black intractable materials, which were probably formed by decomposition of the intermediates (5).

These results confirm the mechanism proposed on page 48. The fact that compounds (4a) and (4b) were isolated in low yield indicates that hydroxide ions do not attack exclusively at the 2'-position of intermediates (5) as do primary amines and hydrazines. We believe that the 1, 2, 3-thiadiazolium rings of intermediates (5) are degraded by the hydroxide ions, generating sulphide ions in the process. These sulphide ions attack the 2'-position of the intermediates (5), giving the dithiadiazapentalenes (2a) and (2b). There are no previous examples of the reactions of 1, 2, 3-thiadiazolium salts with the hydroxide ion, or any other nucleophiles. However, the

reactions of isothiazolium salts with nucleophiles, including the hydroxide ion, have been investigated[144]. It was found that isothiazolium salts were decomposed by the hydroxide ion with no tractable product being isolated.

The reactions of the chlorovinyl intermediates (5) with sodium sulphide and sodium hydrogen sulphide were also investigated. The reason for carrying out these reactions was that the sulphide and hydrogen sulphide ions are strong nucleophiles, and it was hoped to compare their reactions with the reactions of the weaker nucleophiles, aniline, p-anisidine, and p-nitroaniline .

We proposed that the reaction of these amines with the intermediates (5), resulting in the major products (1a-f), was not complete, and that the oxathiadiazapentalenes (4a) and (4b) were formed, in yields of up to 19%, from the reaction of the unreacted intermediates (5) with water (see page 45).

The reaction of the oxathiadiazapentalene (4a), in dimethylformamide, with phosphoryl chloride and treatment of the resulting intermediate (5) with aqueous sodium sulphide gave the dithiadiazapentalene (2a) in 55% yield and the thione (21) in 31% yield. The oxathiadiazapentalene (4a) was not isolated from the reaction, indicating that the reaction of the chlorovinyl intermediate (5a) with the sulphide ions was complete. Nucleophilic attack at the 2'-position of intermediate (5a) gave the major product (2a) and reductive cleavage of the S-N bond of intermediate (5a) produced the thione (21). The mechanism (5a) $\longrightarrow$ (22) $\longrightarrow$ (23) $\longrightarrow$ (21) is proposed for the

formation of this thione. The oxathiadiazapentalene (4b) gave the dithiadiazapentalene (2b). No reduction product was isolated, probably due to the geometric restriction imposed by the 3,4-trimethylene bridge. However, the oxathiadiazapentalene (4b) was also isolated in low yield (3%) from this reaction. It is thought that the minor product is formed by a competing reaction of hydroxide ions, present in the sodium sulphide solution, with the intermediate (5b), although the product (2b) from the reaction of the more nucleophilic sulphide ion predominates. The replacement of sodium sulphide by sodium hydrogen sulphide in these reactions gave the same products in similar yields.

It should be noted that the action of mercuric acetate on the dithiadiazapentalenes (2a) and (2b) gives the oxathiadiazapentalenes (4a) and (4b)[41]. The reverse reactions are effected by the reaction of compounds (4a) and (4b) with phosphoryl chloride and treatment of the resulting intermediates (5) with sodium sulphide or sodium hydrogen sulphide.

B. Synthesis of 6a-Thia-1, 2, 6-triazapentalenes from 5-Formyl Isothiazole

The 6a-thia-1, 2, 6-triazapentalenes so far discussed have been prepared from the corresponding 6, 6a-dithia-1, 2-diazapentalenes in one- or two-step operations. The require dithiadiazapentalenes were prepared by the reaction of 3-methyl(ene)-1, 2-dithiolium salts with arenediazonium fluoroborates[100] (see page 23). The 3-methyl(ene)-1, 2-dithiolium salts were prepared by the reaction of hydrogen disulphide and β-diketones.

A rapid synthesis of 6a-thia-1, 2, 6-triazapentalenes (27a-c) from the commercially available starting material (24) is described here. This synthesis involves three steps which may be carried out conveniently in two operations, and gives compounds (27a), (27b) and (27c) in overall yields of 85%, 85% and 17%, respectively.

5-Formylisothiazole (24) reacted with phenylhydrazine, p-nitrophenylhydrazine and methylhydrazine, in methanol under reflux, to give the hydrazones (25a), (25b) and (25c), respectively, in excellent yield. Prolonged reaction of compounds (25a) and (25b), in methylene chloride, with methyl fluorosulphonate gave the isothiazolium salts (26a) and (26b). These salts, in water/methanol (3:1) solution, were readily deprotonated on addition of aqueous sodium carbonate to give the thiatriazapentalenes (27a) and (27b) in good yield. The latter two steps could conveniently be carried out in one operation. The hydrazone (25c) reacted more rapidly with methyl fluorosulphonate than did the hydrazones (25a) and (25b).

The resulting salt (26c) separated from solution after 10 minutes as a red oil, and was not characterised. Addition of aqueous sodium carbonate to an aqueous solution of the oil (26c) gave the thiatriazapentalene (27c) in low yield. The low yield of compound (27c) is probably due to a competing reaction of the hydroxide ion with the isothiazolium ring of the salt (26c). It is thought that the high yields of the thiatriazapentalenes (27a) and (27b), formed from the salts (26a) and (26b), result from the higher acidity of the N-H protons of these salts, and consequently the salts (26a) and (26b) are exclusively deprotonated by base with no competing reaction taking place at the isothiazolium ring. However, as the N-H proton of the salt (26c) is less acidic this salt is more susceptible to the competing reaction of the isothiazolium ring with base, and hence the thiatriazapentalene (27c) is formed in lower yield. The reactions of isothiazolium salts with base have been investigated previously. Sykes and Ullah[144] found that 2-alkylisothiazolium salts were decomposed rapidly at room temperature by aqueous alkali, and that only intractable tars were isolated from these reactions.

Thiatriazapentalene (27a) has been prepared by a previous synthesis[41], and the compound prepared here was identical (nmr spectrum and melting point) with the previously prepared compound (27a). The nmr spectrum of the parent thiatriazapentalene (27c) showed that the chemical shifts of the 4-H and 5-H protons were δ6.64 and 7.90, respectively. These values may be compared with the chemical shifts of the 4-H and 5-H protons of the parent dithiaazapentalene (28) (δ7.05 and 7.91) and the parent thiadiazapentalene

(29) (δ6.37 and 7.71). It is assumed from these values that the size of the ring-current increases from the thiadiazapentalene (29) to the thiatriazapentalene (27c) to the dithiaazapentalene (28).

Compounds (28) and (29) form 1:1 charge-transfer complexes with 1, 3, 5-trinitrobenzene[39,47], and in a similar manner thiatriazapentalene (27c) formed complex (30a). Also thiatriazapentalene (27a) formed the complex (30b) with trinitrobenzene. The formation of complexes (30a) and (30b) may be regarded as evidence that compounds (27a) and (27c) are electron-rich and behave as π-donors. Complexes (30a) and (30b) were prepared by the same method as complexes (16c) and (16d) (see page 47).

C. Synthesis of 1, 6-Dimethyl-6a-thia-1, 6-diazapentalene, 6-Methyl-1-oxa-6a-thia-6-azapentalene and 6-Methyl-1, 6a-dithia-6-azapentalene from 5-Formylisothiazole

6a-Thia-1, 2, 6-triazapentalenes (27a-c) were synthesised from 5-formylisothiazole. The syntheses of other aza-analogues of trithiapentalenes from 5-formylisothiazole are described here.

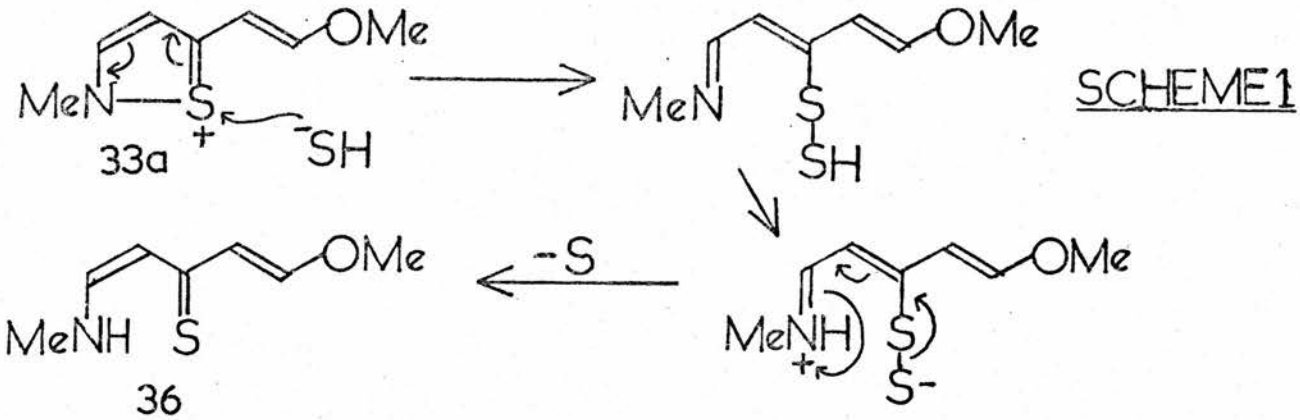
5-Formylisothiazole (24) reacted with the phosphonium ylid (31) in the well-known Wittig reaction[145], to give the cis- (32a) and trans- (32b) methoxyvinyl compounds. The ylid (31) was prepared from the reaction of phenyl lithium with methoxymethyltriphenylphosphonium chloride and was used in situ. Reaction of the ylid (31) with 5-formylisothiazole (24) and distillation of the resulting product gave an inseparable mixture of compounds (32a) and (32b). The nmr spectrum of the distilled reaction product showed that the ratio of the cis- (32a) and trans- (32b) isomers was approximately 1:2. The spectrum also showed weak signals in the range δ7.28-7.64, thought to be due to some trace impurity present which was not separated by distillation. The mass spectrum of the distilled reaction product showed peaks at m/e 154 and 141 which were assigned to the molecular ion peaks of biphenyl and to the methoxyvinyl compounds (32a) and (32b). The trace of biphenyl present in the reaction product doubtless originates from the phenyl lithium solution used in the reaction. The purity of the methoxyvinyl compound (32) was estimated at 98%, by weight, from its nmr spectrum.

As the biphenyl impurity could not be separated by distillation from the methoxyvinyl compound (32), the distilled Wittig reaction product was taken up in methylene chloride and treated with methyl fluorosulphonate. Addition of ether precipitated cis- (33a) and trans- (33b) methoxyvinyl isothiazolium salts which were filtered off, leaving the biphenyl impurity in the methylene chloride/ether solution. The nmr spectrum of the crude isothiazolium salt showed that the ratio of the cis- (33a) and trans- (33b) isomers was still 1:2, and that no impurities were present. The overall yield of the methoxyvinyl isothiazolium salt (33), from 5-formylisothiazole, was 53%. The methoxyvinyl isothiazolium salt (33) reacts with nucleophiles in a similar manner to the chlorovinyl salts (5a) and (5b) already discussed. Attack takes place and the 2'-position with displacement of methoxide ion. The crude salts (33), consisting of a 1:2 mixture of the cis- (33a) and trans-(33b) isomers, as isolated in the previous reaction, were used for subsequent reactions.

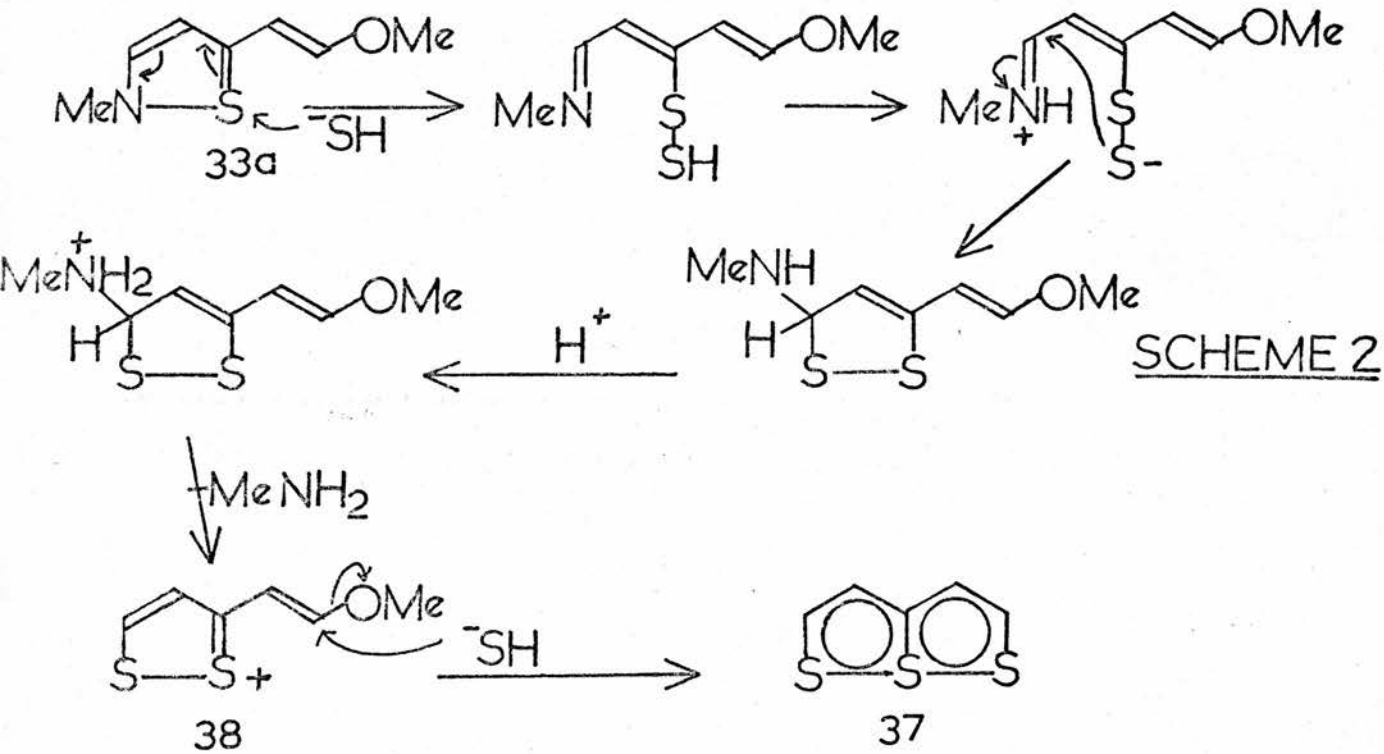
Reaction of the methoxyvinyl isothiazolium salt (33), in acetonitrile solution, with aqueous methylamine gave the 6a-thia-1,6-diazapentalene (29) in 61% yield. This compound had previously been prepared by a different synthetic route[39], but the method described here is more direct and gives compound (29) in a three-step synthesis from a commercially available starting material in an overall yield of 32%. The product obtained in this work was shown to be identical (nmr spectrum and mass spectrum) to the previously prepared compound (29)[39].

Treatment of the methoxyvinyl isothiazolium salt (33) in acetonitrile solution, with aqueous sodium hydroxide gave the 1-oxa-6a-thia-6-azapentalene (34) in low yield (11%). A competing reaction, involving attack of the isothiazolium ring of the salt (33) by hydroxide ions, probably accounts for the low yield of compound (34). A similar competing reaction, involving decomposition of the isothiazolium ring of compound (26c) by base, was proposed to account for the low yield of the thiatriazapentalene (27c) (see page 60). The oxathiaazapentalene (34) was a relatively unstable low melting compound which slowly decomposed on standing at room temperature. No peaks were detected in the normal carbonyl frequency region (1600-1750 cm^{-1}) in the infrared spectrum of compound (34), which rules out the alternative monocyclic structure (35) for this compound and indicates that a sulphur-oxygen interaction is present. The electronic spectrum of the oxathiaazapentalene (34) showed absorptions at 205, 235 and 374 nm.

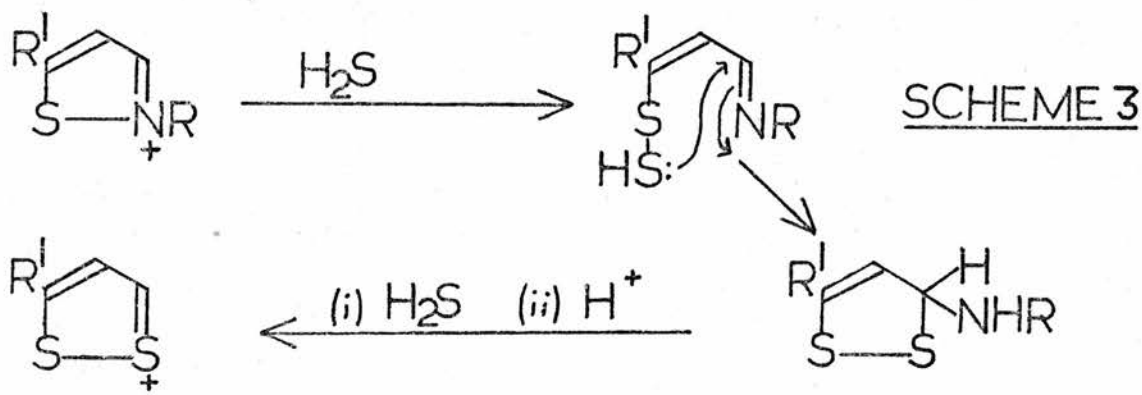
The reaction of a solution of the salt (33) in acetonitrile with sodium hydrogen sulphide gave three products. Nucleophilic attack at the 2'-position of the salt (33) by the hydrogen sulphide ion gave the 1, 6a-dithia-6-azapentalene (28) in 23% yield. Reductive cleavage of the S-N bond of the salt (33) by the hydrogen sulphide ion produced the thione (36) which partially decomposed during the work-up procedure (final yield 8.5%). The nmr spectrum of the thione showed that only the trans-methoxyvinyl isomer (36) was isolated and the mechanism outlined in Scheme 1 is proposed for the formation of



SCHEME 1



SCHEME 2



SCHEME 3

this compound. 1,6,6a-Trithiapentalene (37) was also isolated from this reaction in low yield (2.7%). It is thought that the 1,2-dithiolium intermediate (38) is initially formed by the action of the hydrogen sulphide ion on the isothiazolium ring of the salt (33). Further attack on the 2'-position of the dithiolium intermediate (38), by the hydrogen sulphide ion, results in the trithiapentalene (37). The mechanism outlined in Scheme 2 is proposed for the formation of this compound. 1,2-Dithiolium salts have previously been prepared by the treatment of isothiazolium salts with hydrogen sulphide[144]. A mechanism was also proposed for this reaction (Scheme 3).

Compounds (28) and (37) were shown to be identical (nmr spectrum, mass spectrum and melting point) to previously prepared samples of these compounds[37,47].

D. Synthesis of 1, 6, 6a-Trithia-3-azapentalenes and 6, 6a-Dithia-1, 3-diazapentalenes from 5-Amino-1, 2-dithiole-3-thiones

The work discussed in this section was carried out at the Esso Chemicals Research Centre. The purpose of this work was to synthesise new proprietary compounds for evaluation as potential antioxidants for lubricating oils. 5-Amino-1, 2-dithiole-3-thiones (39a) and (39b), and other products synthesised from these thiones, have been the subject of recent interest at the Esso Chemicals research laboratories, as part of a search for new antioxidant additives. A number of aza-analogues of 1, 6, 6a-trithiapentalenes were synthesised from the 1, 2-dithiole-3-thiones (39a) and (39b) as part of this search and these syntheses are described here.

The 5-amino group of the dithioles (39a) and (39b) is acidic, and these compounds are deprotonated by triethylamine. Treatment of compounds (39a) and (39b) with triethylamine and reaction of the resulting deprotonated 5-amino-1, 2-dithiole-3-thiones with carbon disulphide gave intermediates for which the structures (40a) and (40b) were proposed. *In situ* reaction of intermediates (40a) and (40b) with methyl iodide gave the 1, 6, 6a-trithia-3-azapentalenes (43a) and (43b) in good yield. The intermediates (40a) and (40b) could be separated from the reaction solution on the addition of ether, as red oils, but attempted crystallisation of these oils was unsuccessful and hence the intermediates (40a) and (40b) were not characterised.

We believe that methylation of the intermediates (40) initially takes place at the negatively charged sulphur atom resulting in the neutral compounds (41). Subsequent methylation of compounds (41) gives the salts (42) which undergo loss of HI and accompanying ring-closure to give the trithiaazapentalenes (43a) and (43b). The 2,5-dibenzylmercapto derivative (44) was prepared by a similar process, replacing methyl iodide by benzyl chloride.

The dithioles (39a) and (39b) reacted with phenyl isothiocyanate in the presence of triethylamine to give intermediates thought to be the salts (45). These salts separated from the reaction solution on the addition of ether as red oils, but attempts to crystallise them were unsuccessful. In situ reaction of the intermediates (45) with methyl iodide afforded the trithiaazapentalenes (47) and the dithiadiaza-pentalenes (50). Compounds (50a) and (50b) are the first two examples of 6,6a-dithia-1,3-diazapentalenes, a new class of heterocyclic system.

The following mechanism is proposed to account for the formation of compounds (47) and (50). Methylation of the salts (45'') at the negatively charged sulphur atom resulted in the neutral species (48). Subsequent methylation of species (48) resulted in the salts (49) which on loss of HI and accompanying ring-closure gave the dithiadiazapentalenes (50a) and (50b). Alternatively the salts (45') may undergo a proton transfer to give the intermediates (46), which on methylation gave the trithiaazapentalenes (47a) and (47b).

There is little doubt that trithiaazapentalenes (43a-b), (44) and (47a-b) exist as bicyclic compounds in which the three sulphur atoms are linked by a four-electron three-centre bond. As there are no ring protons in these compounds their nmr spectra give little structural information. The electronic spectra of these compounds show strong absorptions in the visible region in the range 413-439 nm, responsible for the orange colour of these compounds, and also several strong absorptions in the ultraviolet region.

There is also little doubt that the dithiadiazapentalenes (50a) and (50b) exist as bicyclic compounds, with the S-S-N sequence of atoms maintained by a four-electron three-centre bond. Dithiadiazapentalenes (50a) and (50b) are pale yellow compounds and their electronic spectra show strong bands in the visible region at 386 and 400 nm, respectively, as well as several strong bands in the ultraviolet region.

The trithiaazapentalenes (43a-b), (44) and (47a-b) and the dithiadiazapentalenes (50a-b) were insufficiently soluble in mineral oils and hence could not be tested for evaluation of their performance as lubricating oil additives. However, in subsequent work at the Esso Chemicals laboratories, a modification of the synthesis of 1, 6, 6a-trithia-3-azapentalenes described here has been introduced. Methyl iodide has been replaced by long chain alkylating agents and phenylisothiocyanate has been replaced by long chain isothiocyanates. The thiatriazapentalenes prepared by these modified methods were sufficiently soluble in mineral oils to undergo bench testing. The results of these bench tests indicate that trithiaazapentalenes show

promise as antioxidants and antiwear agents in lubricating oils. Certain thiatriazapentalenes, prepared by the methods outlined here, are currently being evaluated by further bench and engine tests. It is thought that the large amount of sulphur present in the thiatriazapentalenes described here result in the good antioxidant and antiwear properties found for these compounds.

E Protonation Studies of 1, 6, 6a-Trithiapentalenes and Pyrrolo[2, 1-b]thiazole thioaldehydes

The protonation of 1, 6, 6a-trithiapentalenes and pyrrolo[2, 1-b]-thiazole thioaldehydes in trifluorcacetic acid solution was studied by ^{1}H nmr spectroscopy. The deuteration of these compounds in deuteriotrifluoroacetic acid solution was also studied in certain cases. The nmr spectra recorded are reproduced in figures 2-11 (see pages 84 to 91).

(a) Protonation of 1, 6, 6a-Trithiapentalenes

Previous studies have shown that the protonation of 1, 6, 6a-trithiapentalenes (51) occurs at the C(3)- and S(1)-positions resulting in the cations (52) and (53), respectively[110] (see Part 1, page 19). Although the spectrum of compound (51a) in trifluoroacetic acid solution was too complex to analyse, the partial H-D exchange at the 3- and 4-positions of a sample of trithiapentalene (51a), recovered from deuteriotrifluoroacetic acid solution, was taken as evidence for the existence of the C(3)-protonation species (52a). This species possesses a thioformyl group. However stable thioformyl compounds are only possible when the C=S linkage is conjugated with an adjacent electron releasing group or heterocyclic system, eg. (54a)$\longleftrightarrow$(54b). In structure (52a) the saturated C(1')-atom interrupts the conjugation of the thioformyl group with the dithiolium ring and it is therefore thought unlikely that the C(3)-protonation product would exist as the thioaldehyde structure (52a).

In an attempt to determine the structure of the C(3)-protonation products (52) of 1,6,6a-trithiapentalenes (51), the protonation of compound (51b) was reinvestigated. In an earlier study[110], the spectrum of compound (51b) in trifluoroacetic acid showed signals which were assigned to the S-protonation product (53b). Protonation of the trithiapentalene was complete after approximately 48 hours. Also very weak signals, which were not interpreted in the earlier study, were observed in the spectrum of compound (51b). These weak signals were of interest as we believed that they could correspond to the C(3)-protonation species (52b). In our reinvestigation the protonation of trithiapentalene (51b) was observed in 1% water/trifluoroacetic acid as it was hoped that the ratio of C:S protonation would increase in this less acidic protonation medium.

In the spectrum of compound (51b) obtained here (figure 2) the signals due to the previously reported S-protonation product (53b) were observed, and further signals which were not interpreted in the earlier study were also observed. The spectrum was recorded approximately 24 hours after preparation of a solution of compound (51b), the protonation being complete in that time. The signals at δ2.41, 2.72, 7.91 and 9.53 were assigned to the cation (53b) as before. The signals thought to correspond to the C(3)-protonation product (52b) occurred at δ1.71, 7.18 and 10.08. The signal at δ1.71 was assigned to the 1'-Me group and was originally thought to be a double doublet with the major splitting (J=7.5 Hz) due to coupling with the 1'-H proton and the minor splitting (J=1.8 Hz) due to coupling with the 2'-H proton. However, irradiation of the signal thought to correspond to the 2'-H proton did not cause the signal at δ1.71 to

collapse to a doublet. We therefore believe that the signal at δ1.71 is due to two superimposed doublets (J=7.5 Hz) corresponding to two distinct 1'-Me groups in different chemical environments. It was hoped that when the spectrum of the compound (51b) was recorded in deuteriotrifluoroacetic acid, the 1'-Me signals would collapse to two singlets due to the replacement of the added 1'-H hydrogen atom by deuterium, eg. structure (55). Unfortunately the spectrum of trithiapentalene (51b) in deuteriotrifluoroacetic acid showed that S-deuteration had taken place exclusively resulting in only the cation (56). S-deuteration of compound (51b) also took place exclusively in a 1% D_2O/deuteriotrifluoroacetic acid solution. The signal due to the added 1'-H proton of species (52b) was not observed. The signal at δ7.18 was though to originate from the 2'-H proton. However it was thought that this signal could not correspond to the thioformyl proton of structure (52b), as the chemical shifts of the thioformyl protons of stable heterocyclic thioaldehydes, even when polarised in the sense $R=\overset{+}{C}H-\bar{S}$, do not fall below δ10.2[45,46]. The possibility that the thioformyl group of structure (52b) had polymerised was then considered. This would account for the 2'-H proton signal occurring at δ7.18. We believe that the signal at δ7.18 occurs as two superimposed doublets (J=6.3 Hz) due to the 2'-H proton being in two distinct chemical environments with the splitting due to coupling with the added 1'-H proton. As the attempted synthesis of aryl thioaldehydes resulted in the formation of α- and β-1,3,5-trithianes[128,129] the possibility of 1,3,5-trithianes being formed here was examined. The formation of the β-trithiane (57a) was ruled out as the trithiane ring protons in

this structure would appear as a doublet, with the splitting due to coupling with the 1'-H proton. As the two doublets observed at δ7.18 are approximately of equal intensity it is unlikely that they correspond to the axial and equatorial ring protons of the α-trithiane (57b). Although we are uncertain of the structure of the species resulting from polymerisation of the unstable C-protonation product (52b) we tentatively suggest the cyclic tetramer (58) in which the 2 and 6 ring-hydrogens occupy equatorial positions and the 4 and 8 ring-hydrogens occupy axial positions. In structure (58) the ring protons are in two distinct chemical environments which would account for the 2'-H proton signal being observed as two superimposed doublets. Similarly the dithiolium rings of structure (58) are in two distinct chemical environments accounting for the observation of the 1'-Me signal as two superimposed doublets. It is thought that the expected trimers (57a) and (57b) are not formed here due to steric hindrance caused by the dithiolium (R) groups in these structures, and hence we have suggested the less hindered tetramer.

The two quartets observed at δ10.07 and 10.10 are assigned to the 5-H proton with the splitting due to coupling with the 4-Me group. It is thought that the 5-H protons are in two distinct chemical environments, due to the dithiolium rings of structure (58) occupying both axial and equatorial positions, and hence two distinct signals are observed for the 5-H proton. The signal at δ10.00 could not be interpreted. Several signals were observed in the range δ2-δ3 but only the signals at δ2.41 and 2.72 were interpreted and assigned to the 4-Me and 1'-Me signals of species (53b). It is thought that the

4-Me signal of species (52b) also occurs in this region. The ratio of C(3)- to S(1)-protonation of trithiapentalene (51b) was estimated at approximately 1:4 from the relative intensities of the signals due to the C(3)- and S(1)-protonation products, (52b) and (53b), respectively.

Trithiapentalenes (51c) and (51d) were synthesised with a view to studying their protonation in trifluoroacetic acid solution by ^{1}H nmr spectroscopy. Compounds (51c) and (51d) were prepared by successive condensation of dimethylthioformamide with 1,2-dithiolium salts (59) in boiling acetic anhydride and treatment of the resulting intermediates (60) with aqueous sodium hydrogen sulphide. It was hoped that the C(3)-protonation products (52c) and (52d) of these trithiapentalenes would predominate over the S-protonation products (53c) and (53d), as it was thought that the unsaturated C(1')-carbon atom of species (53c) and (53d) would introduce strain effects into the 7 and 8 membered rings. In compounds (52c) and (52d) the C(1')-carbon atoms are saturated and therefore the strain present in compounds (53c) and (53d) is not present in compounds (52c) and (52d). Therefore we believed that C(3)-protonation of trithiapentalenes (51c) and (51d) would predominate. Unfortunately, the spectra of compounds (51c) and (51d) were too complex to analyse and no further information about the structure of the unstable C(3)-protonation products (52) was obtained.

(b) Protonation of Pyrrolo[2,1-b]thiazole-7-thioaldehydes

The spectrum of the trithiapentalene (51b) in trifluoroacetic acid solution could not be fully interpreted although it was assumed that C(3)-protonation had taken place. On the basis of the presence of the

signal at δ7.18 we assumed that the C(3)-protonation product (52b) had polymerised, although the structure of the resulting thioaldehyde polymer was uncertain. The spectra of the trithiapentalenes (51c) and (51d) in trifluoroacetic acid provided no more information about the C(3)-protonation products of trithiapentalenes. Attention was therefore turned to the protonation of pyrrolo[2,1-b]thiazole-7-thioaldehydes (61). Since pyrrolo[2,1-b]thiazoles undergo electrophilic substitution preferentially at the 5-position[131], it was hoped that the thioaldehydes (61) would protonate at the 5-position in preference to the sulphur atom of the 7-thioformyl group. The stability of pyrrolo[2,1-b]thiazole thioaldehydes arises from the conjugation of the thioformyl group with the pyrrolo[2,1-b]thiazole system, eg. (61)⟷(62). However in the C-protonation products (63) of compounds (61), the thioformyl group cannot be conjugated with the pyrrolo[2,1-b]-thiazole system since it is insulated from the ring system by the saturated C(5)-carbon atom. Seen in this light, the C-protonation products (63) of pyrrolo[2,1-b]thiazole thioaldehydes (61) are similar to the C-protonation products (52) of 1,6,6a-trithiapentalenes since both species possess an unstable thioformyl group which cannot conjugate with the heterocyclic portion of the molecule. It was hoped that the spectra of compounds (61) in trifluoroacetic acid would provide more information about the fate of the unstable thioaldehyde structures (63) in trifluoroacetic acid solution.

The protonation of the thioaldehydes (61) was observed over a period of time and the nmr spectra recorded are reproduced in figures 3-7. The products arising from the protonation of compounds

(61) will be discussed first, and this will be followed by an interpretation of the nmr spectra reproduced in figures 3-7, from which the structures of the protonation products are deduced.

The spectra of compounds (61a-e) were recorded initially approximately 30 minutes after the preparation of the trifluoroacetic acid solutions. These first spectra showed that both C- and S-protonation had taken place, forming protonation products (63) and (64), respectively. The initial ratios of C- to S-protonation of compounds (61a), (61b), (61c), (61d) and (61e) were respectively; 4:1, 2:3, 2:1, 1:0 and 12:1. These ratios were found to increase with time until a final value was reached. The final ratios of C- to S-protonation of compounds (61a), (61b), (61c), (61d) and (61e) were respectively; 8:1 (after 14 days), 3:1 (after 6 days), 1:0 (after 41 days), 1:0 (after 27 days) and 1:0 (after 13 days). These results indicate that the S-protonation products (64) are slowly being converted into the C-protonation products (63). It is thought that these conversions take place <u>via</u> the unprotonated thioaldehydes (61), with all three species coexisting in equilibrium, eg. (64) $\rightleftharpoons$ (61) $\rightleftharpoons$ (63), and with the equilibrium gradually changing in favour of species (63). It is assumed that the unprotonated thioaldehydes (61) exist in trifluoroacetic acid solution, below the limits of detection by ^{1}H nmr spectroscopy.

The unstable C-protonation products (63) polymerised to give 1,3,5-trithianes. Initially the α-isomers (65) predominated but they were gradually transformed into the β-isomers (66). The initial α:β isomer ratios observed for the 1,3,5-trithianes, formed from the unstable C-protonation products (63a), (63b), (63c), (63d) and (63e)

were respectively; 4:1, 2:1, 5:2, 4:1 and 1:0. The final α:β isomer ratios were respectively; 1:3 (after 14 days), 1:12 (after 6 days), 0:1 (after 41 days), 0:1 (after 27 days) and 0:1 (after 13 days). In the synthesis of 2,4,6-triaryl-1,3,5-trithianes[128,129], it was found that the α-isomers were always formed to a greater extent than the β-isomers, despite the fact that the β-isomers were thermodynamically more stable. A mechanism[128] has been proposed to account for this observation. Here the α-isomers (65) are initially formed to a greater extent than the β-isomers (66), due probably to a kinetically controlled reaction as in the formation of triaryl-trithianes. However, since the protonation of thioaldehydes (61), resulting in 1,3,5-trithianes (65) and (66), is thought to be reversible, the sterically more hindered α-isomers (65) gradually transform into the thermodynamically more stable β-isomers (66). The reversibility of the protonation of the thioaldehydes (61) was demonstrated by quenching trifluoroacetic acid solutions of these compounds with aqueous sodium carbonate. The original thioaldehydes (61) were recovered on extracting the quenched solution with benzene. The trifluoroacetic acid solutions of compounds (61) were allowed to stand for a sufficient length of time to allow the C-protonation products (65) and (66) to become predominant.

The presence of the S-protonation products (64) was assumed from the observation of C<u>H</u>(SH) proton signals in the range δ8.50-9.24. The CH(S<u>H</u>) proton signals were not observed owing to rapid exchange with the solvent. To confirm the assignment of the signal at δ8.60 in the spectrum of the thioaldehyde (61a) in trifluoroacetic acid (see

figure 3) to the CH(SH) signal of species (64a), the corresponding deuteriothioaldehyde (67a) was synthesised by a modification of the Vilsmeier reaction. The spectrum of this compound was identical to the spectrum of compound (61a) except that the signal at δ8.60 was absent in the spectrum of compound (67a), due to the CD(SH) group of the corresponding S-protonation product (68a) of compound (67a). The assignments of the signals at δ8.72, 8.50 and 9.24 to the CH(SH) signals of species (64b) (see figure 4), (64c) (see figure 5) and (64e) (see figure 7), respectively, followed by analogy with the preceding example. Although no direct evidence has been obtained, the S-protonation products of thioaldehydes (61) are assigned the syn-structures (64). The alternative anti- structures (69) are ruled out on the grounds that steric clash would occur between the SH and Me or Bu^t groups in the anti-isomers.

The presence of the C-protonation products (63a-c) of the thioaldehydes (61a-c), substituted in the 5-position, was deduced from the presence of broad signals in the range δ5.36-5.46, assigned to the added 5-H protons. The 5-Me signals of species (63a-c) were split into doublets (J=7.0-7.2 Hz) from coupling with the added 5-H protons. On rerunning the spectra of thioaldehydes (61a–c) in deuteriotrifluoroacetic acid the signals previously observed at δ5.36-5.46 were absent. Also the 5-Me signals of species (63a-c) had collapsed to singlets. The spectra of the thioaldehydes (61d) (figure 6) and (61e) (figure 7), unsubstituted in the 5-position, showed broad singlets at δ5.21 and δ5.36, respectively, due to the 5-CH_2 signals of the C-protonation products (63d) and (63e), respectively. These signals were absent in

the spectra of compounds (61d) and (61e) in deuteriotrifluoroacetic acid.

The conclusion that polymerisation of the unstable C-protonation products (63) had occurred to give the α- and β -1, 3, 5-trithianes (65) and (66) was deduced from the observation of signals in the region δ6.23-6.90, which we assigned to the trithiane ring protons. The formation of the 1, 3, 5-trithianes (70) and (71) was also considered. However these structures were ruled out due to the steric hindrance caused by the bulky pyrrolo [2, 1-b]thiazolium (R) groups occupying two or three axial positions. The signals from the equatorial ring protons occurred at lower field than those from the axial ring protons, and the axial ring protons of the α-isomers (65) occurred at lower field than the axial ring protons of the β -isomers (66). The ratios of the axial to equatorial ring proton signals of the α-isomers (65) were always 2:1. When the spectra of the thioaldehydes (61) in trifluoroacetic acid were observed over a period of time the signals from the α-trithiane ring protons decreased in intensity, while those from the β -trithiane ring protons increased in intensity. The ratios of the α- and β -isomers (65) and (66) present in solution at any given time were estimated from the relative intensities of the trithiane ring protons of the two species. To confirm that the signals at δ6.29, 6.34 and 6.48 in the spectrum of the thioaldehyde (61a) and the signals at δ6.30, 6.33 and 6.48 in the spectrum of thioaldehyde (61d) were in fact due to 1, 3, 5-trithiane ring protons, the spectra of the corresponding deuteriothioaldehydes (67a) and (67b) were recorded. There were no signals in the region δ6.29-6.53 in the spectra of compounds (67a) and (67b). The assignment of signals in the range δ6.23-6.90, in the spectra of the thioaldehydes (61b)

(61c) and (61e), to the trithiane ring protons of structures (65) and (66), followed by analogy with the preceding two examples.

The spectrum of the 5-deuteriomethyl thioaldehyde (72) in trifluoroacetic acid was also of interest. Initially the signal due to the added 5-H proton appeared as a broad singlet at δ5.46. It is thought that this broad singlet arises from two superimposed signals due to the 5-H protons of the equatorial and axial pyrrolo[2,1-b]-thiazolium rings (R) in the derived α- and β-1,3,5-trithianes (73) and (74). The signal at δ.5.46 sharpened with time as the α-isomer (73) slowly transformed to the β-isomer (74). After 6 days the signal due to the 5-H proton of the β-isomer (74) appeared as a sharp singlet. Compound (72) was synthesised from the previously prepared deuteriothioaldehyde (75)[46]. Reduction of compound (75) with lithium aluminium deuteride aluminium chloride gave compound (76) which was thioformylated by means of the Vilsmeier reaction to give the thioaldehyde (72).

(c) Protonation of Pyrrolo[2,1-b]thiazole-5-thioaldehydes

The protonation of pyrrolo[2,1-b]thiazole-5-thioaldehydes (77a-d) in trifluoroacetic acid solution was also studied and the nmr spectra are reproduced in figures 8-11. Possible sites for protonation of compounds (77a-d) were the C(7)-positions and the sulphur atoms of the 5-thioformyl groups. Since pyrrolo[2,1-b]thiazoles also undergo electrophilic attack at the 7-position if the 5-position is blocked we hoped to observe C-protonation of compounds (77a-d) with similar results to those obtained for the protonation of the 7-thioaldehydes (61a-e).

The nmr spectra of compounds (77a-d), in trifluoroacetic acid, showed that S-protonation had taken place, resulting in the cations (78) and (79). The spectra were recorded immediately after preparation of the trifluoroacetic acid solutions, the protonation of the thioaldehydes being completed during preparation. Unlike the spectra of the 7-thioaldehydes (61) the spectra of compounds (77) did not change with time. Protonation at the 5-position of the thioaldehydes (77a-b) resulted in the formation of two isomeric products, namely the syn-isomers (78a-b) and the anti-isomers (79a-b). Protonation at position-5 of the thioaldehydes (77c-d) produced exclusively the anti-isomers (79c-d). The signals at δ8.42 and 8.86 in the spectrum of compound (77a) and the signals at δ8.43 and 8.73 in the spectrum of compound (77b) were assigned to the CH(SH) proton signals of structures (78) and (79). The CH(SH) signals were not observed due to rapid exchange with the solvent. As the CH(SH) protons of the anti-isomers (79a-b) were more subject to the deshielding effect of the isothiazolium ring than the CH(SH) protons of the syn-isomers (78a-b), the CH(SH) signals at lower field (δ8.86 and 8.73) have been assigned to the anti-isomers (79a-b), and the CH(SH) signals at higher field (δ8.42 and 8.43) to the syn-isomers (78a-b). Also the CH(SH) proton signals of the anti-structures (79a-b) appeared as doublets (J=1.2 Hz) since the CH(SH) protons of these structures were in the W-configuration necessary for long-range coupling with the 7-H proton. The CH(SH) proton signals of the syn-structures were observed as singlets. On irradiation of the 7-H proton signals at δ7.03 and 6.94 in the spectra of compounds (77a) and (77b),

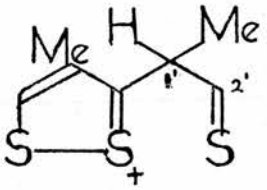
respectively, the CH(SH) proton signals from the anti-structures (79a) and (79b) collapsed to singlets. The syn-isomers (78a) and (78b) predominated over the anti-isomers (79a) and (79b), the syn:anti isomer ratios being approximately 2:1 in both cases.

The spectra of compounds (77c) and (77d) in trifluoroacetic acid solution showed signals at δ8.85 and δ8.87 which we have assigned to the CH(SH) proton signals of the anti-isomers (79c) and (79d), respectively. As these signals are doublets from coupling with the 7-H protons through a W-configuration, the anti-isomers were assumed. Irradiation of the 7-H proton signals at δ6.98 and 7.06, respectively, caused the CH(SH) proton signals to collapse to singlets. The assignment of the signal at δ8.87 in the spectrum of compound (77d) in trifluoroacetic acid to the CH(SH) proton of structure (79d) was confirmed by observing the spectrum of the corresponding deuteriothioaldehyde (80). The corresponding S-protonation product (81) of this compound did not show a signal at δ8.87.

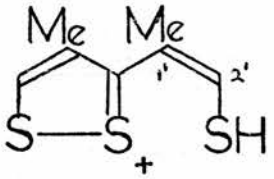
It is thought that the syn-isomers (78a) and (78b) predominate over the anti-isomers (79a) and (79b) due to steric hindrance between the 6-Me groups and the SH groups in the latter structures. We also believe that the anti-isomers (79c) and (79d) are formed exclusively because steric hindrance between the 3-Me groups and SH groups in the syn-isomers (78c) and (78d) is much greater than steric hindrance between the SH groups and the 6-Me groups in the anti-isomers (79c) and (79d).

Although C-protonation resulting in the products (82) was not

directly observed, the 7-H proton signals of species (78) and (79) disappeared due to H-D exchange when the spectra of thioaldehydes (77a-c) were recorded in deuteriotrifluoroacetic acid solution. H-D exchange was complete almost immediately after preparation of the solutions of compounds (77a) and (77b), but completely H-D exchange in compounds (77c) and (77d) took two days. These results indicate that C-protonation of thioaldehydes (77a-d) takes place at concentrations below the limits of detection by nmr spectroscopy. Since the signals arising from C-protonation products were not directly observed the structures of the unstable C-protonation products (82) could not be deduced. However, we believe that the unstable thioaldehydes (82) form α- and β-1, 3, 5-trithianes as in the case of the protonation of pyrrolo[2, 1-b]thiazole-7-thioaldehydes.



52b



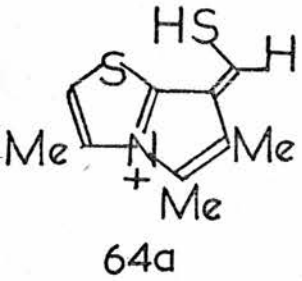
53b

NMR Spectrum of Compound (51b) in Trifluoroacetic Acid

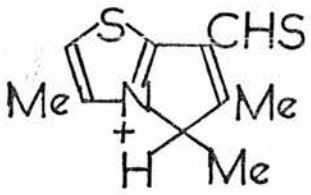
S-6 Protonation Product (53b) - δ2.41 (b, 1'-Me), δ2.72 (b, 4-Me), δ7.91 (b, 2'-H), δ9.53 (b, 5-H)

C-3 Protonation product (52b) - δ1.71 (two superimposed doublets, 1'-Me), δ7.18 (two superimposed doublets, 2'-H), δ10.07 (q, 5-H), δ10.10 (q, 5-H)

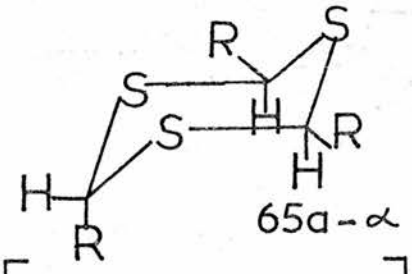
The remaining signals observed in spectrum of compound (51b), in trifluoroacetic acid, could not be interpreted.



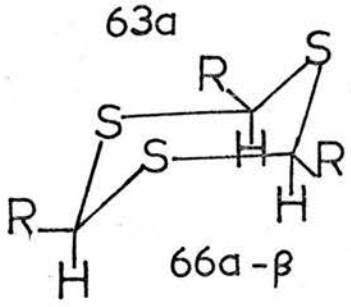
64a



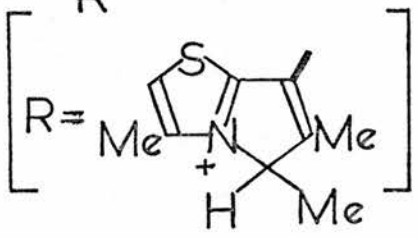
63a



65a-α



66a-β



NMR Spectrum of Compound (61a) in Trifluoroacetic Acid

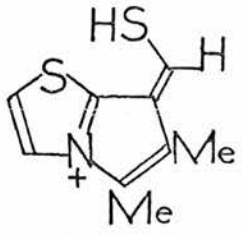
$\delta 1.86^{a+}$ (d b) $J_{5Me,5H}=7.0Hz$	5-Me (65a and 66a)
$\delta 2.23^{-}$ (q)	5-Me or 6-Me (64a)
$\delta 2.47^{+}$	6-Me (65a and 66a, equatorial R-groups)
$\delta 2.52^{-}$	6-Me (65a, axial R-group)
$\delta 2.61^{-}$ (d b)	6-Me or 5-Me (64a)
$\delta 2.70^{+}$	3-Me (65a and 66a)
$\delta 2.81^{-}$	3-Me (64a)
$\delta 5.41^{b+}$ (q b)	5-H (65a and 66a)
$\delta 6.29^{c+}$	axial trithiane ring protons (66a)
$\delta 6.34^{c-}$	axial trithiane ring protons (65a)
$\delta 6.48^{c-}$	equatorial trithiane ring proton (65a)
$\delta 7.55$ (b)	2-H (64a, 65a and 66a)
$\delta 8.60^{c-}$	7-CH(SH) (64a)

a - Signal collapsed to a singlet when the spectrum of compound (61a), in deuteriotrifluoroacetic acid, was recorded

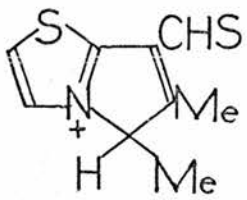
b - Signal disappeared when the spectrum of compound (61a), in deuterio-trifluoroacetic acid, was recorded

c - Signal disappeared when the spectrum of the corresponding deuterio-thioaldehyde (67a), in trifluoroacetic acid, was recorded

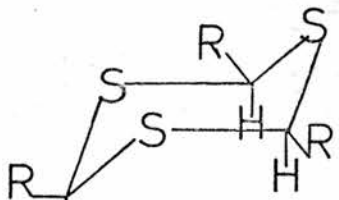
+ - Signal increases in intensity with time, - - Signal decreases in intensity with time



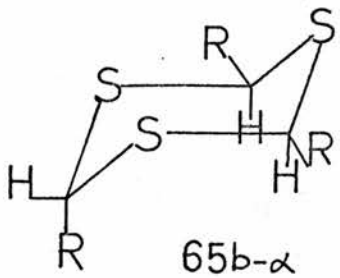
64b



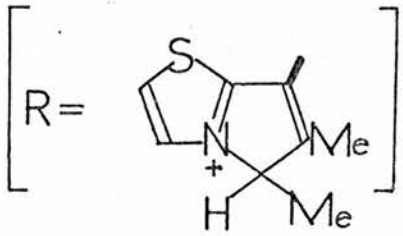
63b



66b-β



65b-α



NMR Spectrum of Compound (61b) in Trifluoroacetic Acid

$\delta 1.88^{a,b,+}$ (d)	$J_{5Me,5H}=7.2Hz$	5-Me (65b and 66b)
$\delta 2.29^{-}$ (q)		6-Me (64b)
$\delta 2.48^{-}$		6-Me (65b, axial R-group)
$\delta 2.52^{+}$ (b)		6-Me (65b and 66b, equatorial R-groups)
$\delta 2.58^{b,-}$		5-Me (64b)
$\delta 5.46^{c,d,+}$ (q b)		5-H (65b and 66b)
$\delta 6.36^{+}$		axial trithiane ring protons (66b)
$\delta 6.40^{-}$		axial trithiane ring protons (65b)
$\delta 6.53^{-}$		equatorial trithiane ring protons (65b)
$\delta 8.01^{+}$ (d)	$J_{2H,3H}=3.9Hz$	2-H (65b and 66b)
$\delta 8.04^{-}$ (d)	$J_{2H,3H}=3.9Hz$	2-H (64b)
$\delta 8.14^{-}$ (d)	$J_{3H,2H}=3.9Hz$	3-H (64b)
$\delta 8.31^{+}$ (d)	$J_{3H,2H}=3.9Hz$	3-H (65b and 66b, equatorial R-groups)
$\delta 8.32^{-}$ (d)	$J_{3H,2H}=3.9Hz$	3-H (65b, axial R-groups only)
$\delta 8.72^{-}$ (d)		5-C<u>H</u>(SH) (64b)

a-Signal collapsed to a singlet when the spectrum of compound (61b), in deuteriotrifluoroacetic acid, was recorded

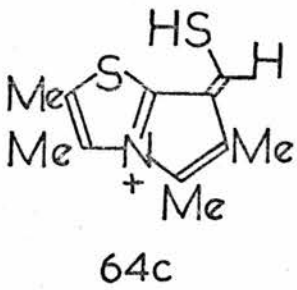
b-Signal disappeared when the spectrum of the corresponding 5-deuteriomethyl thioaldehyde (72), in trifluoroacetic acid, was recorded

c-Signal disappeared when the spectrum of compound (61b), in deuterio-trifluoroacetic acid, was recorded

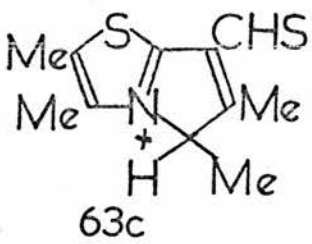
d-Signal collapsed to a broad singlet when sharpened with time when the spectrum of the corresponding 5-deuteriomethyl thioaldehyde (72), in trifluoroacetic acid, was recorded

\+ Signal increases in intensity with time

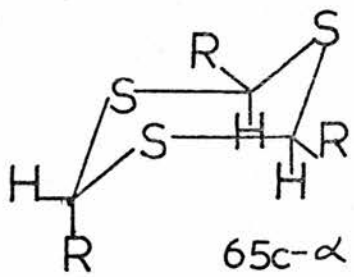
\- Signal decreases in intensity with time



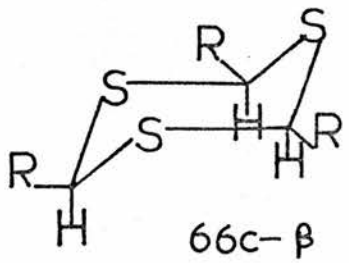
64c



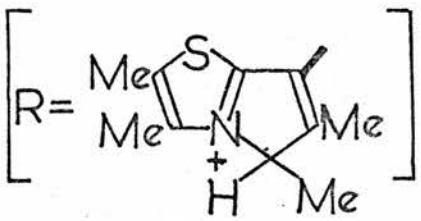
63c



65c-α



66c-β



NMR Spectrum of Compound (61c) in Trifluoroacetic Acid

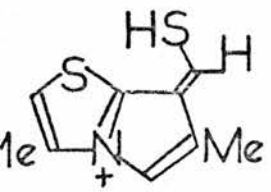
$\delta 1.83^{a+}$ (d)	$J_{5Me,5H}$=7.2Hz	5-Me (65c and 66c)
$\delta 2.21^{-}$ (q)		Exact assignment of signals uncertain
$\delta 2.44^{+}$ (b)		
$\delta 2.50^{-}$ (b)		
$\delta 2.58^{+}$ (b)		2-Me, 3-Me, and 6-Me (65c and 66c)
$\delta 2.62^{-}$ (b)		2-Me, 3-Me, 5-Me and 6-Me (64c)
$\delta 2.71^{-}$ (d)		
$\delta 5.36^{b,+}$ (d b)		5-H (65c and 66c)
$\delta 6.23^{+}$		axial trithiane ring protons (66c)
$\delta 6.28^{-}$		axial trithiane ring protons (65c)
$\delta 6.42^{-}$		equatorial trithiane ring protons (65c)
$\delta 8.50^{-}$		5-CH(SH) (64c)

a - Signal collapsed to a singlet when the spectrum of compound (61c), in deuteriotrifluoroacetic acid, was recorded

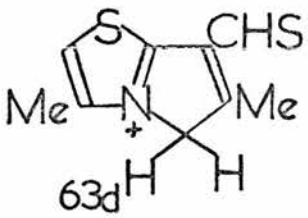
b - Signal disappeared when the spectrum of compound (61c), in deuteriotrifluoroacetic acid, was recorded

+ - Signal increases in intensity with time

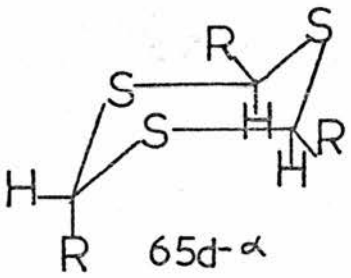
- - Signal decreases in intensity with time



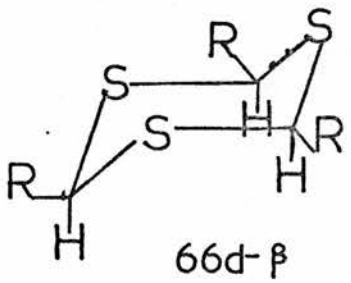
64d



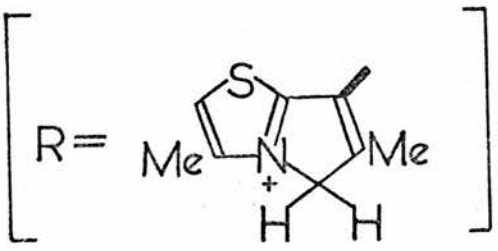
63d



65d-α



66d-β



NMR Spectrum of Compound (61d) in Trifluoroacetic Acid

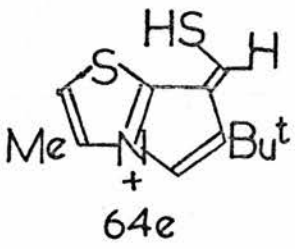
$\delta 2.39^{-}$ (b)	3- and 6-Me (65d, axial R-group)
$\delta 2.54$ (b)	3- or 6-Me (65d and 66d, equatorial R-groups)
$\delta 2.60$ (b)	6- or 3-Me (65d and 66d, equatorial R-groups)
$\delta 5.21^{a}$ (b)	5-CH_2 (65d and 66d)
$\delta 6.30^{b+}$	axial trithiane ring protons (66d)
$\delta 6.33^{b-}$	axial trithiane ring protons (65d)
$\delta 6.48^{b-}$	equatorial trithiane ring proton (65d)
$\delta 7.53$	2-H (65d and 66d)

a - Signal disappeared when the spectrum of compound (61d), in deuteriotrifluoroacetic acid, was recorded

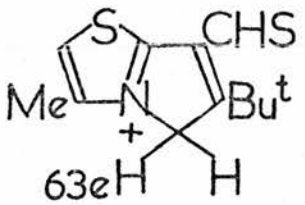
b - Signals disappeared when the spectrum of the corresponding deuteriothioaldehyde (67b), in trifluoroacetic acid, was recorded.

\+ - Signal increases in intensity with time

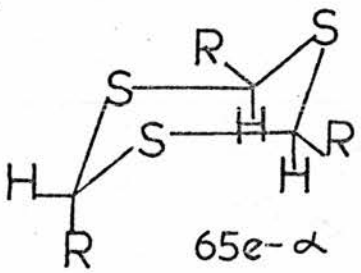
\- - Signal decreases in intensity with time



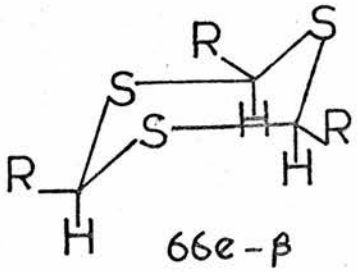
64e



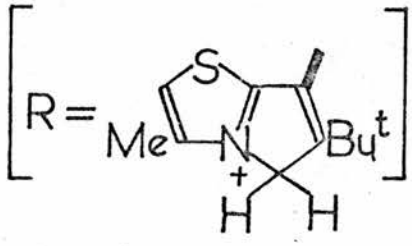
63e



65e-α



66e-β



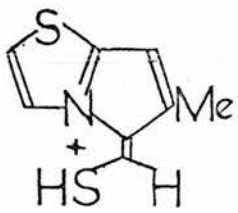
NMR Spectrum of Compound (61e) in Trifluoroacetic Acid

$\delta 1.50^-$	6-Bu^t (64e)
$\delta 1.55^+$	6-Bu^t (66e)
$\delta 1.58^-$	6-Bu^t (65e, equatorial R-groups)
$\delta 1.60^-$	6-Bu^t (65e, axial R-group)
$\delta 2.60^-$ (b)	3-Me (65e, axial R-group)
$\delta 2.62^+$ (b)	3-Me (65e and 66e, equatorial R-groups)
$\delta 2.68^-$ (b)	3-Me (64e)
$\delta 5.35^a$	5-CH_2 (65e and 66e)
$\delta 6.60^+$	axial trithiane ring protons (66e)
$\delta 6.62^-$	axial trithiane ring protons (65e)
$\delta 6.90^-$	equatorial trithiane ring protons (65e)
$\delta 7.37^-$	2-H (64e)
$\delta 7.57^-$	2-H (65e, axial R-group)
$\delta 7.58^+$	2-H (66e)
$\delta 7.60^-$	2-H (65e, equatorial R-groups)
$\delta 9.24^-$	5-C<u>H</u>(SH) (64e)

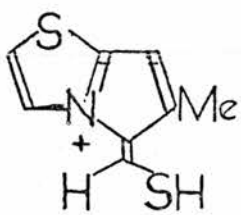
a - Signal disappeared when the spectrum of compound (61e), in deuteriotrifluoroacetic acid, was recorded

\+ - Signal increases in intensity with time

\- - Signal decreases in intensity with time



78a

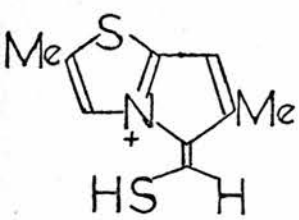


79a

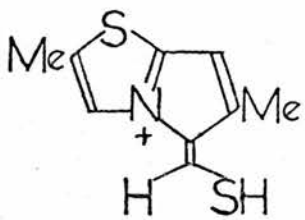
NMR Spectrum of Compound (77a) in Trifluoroacetic Acid

Syn-isomer (78a) - δ2.48[a] (d, $J_{6\text{-Me, 7H}}$=1.4Hz, 6-Me), δ7.03[b] (d b, 7-H), .78 (d, $J_{2H, 3H}$=4.1Hz, 2-H), δ8.42 [5-C<u>H</u>(SH)], δ8.49[c] (dd, $J_{3H, 2H}$=4.1Hz, H, 7H=0.6Hz, 3-H)

Anti-isomer (79a) - δ2.66[a] (d, $J_{6Me, 7H}$=1.4Hz, 6-Me), δ7.03[b] (d b, 7-H), .58 (d, $J_{2H, 3H}$=4.1Hz, 2-H), δ8.27[c] (dd, $J_{3H, 2H}$=4.1Hz, $J_{3H, 7H}$=0.6Hz, 3-H), .86[a] (d, $J_{C\underline{H}(SH), 7H}$=1.2Hz, 5-C<u>H</u>(SH))



78b



79b

NMR Spectrum of Compound (77b) in Trifluoroacetic Acid

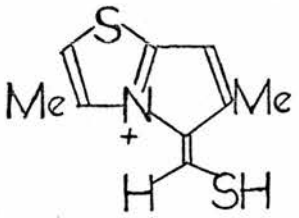
Syn-isomer (78b) - δ2.44[a] (d, $J_{6Me, 7H}$=1.4Hz, 6-Me), δ2.69 (d, $J_{2Me, 3H}$= 4Hz, 2-Me), δ6.94[b] (b, 7-H), δ8.19 (q, 3-H), δ8.43 [5-C<u>H</u>(SH)]

Anti-isomer (79b) - δ2.59 (d, $J_{2Me, 3H}$=1.4Hz, 2-Me), δ2.61[a] (d, $J_{6Me, 7H}$=1.4Hz, 6-Me), δ6.94[b] (b, 7-H), 95 (q, 3-H), δ8.73[a] [d, $J_{C\underline{H}(SH), 7H}$=1.2Hz, 5-C<u>H</u>(SH)]

Signal collapsed to a singlet when the spectrum of the thioaldehyde (77), in deuteriotrifluoroacetic acid, was recorded

Signal disappeared when the spectrum of the thioaldehyde (77), in deuteriotrifluoroacetic acid, was recorded

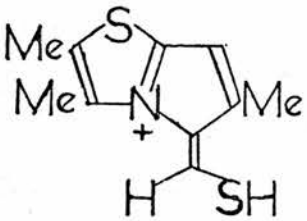
Signal collapsed to a doublet when the spectrum of the thioaldehyde (77), in deuteriotrifluoroacetic acid, was recorded



79c

NMR Spectrum of Compound (77c) in Trifluoroacetic Acid

Anti-isomer (79c) - δ2.68 (d, $J_{6Me,7H}$=1.4Hz, 6-Me), δ2.76 (d, $J_{3Me,2H}$=1.0Hz, 3-Me), δ7.06[a] (q b, 7-H), δ7.25 (q, 2-H), δ8.87[b] [d, $J_{C\underline{H}(SH),7H}$=0.6Hz, 5-C$\underline{H}$(SH)]



79d

NMR Spectrum of Compound (77d) in Trifluoroacetic Acid

Anti-isomer (79d) - δ2.52 (b, 2-Me), δ2.64 (b, 3- and 6-Me), δ6.98[a] (q b, 7-H), δ8.85 [d, $J_{C\underline{H}(SH),7H}$=0.6Hz, 5-C$\underline{H}$(SH)]

a - Signal disappeared after 48 hours when the spectrum of the thioaldehyde (77), in deuteriotrifluoroacetic acid, was recorded

b - Signal disappeared when the spectrum of the corresponding deuteriothioaldehyde (80), in trifluoroacetic acid, was recorded

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 or a Perkin-Elmer 402 spectrophotometer.

Infrared spectra were recorded with a Perkin-Elmer 621 spectrometer, and refer to solids dispersed in KBr discs.

Mass spectra were obtained with an AEI MS902 instrument.

^{1}H nmr spectra were recorded at ca 31.4°, unless otherwise stated, with a Varian HA100 spectrometer operating at 100 MHz. Solutions in deuteriochloroform were 0.4M; those in hexadeuteriodimethylsulphoxide, trifluoroacetic acid and deuteriotrifluoroacetic acid were 0.6M. When these concentrations could not be attained saturated solutions were employed. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane as internal reference. J values were measured on the 100 Hz scale. Multiplicity refers to the appearance of spectra on the 100 Hz scale. Unless otherwise stated (d=doublet, t=triplet, q=quartet dd=double doublet, m=multiplet, and b=broad peak) chemical shift values refer to singlet absorptions.

Carbon, hydrogen and nitrogen elemental microanalyses were carried out by Mr. J. Bews, Department of Chemistry, University of St. Andrews. Sulphur elemental analysis were carried out by Dr. A. Bernhardt, Mulheim, West Germany.

Procedures Criteria used in the identification of products included melting points, tlc behaviour, and nmr and mass spectra.

Thin layer chromatography (tlc) was carried out with silica (MN Kieselgel-G) coated plates (ca 0.25 mm thick). Alumina for column chromatography was Laporte type H (100-200 mesh), unless otherwise stated. Silica for chromatography was Sorbsil Silica Gel. Solvent mixtures are described in ratios by volume. Alumina for dry column chromatography was 'Woelm' neutral grade, activity 111/20 mm.

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

Materials "Petroleum" refers to petroleum ether of boiling range 40-60° and "ether" refers to diethyl ether. Acetic acid, acetic anhydride, acetone, cyclohexane, ethanol, methanol, n-hexane and petroleum were all redistilled commercial solvents.

Ether and tetrahydrofuran were refluxed over sodium wire for 1 hour and then distilled to give the dry solvents. These solvents were stored over sodium wire. The crude solvents were pre-dried over calcium chloride for ca 3 days before refluxing and distilling.

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 and then distilled.

Methylene chloride and 1,2-dichloroethane were refluxed over phosphoric anhydride for 1 hour and then distilled.

Acetonitrile was refluxed over sodium hydride (50% dispersion in oil, 2 g/litre) for 30 minutes, distilled, then refluxed over phosphoric anhydride for 1 hour, distilled and redistilled.

Dimethylformamide was dried for ca 1 week over powdered calcium hydride and then distilled at 15 mm Hg.

Aniline, benzyl chloride, t-butylamine, 5-formylisothiazole, N,N-dimethylhydrazine, methylhydrazine, phenylhydrazine, phenylisothiocyanate, phosphoryl chloride and triethylamine were all distilled commercial reagents. Methylfluorosulphonate was a distilled commercial reagent and was stored in a polythene bottle. Carbon disulphide was analar grade.

Aqueous methylamine was 25-30% (w/v) methylamine. Perchloric acid refers to 70-72% (w/w) perchloric acid.

Aqueous 2M-sodium hydrogen sulphide solutions were prepared by saturating aqueous 2M-sodium sulphide solutions with hydrogen sulphide. Potassium selenosulphate was prepared by the reported method[146]. Hydrogen disulphide was prepared as described by Feher, Laue, and Winkhaus[147]. Dimethylthioformamide was prepared by the method of Willstätter and Wirth[148], modified by Pettit and Garson[149]. Phenyl lithium was prepared by the reported method[150]. The phenyl lithium solution was standardised by adding a 5 ml aliquot to water and titrating the resulting solution with standard 0.1 N-hydrochloric acid, using phenolphthalein as an indicator.

A Synthesis of 6a-Thia-1,2,6-triazapentalenes and Related Compounds from 6-Oxa-6a-thia-1,2-diazapentalenes

3,4-Dimethyl-1-phenyl-(4a) and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) were prepared by the method described by Christie[41].

(1) Preparation of 5-(2-chlorovinyl)-1,2,3,-thiadiazolium perchlorates

Method A (Using dimethylformamide)

Phosphoryl chloride (0.5 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1,2-diazapentalene (5 mmol) in dimethylformamide (10 ml) at 50° and the solution was stirred at that temperature for 10 minutes before being cooled to room temperature. Ether (ca 250 ml) was then gradually added to the solution, separating an oil. The ether was then decanted off and the residual oil was washed with ether. The ether washings were then decanted off and the oil was taken up in acetic acid (25 ml). Perchloric acid (1.26 ml, 15 mmol) was then added to the solution and the resulting perchlorate salt was precipitated from solution by gradual addition of ether. The salt was then filtered, washed thoroughly with ether, and dried in vacuo over potassium hydroxide.

Method B (Using 1,2-dichloroethane)

As method A except that 1,2-dichloroethane (10 ml) was used in place of dimethylformamide.

4-Methyl-5-(1 -methyl-2 -chlorovinyl)-2-phenyl-1, 2, 3-thiadiazolium perchlorate (6a)

Method A was used with 3, 4-dimethyl-1-phenyl- 6-oxa-6a-thia-1 ,2 -diazapentalene (4a) (1.160 g, 5 mmol), and gave 4-methyl-5-(1 -methyl-2 -chlorovinyl)-2-phenyl-1, 2, 3-thiadiazolium perchlorate (6a) (1.210 g, 69%). A portion of this salt (ca 0.2 g) was recrystallised as pale yellow prisms from acetic acid for characterisation, mp = 115-117°

Found C, 41.34; H, 3.69; N, 7.81 %

$C_{12}H_{12}NSClO_4$ requires C, 41.04; H, 3.45; N, 7.98 %

[Nmr spectrum;CF_3COOH, δ2.46 (3H, d $J_{1'\text{-Me}, 2'\text{-H}}$=1.6 Hz, 1'-Me), δ2.94 (3H, 4-Me), δ7.25 (1H, q, 2'-H), δ7.63-7.73 and 7.89-8.04 (5H, m, 2-Ph) signals due to minor isomer, δ2.74 (d, $J_{1'\text{-Me}, 2'\text{-H}}$=1.6 Hz, 1'-Me), δ3.02 (4-Me)]

[UV spectrum;methanol, λ_{max}(nm) 372, 345(sh), 245(sh), 208 (log ε 4.08, 3.95, 3.63, 4.15)]

Method B was used with 3, 4-dimethyl-1-phenyl- 6-oxa-6a-thia-1, 2-diazapentalene (4a) (1.160 g, 5 mmol) and gave 4-methyl-5-(1 -methyl-2 -chlorovinyl)-2-phenyl-1, 2, 3-thiadiazolium perchlorate (6a) (1.479 g, 84%). A portion of this salt (ca 0.2 g) was recrystallised as pale yellow prisms from acetic acid for characterisation. Product identical (nmr spectrum) with sample of salt (6a) prepared by method A.

4, 5, 6, 7-Tetrahydro-7-chloromethylene-2-phenylbenzo[d][1, 2, 3]-thiadiazolium perchlorate (6b)

Method A was used with 3, 4-trimethylene-1 -phenyl-6 -oxa-6a-thia-1, 2-diazapentalene (4b) (1.220 g, 5 mmol) and gave

4,5,6,7-tetrahydro-7-chloromethylene-2-phenylbenzo[d][1,2,3]-thiadiazolium perchlorate (6b) (1.743 g, 96%). A portion of this salt (ca 0.2 g) was recrystallised as pale yellow prisms from acetic acid, mp = 201-203° (sample chars on melting).

Found C, 43.01; H, 3.34; N, 7.79%

$C_{13}H_{12}N_2SClO_4$ requires C, 42.99; H, 3.33; N, 7.71%

[Nmr spectrum; CF_3COOH, δ2.25 (2H, q, 5-CH_2), δ3.00 (2H, t, 6-CH_2), δ3.46 (2H, t, 4-CH_2), δ7.25 (1H, t, 7-CCl<u>H</u>), δ7.66-7.80 and 8.00-8.10 (5H, m, 2-Ph)]

[UV spectrum; methanol, λ_{max} (nm) 397 (br), 240 (sh), 207 (log ε 4.21, 3.75, 4.12)]

Method B was used with 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) and gave 4,5,6,7-tetrahydro-7-chloromethylene-2-phenylbenzo[d][1,2,3]thiadiazolium perchlorate (6b) (1.727 g, 95%). A portion of this salt (ca 0.2 g) was recrystallised as pale yellow prisms from acetic acid. Product identical (nmr spectrum) with sample of salt (6b) prepared by method A.

(2) Synthesis of 1,6-Diaryl-6a-thia-1,2,6-triazapentalenes

General Procedure

Method A - Phosphoryl chloride (0.5 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1,2-diazapentalene (5 mmol) in dimethylformamide (25 ml) at 50° and the solution was stirred at that temperature for 10 minutes. The aromatic amine (10 mmol) in dimethylformamide (10 ml) was then added and the solution was stirred for a further 10 minutes at 50°C. The solution was then cooled,

diluted with water and extracted with benzene. The extracts were washed with water (x6), dried (Na_2SO_4) and evaporated. Chromatography (alumina 40 x 3.2 cm) of the residue with benzene brought through red eluates which afforded the 6a-thia-1,2,6-triazapentalene. Further elution with benzene-ether (4:1) gave yellow eluates which afforded the recovered 6-oxa-6a-thia-1,2-diazapentalene.

Method A' - Procedure as in method A, except that chromatography and subsequent procedure is described for individual cases.

Method B - Phosphoryl chloride (0.50 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1,2-diazapentalene (5 mmol) in dimethylformamide (25 ml) at 50° and the solution was stirred at that temperature for 10 minutes. p-Nitroaniline (1.381 g, 10 mmol) in dimethylformamide (25 ml) was then added and the solution was stirred for a further hour at 50°C. The solution was then cooled, diluted with water and extracted with benzene. The extracts were washed with water (x6), dried (Na_2SO_4) and evaporated. Subsequent procedure is described for individual cases.

3,4-Dimethyl-1,6-diphenyl-6a-thia-1,2,6-triazapentalene (1a)

Method A was used with 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) and aniline (0.92 ml, 10 mmol, added to the solution neat) and gave 3,4-dimethyl-1,6-diphenyl-6a-thia-1,2,6-triazapentalene (1a) (1.357g, 88%) as red needles from cyclohexane, mp = 128-129° ,

Found C, 70.50; H, 5.65; N, 13.69; S, 10.21%

$C_{18}H_{17}N_3S$ requires C, 70.33; H, 5.58; N, 13.67; S, 10.43%

[Nmr spectrum; see Appendix A, table 1]

[UV spectrum; see Appendix B, table 1]

and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (0.120 g, 11%) (identified by tlc).

3,4-Trimethylene-1,6-diphenyl-6a-thia-1,2,6-triazapentalene (1b)

Method A was used with 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) and aniline (0.92 ml, 10 mmol, added to the solution neat) and gave 3,4-trimethylene-1,6-diphenyl-6a-thia-1,2,6-triazapentalene (1b) (1.541 g, 97%) as red cubes from cyclohexane, mp = 146-147°C.

Found C, 71.04; H, 5.27; N, 13.24; S, 9.96%

$C_{19}H_{17}N_3S$ requires C, 71.44; H, 5.37; N, 13.15; S, 10.04%

[Nmr spectrum; see Appendix A, table 1]

[UV spectrum; see Appendix B, table 1]

(No 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) recovered from the reaction)

6-p-Methoxyphenyl-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1c)

Method A was used with 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) and p-anisidine (1.232 g, 10 mmol) and gave 6-p-methoxyphenyl-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1c) (1.419 g, 84%) as red needles from cyclohexane, mp = 115-116°,

Found C, 67.66; H, 5.68; N, 12.36%

$C_{19}H_{19}N_3SO$ requires C, 67.63; H, 5.68; N, 12.45%

[Nmr spectrum; see Appendix A, table 1]

[UV spectrum; see Appendix B, table 1]

and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (0.052 g, 5%) (identified by tlc).

6-p-Methoxyphenyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1d)

Method A was used with 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5mmol) and p-anisidine (1.232 g, 10 mmol) and gave 6-p-methoxyphenyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1d) (1.601 g, 92%) as red needles from cyclohexane, mp = 131-132.5°,

Found C, 68.64; H, 5.28; N, 11.98%

$C_{20}H_{19}N_3SO$ requires C, 68.74; H, 5.48; N, 12.02%

[Nmr spectrum; see Appendix A, table 1]

[UV spectrum; see Appendix B, table 1]

and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (0.050 g, 4%) (identified by tlc).

3,4-Dimethyl-6-p-nitrophenyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1e)

Method B was used and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) gave a dark red residue on evaporation of the benzene extracts. The residue was recrystallised from benzene and gave the thiatriazapentalene (1e) (1.075 g) as

brown needles. The mother liquors were evaporated and chromatography (alumina 60 x 2.7 cm) of the residue with benzene brought through red eluates which afforded a further crop of the thiatriazapentalene (1e) (0.094 g). Continued elution with benzene gave red eluates which afforded a mixture of the thiatriazapentalene (1e) and the oxathiadiazapentalene (4a). Elution with benzene-ether (4:1) brought through yellow eluates which gave the oxathiadiazapentalene (4a) (0.103 g). The mixture of compounds (1e) and (4a) was rechromatographed (alumina 40 x 3.2 cm) and elution with benzene gave purple eluates which afforded a third crop of the thiatriazapentalene (1e) (0.107 g). Further elution with benzene-ether (4:1) gave yellow eluates which gave a second crop of the oxathiadiazapentalene (4a) (0.092 g).

Total yield of 3,4-dimethyl-6-p-nitrophenyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1e) (1.276 g, 72%) as brown needles from benzene, mp = 215-216° .

Found C, 61.40; H, 4.63; N, 15.82%

$C_{18}H_{16}N_4O_2S$ requires C, 61.35; H, 4.58; N, 15.90%

M^+ at m/e 352

[UV spectrum; see Appendix B, table 1]

Total yield of recovered 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (0.195 g, 17%) (identified by tlc).

3,4-Trimethylene-6-p-nitrophenyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1f)

Method B was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) gave a dark red residue on

evaporation of the benzene extracts. Chromatography (alumina 25 x 3.7 cm) of the residue with benzene gave purple eluates which afforded 3,4-trimethylene-6-p-nitrophenyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1f) (1.562 g, 86%) as brown prisms from benzene, mp = 217-218° .

Found C, 62.43; H, 4.36; N, 15.13%

$C_{19}H_{16}N_4O_2S$ requires C, 62.62; H, 4.43; N, 15.37%

M^+ at m/e 364

[UV spectrum; see Appendix B, table 1]

Further elution with benzene-ether (4:1) gave yellow eluates which afforded recovered 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (0.131 g, 11%) (identified by tlc).

6-o-Aminophenyl-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1g)

Method A' was used and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) and o-phenylenediamine (1.081 g, 10 mmol) gave a dark red residue on evaporation of the benzene extracts. Chromatography (alumina 40 x 3.2 cm) of the residue with benzene brought through dark red eluates which afforded 6,6'-o-phenylene-bis-(3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene) (12a) (0.373 g, 28%) as dark red prisms from n-hexane, mp = 200-202° .

Found C, 66.98; H, 5.23; N, 15.58%

$C_{30}H_{28}N_6S_2$ requires C, 67.14; H, 5.26; N, 15.67%

[Nmr spectrum; see Appendix A, table 2]

M^+ at m/e 536

[UV spectrum; see Appendix B, table 1]

Further elution with benzene-ether (1:1) gave red eluates which afforded a mixture of the thiatriazapentalenes (1g) and (13a). Chromatography (silica 30 x 3.7 cm) of the mixture with benzene gave red eluates which afforded 6-o-aminophenyl-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1g) as red prisms from cyclohexane, mp = 182-184°. (Yield 0.773 g, 46%)

Found C, 66.82; H, 5.66; N, 17.47%

$C_{18}H_{18}N_4S$ requires C, 67.05; H, 5.63; N, 17.38%

[Nmr spectrum; see Appendix A, table 1]

M^+ at m/e 322

ν_{max} (KBr disc) 3400 (N-H) cm^{-1}

[UV spectrum; see Appendix B, table 1]

Further elution with methanol gave orange eluates which afforded 3,4-dimethyl-6-o-dimethylaminomethyleneaminophenyl-1-phenyl-6a-thia-1,2,6-triazapentalene (13a) (0.110 g, 5.8%) as red prisms from cyclohexane, mp = 160-161°.

Found C, 66.64; H, 6.27; N, 18.58%

$C_{21}H_{23}N_5S$ requires C, 66.82; H, 6.14; N, 18.55%

[Nmr spectrum; see Appendix A, table 1]

M^+ at m/e 377

[UV spectrum; see Appendix B, table 1]

6-o-Aminophenyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1h)

Method A' was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) and o-phenylene diamine (1.081 g, 10 mmol) gave a dark red residue on evaporation of the

benzene extracts. Chromatography (alumina 40 x 3.2 cm) of the residue with benzene brought through dark red eluates which afforded 6,6'-o-phenylene-bis(3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene) (12b) (0.505 g, 36%) as red prisms from n-hexane, mp = 207-209° .

Found C, 68.25; H, 5.01; N, 14.90%

$C_{32}H_{28}N_6S_2$ requires C, 68.54; H, 5.03; N, 14.99%

[Nmr spectrum; see Appendix A, table 2]

[UV spectrum; see Appendix B, table 1]

Further elution with benzene-ether (1:1) gave red eluates which afforded a mixture of thiatriazapentalenes (1h) and (13b). Chromatography (silica 30 x 3.7 cm) with benzene gave red eluates which afforded 6-o-aminophenyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1h) (0.637 g, 54%) as brown needles from cyclohexane, mp = 152-153.5° .

Found C, 68.54; H, 5.58; N, 16.43%

$C_{19}H_{18}N_4S$ requires C, 68.23; H, 5.43; N, 16.76%

[Nmr spectrum; see Appendix A, table 1]

ν_{max} (KBr disc) 3430 (N-H) cm^{-1}

[UV spectrum; see Appendix B, table 1]

Further elution with methanol gave orange eluates which afforded 3,4-trimethylene-6-o-dimethylaminomethyleneaminophenyl-1-phenyl-6a-thia-1,2,6-triazapentalene (13b) (0.030 g, 1.5%)

M^+ at m/e 389.

(An insufficient quantity of compound (13b) was isolated to obtain an nmr spectrum, a uv spectrum, and a C,H,N elemental microanalysis.)

(3) Preparation of 1, 3, 5-Trinitrobenzene Complexes of 6a-Thia-1, 2, 6-triazapentalenes (1a-d)

Trinitrobenzene Complex of 3, 4-Dimethyl-1, 6-diphenyl-6a-thia-1, 2, 6-triazapentalene (3:2) (16a)

A boiling solution of 1, 3, 5-trinitrobenzene (0.320 g, 1.5 mmol) in ethanol (5 ml) was added to a boiling solution of 3, 4-dimethyl-1, 6-diphenyl-6a-thia-1, 2, 6-triazapentalene (1a) (0.307 g, 1 mmol) in ethanol (20 ml) and the resulting solution was allowed to cool to room temperature. The resulting precipitate was filtered, dried in vacuo over P_2O_5, and shown to be a mixture of the complex (16a) and unreacted base (1a) by nmr. The mother liquors were evaporated to low volume and the resulting solid was filtered, dried in vacuo over P_2O_5 and shown to be the 3:2 complex (16a) by nmr. The trinitrobenzene complex of 3, 4-dimethyl-1, 6-diphenyl-6a-thia-1, 2, 6-triazapentalene (0.095 g, 15%) was obtained as purple prisms, mp = 116-118° .

Found C, 51.53; H, 3.36; N, 16.73%

$C_{54}H_{43}N_{15}O_{18}S_2$ requires C, 51.72; H, 3.46; N, 16.76%

[Nmr spectrum ($CDCl_3$); δ2.54 (6H, d, $J_{4Me, 5H}$=0.5Hz, 4-Me), δ2.71 (6H, 3-Me), δ6.92-7.44 (20H, m, 1- and 6-Ph), δ7.98 (2H, q, 5-H), δ9.10 (9H, trinitrobenzene protons)]

Trinitrobenzene Complex of 3, 4-Trimethylene-1, 6-diphenyl-6a-thia-1, 2, 6-triazapentalene (1:1) (16b)

A boiling solution of 1, 3, 5-trinitrobenzene (0.213 g, 1 mmol) in ethanol (5 ml) was added to a boiling solution of 3, 4-trimethylene-1, 6-diphenyl-6a-thia-1, 2, 6-triazapentalene (1b) (0.319 g, 1 mmol)

in ethanol (30 ml) and the resulting solution was allowed to cool to room temperature. The resulting precipitate was filtered, dried in vacuo over P_2O_5, and shown to be a mixture of the complex (16b) and unreacted base (1b) by nmr. The mother liquors were evaporated to low volume and the resulting solid was filtered, dried in vacuo over P_2O_5, and shown to be the 1:1 complex (16b) by nmr. The trinitrobenzene complex of 3,4-trimethylene-1,6-diphenyl-6a-thia-1,2,6-triazapentalene (0.076 g, 13%) was obtained as black prisms, mp = 126.5-127.5° .

Found C, 56.28; H, 3.62; N, 15.98%

$C_{25}H_{20}N_6O_6S$ requires C, 56.39; H, 3.79; N, 15.78%

[Nmr spectrum ($CDCl_3$); δ2.12 (2H, q, β-CH_2), δ2.82 (2H, t, γ-CH_2), δ3.02 (2H, t, α-CH_2), δ6.95-7.46 (10H, m, 1- and 6-Ph), δ8.15 (1H, 5-H), δ9.10 (3H, trinitrobenzene protons)]

Trinitrobenzene Complex of 6-p-Methoxyphenyl-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1:1) (16c)

A boiling solution of 1,3,5-trinitrobenzene (0.213 g, 1 mmol) in ethanol (5 ml) was added to a boiling solution of 6-p-methoxyphenyl-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1c) (0.337 g, 5 mmol) in ethanol (30 ml) and the solution was allowed to cool to room temperature. The resulting solid was filtered, dried in vacuo over P_2O_5, and shown to be the (1:1) complex (16c) by nmr. The trinitrobenzene complex of 6-p-methoxyphenyl-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (0.465 g, 85%) was obtained as black prisms, mp = 135-136° .

Found C, 54.77; H, 3.88; N, 15.11%

$C_{25}H_{22}N_6O_7S$ requires C, 54.54; H, 4.03; N, 15.27%

[Nmr spectrum ($CDCl_3$); δ2.58 (3H, b, 4-Me), δ2.76 (3H, 3-Me), δ3.81 (3H, 6-C_6H_4OMe), δ6.86-7.52 (9H, m, 1-Ph and 6-C_6H_4OMe), δ7.96 (1H, 5-H), δ9.07 (3H, trinitrobenzene protons)]

Trinitrobenzene Complex of 6-p-Methoxyphenyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1:1) (16d)

A boiling solution of 1,3,5-trinitrobenzene (0.213 g, 1 mmol) in ethanol (5 ml) was added to a boiling solution of 6-p-methoxyphenyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1d) (0.349 g, 1 mmol) in ethanol (40 ml) and the solution was allowed to cool to room temperature. The resulting solid was filtered, dried in vacuo over P_2O_5, and shown to be the 1:1 complex (16d) by nmr. The trinitrobenzene complex of 6-p-methoxyphenyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (0.494 g, 88%) was obtained as black prisms, mp = 155.5-157.5° .

Found C, 55.64; H, 3.92; N, 14.88%

$C_{26}H_{22}N_6O_7S$ requires C, 55.51; H, 3.94; N, 14.94%

[Nmr spectrum ($CDCl_3$); δ2.16 (2H, q, β-CH_2), δ2.84 (2H, t, γ-CH_2), δ3.04 (2H, t, α-CH_2), δ3.82 (3H, 6-MeOC_6H_4), δ6.85-7.45 (9H, m, 1-Ph and 6-MeOC_6H_4), δ8.14 (1H, 5-H), δ9.19 (3H, trinitrobenzene protons)]

(4) Synthesis of 1-Aryl-6-alkyl-6a-thia-1,2,6-triazapentalenes

General Procedure

Phosphoryl chloride (0.50 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1,2-diazapentalene (5 mmol) in

dimethylformamide (25 ml) at 50° and the solution was stirred at that temperature for 10 minutes before being cooled to room temperature. Aqueous methylamine (25 ml) was then added and the solution was stirred for a further 10 minutes at room temperature before being diluted with water and extracted with benzene. The extracts were washed with water (x6), dried (Na_2SO_4) and evaporated. Chromatography (alumina, 40 x 2.7 cm) of the residue with petroleum-benzene (2:1) gave red eluates which afforded the 6, 6a-dithia-1, 2-diazapentalene. Further elution with benzene gave orange eluates which afforded the 6a-thia-1, 2, 6-triazapentalene. Continued elution with benzene-ether (4:1) gave yellow eluates which afforded recovered 6-oxa-6a-thia-1, 2-diazapentalene.

3, 4, 6-Trimethyl-1-phenyl-6a-thia-1, 2, 6-triazapentalene (1i)

The general procedure was used and 3, 4-dimethyl-1-phenyl-6-oxa-6a-thia-1, 2-diazapentalene (4a) (1.160 g, 5 mmol) gave 3, 4-dimethyl-1-phenyl-6, 6a-dithia-1, 2-diazapentalene (2a) (0.089 g, 14%) [Nmr spectrum of product identical with nmr spectrum of an authentic sample of compound (2a)[100]]; 3, 4, 6-trimethyl-1-phenyl-6a-thia-1, 2, 6-triazapentalene (1i) (0.286 g, 23%), mp = 75-77° (lit. 70.5-71.5°[41]) [Nmr spectrum of product identical with nmr spectrum of an authentic sample of compound (1i)[41]]; and 3, 4-dimethyl-1-phenyl-6-oxa-6a-thia-1, 2-diazapentalene (4a) (0.041 g, 3.5%) (identified by tlc).

6-Methyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1j)

The general procedure was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) gave 3,4-trimethylene-1-phenyl-6,6a-dithia-1,2-diazapentalene (2b) (0.005 g, 0.8%) (identified by tlc), and 6-methyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1j) (0.583 g, 44%), mp = 100-102° (lit. 102-103.5° [41]). [Nmr spectrum of product identical with nmr spectrum of an authentic sample of compound (1j)[41]] (No 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) recovered from the reaction.)

Attempted Synthesis of 6-t-Butyl-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1k)

Phosphoryl chloride (0.5 ml, 5.5 mmol) was added to a solution of 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) in dimethylformamide (25 ml) at 50°C and the solution was stirred at that temperature for 10 minutes before being cooled to room temperature. t-Butylamine (1.05 ml, 10 mmol) in dimethylformamide (25 ml) was then added to the solution. The solution was then diluted with water and extracted with benzene. The extracts were washed with water (x6), dried (Na_2SO_4) and evaporated leaving a black intractable tar. The reaction was abandoned.

(5) Synthesis of 6a-Thia-1,2,6-triazapentalenes with 6-Substituents other than Alkyl and Aryl

Method A

Phosphoryl chloride (0.5 ml, 5.5 mmol) was added to a solution

of 6-oxa-6a-thia-1, 2-diazapentalene (5 mmol) in dimethylformamide (25 ml) at 50°C and the mixture was stirred at that temperature for 10 minutes before being cooled to room temperature. A solution of hydroxylamine hydrochloride (3.475 g, 50 mmol) and sodium carbonate (3.150 g, 30 mmol) in water (25 ml) was then added and the solution was stirred for 30 minutes at room temperature. The solution was then diluted with water and extracted with benzene. The extracts were washed with water (x6), dried (Na_2SO_4), and evaporated. Chromatography (alumina, Merck grade II-III, 30 x 3.2 cm) of the residue with benzene gave red eluates which afforded the 6, 6a-dithia-1, 2-diazapentalene. Further elution with benzene-ether (4:1) gave yellow eluates which afforded the 6-oxa-6a-thia-1, 2-diazapentalene. Continued elution with ether-methanol (50:1) gave yellow eluates which afforded the 6a-thia-1, 2, 6-triazapentalene.

6-Hydroxy-3, 4-dimethyl-1-phenyl-6a-thia-1, 2, 6-triazapentalene (11)

Method A was used and 3, 4-dimethyl-1-phenyl-6-oxa-6a-thia-1, 2-diazapentalene (4a) (1.160 g, 5 mmol) gave 3, 4-dimethyl-1-phenyl-6, 6a-dithia-1, 2-diazapentalene (2a) (0.121 g, 20%), [Nmr spectrum of product identical to nmr spectrum of an authentic sample of compound (2a)[100]], 3, 4-dimethyl-1 -phenyl-6-oxa-6a-thia-1, 2-diazapentalene (4a) (0.331 g, 29%) (identified by tlc), and 6-hydroxy-3, 4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene(11) (0.349 g, 28%), as orange prisms from cyclohexane, mp = 113-115° .

Found C, 58.17; H, 5.27; N, 16.91%

$C_{12}H_{13}N_3SO$ requires C, 58.28; H, 5.30; N, 16.99%

[Nmr spectrum; see Appendix A, table 3]

ν_{max} (KBr disc) 3340 (O-H) cm^{-1}

[UV spectrum; see Appendix B, table 1]

6-Hydroxy-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1m)

Method A was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) gave 3,4-trimethylene-1-phenyl-6,6a-dithia-1,2-diazapentalene (2b) (0.048 g, 8%) (identified by tlc), 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (0.432 g, 35%) (identified by tlc), and 6-hydroxy-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1m) (0.663 g, 51%) as orange prisms from n-hexane, mp = 126-128° .

Found C, 59.97; H, 5.02; N, 16.21%

$C_{13}H_{13}N_3SO$ requires C, 60.21; H, 5.05; N, 16.20%

[Nmr spectrum; see Appendix A, table 3]

ν_{max} (KBr disc) 3290 (O-H) cm^{-1}

[UV spectrum; see Appendix B, table 1]

Method B

Phosphoryl chloride (0.50 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1,2-diazapentalene (5 mmol) in dimethylformamide (25 ml) at 50° and the solution was stirred at that temperature for 10 minutes before being cooled to room temperature. A solution of methoxyamine hydrochloride (4.175 g, 50 mmol) and sodium carbonate (3.150 g, 30 mmol) in water (25 ml) was then added and the solution was stirred for 30 minutes at room temperature. The solution was

then diluted with water and extracted with benzene. The extracts were washed with water (x6), dried (Na_2SO_4), and evaporated. Chromatography (alumina 10 x 3.7 cm) of the residue with benzene gave yellow eluates which afforded the 6a-thia-1,2,6-triazapentalene.

6-Methoxy-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1n)

Method B was used and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) gave 6-methoxy-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1n) (1.246 g, 95%) as red prisms from petroleum, mp = 89-91° .

Found C, 59.85; H, 5.85; N, 15.96%

$C_{13}H_{15}N_3SO$ requires C, 59.75; H, 5.79; N, 16.07%

[Nmr spectrum; see Appendix A, table 3]

[UV spectrum; see Appendix B, table 1]

6-Methoxy-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1o)

Method B was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) gave 6-methoxy-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1o) (1.349 g, 99%) as red cubes from petroleum, mp = 78-80° .

Found C, 61.64; H, 5.59; N, 15.39%

$C_{14}H_{15}N_3SO$ requires C, 61.51; H, 5.53; N, 15.37%

[Nmr spectrum; see Appendix A, table 3]

[UV spectrum; see Appendix B, table 1]

Attempted Synthesis of 6-Dimethylamino-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1p)

Phosphoryl chloride (0.50 ml, 5.5 mmol) was added to a solution of 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) in dimethylformamide (25 ml) at 50° and the solution was stirred at that temperature for 10 minutes before being cooled to room temperature. N,N-dimethylhydrazine (0.76 ml, 10 mmol) in dimethylformamide (25 ml) was then added and the resulting solution was stirred for 10 minutes at room temperature. The solution was then diluted with water and extracted with benzene. The extracts were washed with water (x 6), dried (Na_2SO_4), and evaporated. The product decomposed on attempted chromatography and the reaction was abandoned.

Attempted Synthesis of 6-Anilino-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1q)

Procedure as in attempted synthesis of 6a-thia-1,2,6-triazapentalene (1p) replacing N,N-dimethylhydrazine by phenylhydrazine (1.00 ml, 10 mmol). The resulting product decomposed on attempted chromatography and the reaction was abandoned.

Method C

Phosphoryl chloride (0.50 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1,2-diazapentalene (5 mmol) in dimethylformamide (25 ml) at 50°C and the solution was stirred at that temperature for 10 minutes. The hydrazine (10 mmol or 25 mmol) in dimethylformamide (25 ml) was then added and the resulting solution was stirred for a

further 10 minutes at 50°C. Water (ca 250 ml) was then added and the resulting solid was filtered, washed well with water, and dried in vacuo over P_2O_5. Subsequent procedure is given for individual cases.

3,4-Dimethyl-6-p-nitrophenylamino-1-phenyl-6a-thia-1,2,6-triazapentalene (1r)

Method C was used and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) and p-nitrophenylhydrazine (1.531 g, 10 mmol) gave a black solid which was recrystallised from ethanol affording the 6a-thia-1,2,6-triazapentalene (1r) (0.531 g) as black prisms. The mother liquors were evaporated to low volume and then reheated to 80°. On cooling, the solution was filtered giving a further crop of compound (1r) (0.344 g). The mother liquors were then evaporated and chromatography (alumina 15 x 3.2 cm) of the residue with benzene gave pale purple eluates which were discarded. Further elution with benzene-ether (4:1) gave yellow eluates which afforded 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (0.221 g, 19%) (identified by tlc). Continued elution with ether-methanol (100:1) gave red eluates which afforded the 6a-thia-1,2,6-triazapentalene (1r) (0.048 g).

Total yield of 3,4-dimethyl-6-p-nitrophenylamino-1-phenyl-6a-thia-1,2,6-triazapentalene (1r) (1.412 g, 77%) as black prisms from ethanol, mp = 185-186°.

Found C, 58.77; H, 4.64; N, 19.06%

$C_{18}H_{17}N_5O_2S$ requires C, 58.84; H, 4.66; N, 19.06%

[Nmr spectrum; see Appendix A, table 3]

M^+ at m/e 367

ν_{max} (KBr disc) 3270 (N-H) cm^{-1}

[UV spectrum; see Appendix B, table 1]

3,4-Trimethylene-6-p-nitrophenylamino-1-phenyl-6a-thia-1,2,6-triazapentalene (1s)

Method C was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) and p-nitrophenylhydrazine (1.531 g, 10 mmol) gave a black solid which was recrystallised from ethanol affording the 6a-thia-1,2,6-triazapentalene (1s) (1.135 g) as black prisms. The mother liquors were evaporated, to low volume and then reheated to 80°. On cooling, the solution was filtered giving a further crop of compound (1s) (0.058 g). The mother liquors were then evaporated and chromatography (alumina 15 x 3.2 cm) of the residue with benzene gave pale purple eluates which were discarded. Further elution with benzene-ether (4:1) gave yellow eluates which gave 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (0.201 g, 16.5%) (identified by tlc). Continued elution with ether-methanol (100:1) gave red eluates which afforded the 6a-thia-1,2,6-triazapentalene (1s) (0.201 g).

Total yield of 3,4-trimethylene-6-p-nitrophenylamino-1-phenyl-6a-thia-1,2,6-triazapentalene (1s) (1.490 g, 79%) as black prisms from ethanol, mp = 193-195°C.

Found C, 59.82; H, 4.38; N, 18.32%

$C_{19}H_{17}N_5O_2S$ requires C, 60.14; H, 4.52; N, 18.46%

[Nmr spectrum; see Appendix A, table 3]

M^+ at m/e 379

ν_{max} (KBr disc) 3270 (N-H) cm^{-1}

[UV spectrum; see Appendix B, table 1]

6-Acetamido-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1t)

Method C was used and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5mmol) and acethydrazine (1.850 g, 25 mmol) gave a red solid which was recrystallised from methanol affording the 6a-thia-1,2,6-triazapentalene (1t) (0.811 g) as red spars. The mother liquors were evaporated to low volume and then heated to 60°. On cooling, the solution was filtered giving a further crop of compound (1t) (0.207 g). The mother liquors were then evaporated and chromatography (alumina 5 x 3.2 cm) of the residue with benzene-ether (4:1) gave 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (0.006 g, 0.5%) (identified by tlc). Further elution with ether-methanol (25:1) gave red eluates which afforded the 6a-thia-1,2,6-triazapentalene (1t) (0.201 g).

Total yield of 6-acetamido-3,4-dimethyl-1-phenyl-6a-thia-1,2,6-triazapentalene (1t) (1.219 g, 85%) as red spars from methanol, mp = 221-223° (decomp.).

Found C, 58.23; H, 5.57; N, 19.51; S, 10.86%

$C_{14}H_{16}N_4SO$ requires C, 58.31; H, 5.59; N, 19.43; S, 11.12%

M^+ at m/e 288

ν_{max} (KBr disc) 1650 (C=O) cm^{-1}, 3180 (N-H) cm^{-1}

[UV spectrum; see Appendix B, table 1]

6-Acetamido-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1u)

Method C was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) and acethydrazine (1.850 g, 5 mmol) gave a red solid which was recrystallised from methanol affording the 6a-thia-1,2,6-triazapentalene (1u) (0.531 g) as orange cubes. The mother liquors were evaporated to low volume and then reheated to 60°. On cooling, the solution was filtered giving a further crop of compound (1u) (0.338 g). This process was repeated giving a third crop of compound (1u) (0.225 g). The mother liquors were then evaporated and chromatography (alumina 5 x 3.2 cm) of the residue with benzene-ether (4:1) gave yellow eluates which afforded 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (0.014 g, 1.2%) (identified by tlc). Further elution with ether-methanol (25:1) gave yellow eluates which afforded the 6a-thia-1,2,6-triazapentalene (1u) (0.059 g).

Total yield of 6-acetamido-3,4-trimethylene-1-phenyl-6a-thia-1,2,6-triazapentalene (1u) (1.153 g, 77%) as orange cubes from methanol, mp = 212° (decomp.).

Found C, 59.68; H, 5.50; N, 18.73; S, 10.31%

$C_{15}H_{16}N_4SO$ requires C, 59.98; H, 5.37; N, 18.65; S, 10.67%

M^+ at m/e 300

ν_{max} (KBr disc) 1650 (C=O) cm^{-1}; 3200 (N-H) cm^{-1}

[UV spectrum; see Appendix B, table 1]

(6) Synthesis of 6a-Thia-6-selena-1,2-diazapentalenes

General Procedure

Phosphoryl chloride (0.50 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1,2-diazapentalene (5 mmol) in dimethylformamide (25 ml) at 50° and the mixture was stirred at that temperature before being cooled in an ice-water bath. A solution of potassium selenosulphate (2.375 g, 10 mmol) in water (5 ml) at 65° was then added to the solution. The solution was then diluted with much benzene and water and then filtered to remove selenium. The aqueous layer was basified with sodium bicarbonate and extracted with benzene (x 4). The extracts were combined with the original benzene extract, washed with water (x 6), dried (Na_2SO_4) and evaporated. Chromatography (alumina 30 x 3.2 cm) of the residue with benzene gave purple eluates which afforded the 6a-thia-6-selena-1,2-diazapentalene. Further elution with benzene-ether (4:1) gave yellow eluates which afforded the 6-oxa-6a-thia-1,2-diazapentalene.

3,4-Dimethyl-1-phenyl-6a-thia-6-selena-1,2-diazapentalene (19a)

The general procedure was used and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) gave 3,4-dimethyl-1-phenyl-6a-thia-6-selena-1,2-diazapentalene (19a) (0.765 g, 52%) as dark red needles from cyclohexane, mp = 144.5-146° ,

Found C, 49.12; H, 4.06; N, 9.44%

$C_{12}H_{12}N_2SSe$ requires C, 48.81; H, 4.10; N, 9.49%

[Nmr spectrum; see Appendix A, table 4]

[UV spectrum; see Appendix B, table 2]

and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (0.047 g, 4%) (identified by tlc).

3,4-Trimethylene-1-phenyl-6a-thia-6-selena-1,2-diazapentalene (19b)

The general procedure was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) gave 3,4-trimethylene-1-phenyl-6a-thia-6-selena-1,2-diazapentalene (19b) (1.008 g, 66%) as dark green prisms from n-hexane, mp = 95-97°,

Found C, 50.61; H, 3.93; N, 9.06%

$C_{13}H_{12}N_2SSe$ requires C, 50.81; H, 3.94; N, 9.12%

[Nmr spectrum; see Appendix A, table 4]

[UV spectrum; see Appendix B, table 2]

and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (0.060 g, 5%) (identified by tlc).

(7) Reaction of Intermediates (5) with Sodium Hydroxide

General Procedure

Phosphoryl chloride (0.50 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1,2-diazapentalene (5 mmol) in dimethylformamide (25 ml) at 50° and the solution was stirred at that temperature for 10 minutes before being cooled to room temperature. Aqueous 2M-sodium hydroxide (12.5 ml, 25 ml) was then added and the resulting solution was diluted with water and extracted with benzene. The extracts were washed with water (x6), dried (Na_2SO_4) and evaporated. Chromatography (alumina 40 x 2.7 cm) of the residue with benzene gave

red eluates which afforded the 6, 6a-dithia-1, 2-diazapental ene. Further elution with benzene-ether (4:1) gave yellow eluates which afforded the 6-oxa-6a-thia-1, 2-diazapentalene.

Reaction of intermediate (5a)

The general procedure was used and 3, 4-dimethyl-1-phenyl-6-oxa-6a-thia-1, 2-diazapentalene (4a) (1.160 g, 5 mmol) gave 3, 4-dimethyl-1-phenyl-6, 6a-dithia-1, 2-diazapentalene (2a) (0.054 g, 8.4%) (identified by tlc and nmr) and the starting compound (4a) (0.144 g, 12%) (identified by tlc and nmr). A large amount of slow moving dark intractable material adhered to the top of the column on chromatography.

Reaction of intermediate (5b)

The general procedure was used and 3, 4-trimethylene-1-phenyl-6-oxa-6a-thia-1, 2-diazapentalene (4b) (1.220 g, 5 mmol) gave 3, 4-trimethylene-1-phenyl-6, 6a-dithia-1, 2-diazapentalene (2b) (0.045 g, 7.0%) (identified by tlc and nmr) and the starting compound (4b) (0.305 g, 25%) (identified by tlc and nmr). A large amount of slow moving dark intractable material adhered to the top of the column on chromatography.

(8) Reaction of Intermediates (5) with Sodium Sulphide and Sodium Hydrogen Sulphide

General Procedure

Phosphoryl chloride (0.50 ml, 5.5 mmol) was added to a solution of the 6-oxa-6a-thia-1, 2-diazapentalene (5 mmol) in dimethylformamide (25 ml) at 50°C and the solution was stirred at that temperature for

10 minutes and was then cooled in an ice bath. Aqueous 2M-sodium sulphide (12.5 ml, 25 mmol) or aqueous 2M-sodium hydrogen sulphide (12.5 ml, 25 mmol) was then added and the resulting mixture was diluted with water and extracted with benzene. The extracts were washed with water (x6), dried (Na_2SO_4) and evaporated. Subsequent procedure given for individual cases.

Reaction of Intermediate (5a) with Sodium Sulphide

The general procedure was used and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) and 2M-sodium sulphide (12.5 ml, 25 mmol) gave a dark red residue on evaporation of the benzene extracts. Chromatography (alumina 40 x 3.2 cm) of the residue with benzene gave red eluates which afforded 3,4-dimethyl-1-phenyl-6,6a-dithia-1,2-diazapentalene (2a) (0.693 g, 54%) (identified by tlc and nmr). Further elution with benzene-ether (4:1) gave yellow eluates which afforded 3,5-dimethyl-1-phenyl-pyridazine-4-thione (21) (0.363 g, 34%) as golden yellow needles from cyclohexane, mp = 118.5--120° .

Found C, 66.28; H, 5.61; N, 12.96%

$C_{12}H_{12}N_2S$ requires C, 66.63; H, 5.59; N, 12.95%

[Nmr spectrum ($CDCl_3$); δ2.42 (3H, d, $J_{5\text{-Me, 6H}}$=0.6Hz, 5-Me), δ2.74 (3H, 3-Me), δ7.56-7.80 (5H, m, 1-Ph), δ8.30 (1H, q, 6-H)]

[UV spectrum, cyclohexane; λ_{max} (nm) 203, 251, 391 (log ε 4.18, 3.69, 4.54)]

Reaction of Intermediate (5a) with Sodium Hydrogen Sulphide

The general procedure was used and 3,4-dimethyl-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4a) (1.160 g, 5 mmol) and 2M-sodium hydrogen sulphide (12.5 ml, 25 mmol) gave a dark red residue on evaporation of the benzene extracts. Chromatography (alumina 40 x 3.2 cm) of the residue with benzene gave red eluates which afforded 3,4-dimethyl-1-phenyl-6,6a-dithia-1,2-diazapentalene (2a) (0.781 g, 63%) (identified by tlc and nmr). Further elution with benzene-ether (4:1) gave yellow eluates which afforded 3,5-dimethyl-1-phenyl-pyridazine-4-thione (21) (0.338 g, 31%) as golden yellow needles from cyclohexane. (A sample of compound (21) prepared here ran concurrently on tlc with a sample of compound (21), prepared by the previous method.)

Reaction of Intermediate (5b) with Sodium Sulphide

The general procedure was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5 mmol) and 2M-sodium sulphide (12.5 ml, 25 mmol) gave a dark red residue on evaporation of the benzene extracts. Chromatography (alumina 40 x 3.2 cm) of the residue with benzene gave red eluates which afforded 3,4-trimethylene-1-phenyl-6,6a-dithia-1,2-diazapentalene (2b) (1.212 g, 93%) (identified by tlc and nmr). Further elution with benzene-ether (4:1) gave yellow eluates which afforded 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (0.040 g, 3.3%) (identified by tlc).

Reaction of Intermediate (5b) with Sodium Hydrogen Sulphide

The general procedure was used and 3,4-trimethylene-1-phenyl-6-oxa-6a-thia-1,2-diazapentalene (4b) (1.220 g, 5mmol) and 2M-sodium hydrogen sulphide (12.5 ml, 25 mmol) gave a dark red residue on evaporation of the benzene extracts. Chromatography (alumina 40 x 3.2 cm) of the residue with benzene gave red eluates which afforded 3,4-trimethylene-1-phenyl-6,6a-dithia-1,2-diazapentalene (2b) (1.258 g, 98%) (identified by tlc).

B Synthesis of 6a-Thia-1, 2, 6-triazapentalenes from 5-Formylisothiazole

5-Formylisothiazole phenylhydrazone (25a)

A solution of phenylhydrazine (1.08 ml, 11 mmol), concentrated hydrochloric acid (0.2 ml) and water (0.5 ml) in methanol (5 ml) was added to a solution of 5-formylisothiazole (24) (1.130 g, 10 mmol) in methanol (5 ml) and the resulting solution was heated under reflux for 10 minutes. The solution was then cooled in an ice/water bath and filtered, affording 5-formylisothiazole phenylhydrazone (25a) which was dried in vacuo over P_2O_5 (yield 1.777 g, 88%). A small portion of the product (ca 0.2 g) was recrystallised, as golden yellow prisms, from ethanol for characterisation, mp = 135-137° .

Found C, 58.94; H, 4.29; N, 20.97%

$C_{10}H_9N_3S$ requires C, 59.09; H, 4.46; N, 20.67%

[Nmr spectrum (d^6-dimethylsulphoxide); δ6.71-7.32 (5H, m, Ph), δ7.38 (1H, dd, $J_{4H, 3H}$=1.8Hz, $J_{4H, C\underline{H}=N}$=0.4Hz, 4-H), δ8.11 (1H, b, -C<u>H</u>=N-), δ8.46 (1H, d, $J_{3H, 4H}$=1.8Hz, 3-H), δ10.78 (1H, b-N<u>H</u>Ph)]

ν_{max} (KBr disc) 3220 (N-H) cm^{-1}.

5-formylisothiazole p-nitrophenylhydrazone (25b)

A boiling solution of p-nitrophenylhydrazine (1.650 g, 11 mmol), concentrated hydrochloric acid (0.2 ml) and water (2.0 ml), in methanol (20 ml) was added to a boiling solution of 5-formylisothiazole (24) (1.130 g, 10 mmol) in methanol (10 ml) and the resulting solution was heated under reflux for 10 minutes. The solution was then cooled in an ice/water bath and filtered affording 5-formylisothiazole

p-nitrophenylhydrazone (25b) which was washed with ether and dried in vacuo over P_2O_5 (yield 2.156 g, 88%). A small portion of the product (ca 0.2 g) was recrystallised, as golden yellow needles, from ethanol for characterisation, mp = 209-211° .

Found C, 48.41; H, 3.31; N, 22.77%

$C_{10}H_8N_4O_2S$ requires C, 48.38; H, 3.25; N, 22.57%

[Nmr spectrum (d^6-dimethylsulphoxide); δ7.13 (2H, d, J=9.7Hz, $C_6\underline{H}_4NO_2$ ortho or meta H), δ7.55 (1H, d, $J_{4H, 3H}$=1.8Hz, 4-H), δ8.13 (2H, d, J=9.7Hz, $C_6\underline{H}_4NO_2$ ortho or meta H), δ8.25 (1H, b, -C$\underline{H}$=N-), δ8.54 (1H, d, $J_{3H, 4H}$=1.8Hz, 3-H), δ11.54 (1H, b, N$\underline{H}C_6H_4NO_2$)]

ν_{max} (KBr disc) 3270 (N-H) cm^{-1}.

5-Formylisothiazole methylhydrazone (25c)

A solution of methylhydrazine (0.920 g, 20 mmol) and acetic acid (0.5 ml) in methanol (10 ml) was added to a solution of 5-formylisothiazole (24) (1.130 g, 10 mmol) in methanol (10 ml) and the resulting solution was heated under reflux for 10 minutes. The solution was then cooled to room temperature, diluted with water, made alkaline with sodium carbonate and extracted with ether. The extracts were dried (Na_2CO_3) and evaporated. The residual oil was distilled at reduced pressure (oil pump) using a heating block affording 5-formylisothiazole methylhydrazone (1.306 g, 93%) as an orange liquid (bp = 135° at 0.1 mm Hg).

Found C, 42.71; H, 5.09; N, 29.76%

$C_5H_7N_3S$ requires C, 42.53; H, 5.00; N, 29.76%

[Nmr spectrum ($CDCl_3$); δ2.95 (3H, d, $J_{Me, H}$=0.9Hz, NH$\underline{Me}$), δ6.28 (1H, b, N$\underline{H}$Me), δ7.10 (1H, dd, $J_{4H, 3H}$=1.8Hz, $J_{4H, CH=N}$=0.5Hz, 4-H), δ7.56 (1H, b, -C$\underline{H}$=N-), δ8.38 (1H, d, $J_{3H, 4H}$=1.8Hz, 3-H)]

2-Methyl-5-formylisothiazolium phenylhydrazone fluorosulphonate (26a)

Methyl fluorosulphonate (0.80 ml, 10 mmol) was added to a solution of 5-formylisothiazole phenylhydrazone (25a) (1.015 g, 5 mmol) in methylene chloride (50 ml) and the solution was stirred overnight (ca 15 hours) with the resulting fluorosulphonate salt (26a) separating from solution. Separation of the salt was completed by the addition of a large excess of ether and the 2-methyl-5-formylisothiazolium phenylhydrazone fluorosulphonate (26a) was filtered, washed well with ether and dried in vacuo over P_2O_5 (yield 1.545 g, 97%). A small portion of the product (ca 0.2 g) was recrystallised, as orange needles, from ethanol for characterisation, mp = 145-147° .

Found C, 41.66; H, 3.92; N, 13.40%

$C_{11}H_{12}N_3O_3S_2F$ requires C, 41.63; H, 3.81; N, 13.24%

[Nmr spectrum (CF_3COOH); δ4.14 (3H, 2-Me), δ7.08-7.44 (6H, m, NHPh and 4-H), δ7.64 (1H, b, NHPh), δ7.82 (1H, CH=N), δ8.42 (1H, dd, $J_{3H,4H}$=3.2Hz, $J_{3H,2Me}$=0.4Hz, 3-H)]

[UV spectrum, methanol; λ_{max} (nm) 202, 244(sh), 257, 444 (log ε 4.12, 4.10, 4.14, 4.42)]

2-Methyl-5-formylisothiazolium p-nitrophenylhydrazone fluorosulphonate (26b)

Methyl fluorosulphonate (0.80 ml, 10 mmol) was added to a suspension of 5-formylisothiazole p-nitrophenylhydrazone (25b) (1.240 g, 5 mmol) in methylene chloride (50 ml) and the suspension was stirred overnight (ca 15 hours). A large excess of ether was then added to the suspension and the 2-methyl-5-formylisothiazolium p-nitrophenylhydrazone fluorosulphonate (26b) was filtered, washed well with ether and dried

in vacuo over P_2O_5 (yield 1.545 g, 97%). A small portion of the product (ca 0.2 g) was recrystallised, as orange prisms, from methanol for characterisation, mp = 226° (decomp).

Found C, 36.78; H, 3.46; N, 15.69%

$C_{11}H_{11}N_4O_5S_2F$ requires C, 36.48; H, 3.06; N, 15.46%

[Nmr spectrum (CF_3COOH); δ4.36 (3H, b, 2-Me), δ7.33 (2H, d, J=9.7Hz, $C_6\underline{H}_4NO_2$ ortho or meta H), δ7.52 (1H, d, $J_{4H,\,3H}$=2.7Hz, 4-H), δ8.18 (1H, C$\underline{H}$=N), δ8.30 (2H, d, J=9.7Hz, $C_6\underline{H}_4NO_2$ ortho or meta H), δ8.75 (1H, dd, $J_{3H,\,4H}$=2.7Hz, $J_{3H,\,2Me}$=0.6Hz, 3-H)]

[UV spectrum, methanol; λ_{max} (nm) 201, 245, 332, 432 (log ε 4.16, 4.03, 3.88, 4.59)]

6-Methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (27a)

An excess of sodium carbonate was added to a solution of 2-methyl-5-formylisothiazolium phenylhydrazone fluorosulphonate (26a) (1.585 g, 5 mmol) in water (750 ml) and methanol (250 ml). The resulting mixture was extracted with benzene and the extracts were washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 30 x 3.2 cm) of the residue with benzene gave orange eluates which afforded 6-methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (27a) (1.017 g, 94%) as red prisms from petroleum, mp = 92-93° (90-92° lit.[41]). (Nmr spectrum of compound (27a) isolated here identical to nmr spectrum of a sample of compound (27a) previously prepared[41].)

6-Methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (27a) (prepared directly from 5-formylisothiazole phenylhydrazone)

Methyl fluorosulphonate (0.80 ml, 10 mmol) was added to a

solution of 5-formylisothiazole phenylhydrazone (25a) (1.015 g, 5 mmol) in methylene chloride (50 ml) and the solution was stirred overnight (ca 15 hours). Water (1 l) was then added and the aqueous solution was washed with ether (x2), the ether washings being discarded. An excess of sodium carbonate was added to the solution which was then extracted with benzene. The extracts were washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 30 x 3.2 cm) of the residue with benzene gave orange eluates which afforded 6-methyl-1-phenyl-6a-thia-1,2,6-triazapentalene (27a) (1.047 g, 97%) as red prisms from petroleum. (A sample of compound (27a) prepared by this method ran concurrently on tlc with a sample of compound (27a) prepared by the previous method.)

6-Methyl-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (27b)

An excess of sodium carbonate was added to a solution of 2-methyl-5-formylisothiazolium phenylhydrazone fluorosulphonate (26b) (1.240 g, 5 mmol), in water (750 ml) and methanol (250 ml). Methylene chloride (750 ml) was then added and the resulting mixture was stirred for 30 minutes at room temperature. The aqueous layer was separated from the methylene chloride layer and then extracted with more methylene chloride. The combined methylene chloride solution was washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 30 x 3.2 cm) of the residue with benzene-ether (4:1) gave red eluates which afforded 6-methyl-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (27b) (1.301 g, 99%) as dark red spars from cyclohexane-benzene (4:1), mp = 185-187°.

Found C, 50.26; H, 3.81; N, 21.51%

$C_{11}H_{10}N_4O_2S$ requires C, 50.37; H, 3.84; N, 21.36%

[Nmr spectrum; see Appendix A, table 5]

[UV spectrum; see Appendix B, table 3]

6-Methyl-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (27b)
(prepared directly from 5-formylisothiazole p-nitrophenylhydrazone)

Methyl fluorosulphonate (0.80 ml, 10 mmol) was added to a suspension of 5-formylisothiazole p-nitrophenylhydrazone (25b) (1.240 g, 5 mmol) in methylene chloride (50 ml) and the suspension was stirred overnight (ca 15 hours). Water (1 l) was then added and the aqueous solution was washed with ether (x2), the ether washings being discarded. An excess of sodium carbonate and methylene chloride (750 ml) were then added to the solution and the resulting mixture was stirred for 30 minutes at room temperature. The aqueous layer was separated from the methylene chloride layer and then extracted with more methylene chloride. The combined methylene chloride solution was washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 30 x 3.2 cm) of the residue with benzene-ether (4:1) gave red eluates which afforded 6-methyl-1-p-nitrophenyl-6a-thia-1,2,6-triazapentalene (27b) (1.281 g, 98%) as dark red spars from cyclohexane-benzene (4:1). (A sample of compound (27b) prepared by this method ran concurrently on tlc with a sample of compound (27b) prepared by the previous method.)

1,6-Dimethyl-6a-thia-1,2,6-triazapentalene (27c)

Methyl fluorosulphonate (0.80 ml, 10 mmol) was added to a solution of 5-formylisothiazole methylhydrazone (25c) (0.705 g, 5 mmol) in methylene chloride (10 ml), the solution was stirred for 10 minutes

at room temperature, and a red oil separated from solution. Water (1 l) was then added and the aqueous solution was washed with ether (x2), the ether washings being discarded. An excess of sodium carbonate was added to the solution which was then extracted with benzene. The extracts were washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 30 x 3.2 cm) of the residue with benzene gave pale yellow eluates which afforded a yellow oil on evaporation. The oil was distilled at reduced pressure (oil pump) using a heating block, giving 1,6-dimethyl-6a-thia-1,2,6-triazapentalene (27c) (0.145 g, 19%), as a yellow oil (bp = 65° at 0.1 mm Hg) which crystallised as pale yellow prisms on cooling, mp = 42-44° .

Found C, 46.69; H, 5.66; N, 27.10%

$C_6H_9N_3S$ requires C, 46.43;, H, 5.84; N, 27.07%

[Nmr spectrum; see Appendix A, table 5]

M^+ at m/e 155

[UV spectrum; see Appendix B, table 3]

Trinitrobenzene Complex of 1,6-Dimethyl-6a-thia-1,2,6-triazapentalene (1:1) (30a)

A boiling solution of 1,3,5-trinitrobenzene (0.213 g, 1 mmol) in ethanol (5 ml) was added to a boiling solution of 1,6-dimethyl-6a-thia-1,2,6-triazapentalene (27c) (0.155 g, 1 mmol) in ethanol (5 ml). On cooling the solution a solid separated. The solid was filtered, dried in vacuo over P_2O_5 and shown to be the 1:1 complex by nmr (yield 0.252 g, 69%). The trinitrobenzene complex of 1,6-dimethyl-6a-thia-1,2,6-triazapentalene (30a) was obtained as brown needles, mp = 129-132° .

Found C, 38.93; H, 3.22; N, 23.09%

$C_{12}H_{12}N_6O_6S$ requires C, 39.13; H, 3.28; N, 22.82%

[Nmr spectrum ($CDCl_3$); δ3.52 (3H, b, 6-Me), δ3.66(3H, 1-Me), δ6.56(1H, d, $J_{4H, 5H}$=4.2Hz, 4-H), δ7.87 (1H, d b, 5-H), δ7.90 (1H, 3H), δ9.27 (3H, t r initrobenzene protons)]

Trinitrobenzene Complex of 6-Methyl-1-phenyl-6a-thia-1, 2, 6-triazapentalene (1:1) (30b)

A boiling solution of 1, 3, 5-trinitrobenzene (0.213 g, 1 mmol) in ethanol (5 ml) was added to a boiling solution of 6-methyl-1-phenyl-6a-thia-1, 2, 6-triazapentalene (27a) (0.217 g, 1 mmol) in ethanol (10 ml). On cooling the solution a solid separated. The solid was filtered, dried in vacuo over P_2O_5 and shown to be the 1:1 complex (30b) by nmr (yield 0.316 g, 73%). The trinitrobenzene complex of 6-methyl-1-phenyl-6a-thia-1, 2, 6-triazapentalene (30b) was obtained as black needles, mp = 140-141° .

Found C, 47.27; H, 3.22; N, 19.78%

$C_{17}H_{14}N_6O_6S$ requires C, 47.44; H, 3.28; N, 19.53%

[Nmr spectrum ($CDCl_3$); δ3.60 (3H, d, $J_{6Me, 5H}$=0.8Hz, 6-Me), δ6.78 (1H, d, $J_{4H, 5H}$=3.9Hz, 4-H), δ6.98-7.54 (5H, m, 1-Ph), δ7.92 (1H, dd, $J_{5H, 4H}$=3.8Hz, $J_{5H, 6Me}$=0.8Hz, 5-H), δ8.03 (1H, 3-H), δ9.10 (3H, trinitrobenzene protons)]

C Synthesis of 1,6-Dimethyl-6a-thia-1,6-diazapentalene, 6-Methyl-1-oxa-6a-thia-6-azapentalene and 6-Methyl-1,6a-dithia-6-azapentalene from 5-Formylisothiazole

2-Methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate (33)

A freshly prepared and standardised solution of phenyl lithium in ether (1.05 M, 71.4 ml ≡ 75 mmol of PhLi) was added to a suspension of methoxymethyl triphenylphosphonium chloride (34.280 g, 100 mmol) in dry tetrahydrofuran (200 ml) (under nitrogen) and the resulting solution was stirred for 30 minutes at room temperature. A solution of 5-formylisothiazole (24) (5.650 g, 50 mmol) in dry tetrahydrofuran (25 ml) was then added and the resulting solution was stirred (under nitrogen) for 1 hour at room temperature. The solution was then filtered and the residual solid was washed thoroughly with ether and then discarded. The tetrahydrofuran solution and the ether washings were then combined and evaporated leaving a sticky oil. Ether (250 ml) was then added to the oil and the resulting mixture was stirred vigorously for 5 minutes. The ether was then decanted from the oil. The oil was extracted with ether in this manner five more times. The combined ether extracts were evaporated leaving a red viscous liquid which contained 5-(2-methoxyvinyl)isothiazole (32).

The above process was repeated using a new solution of phenyl lithium in ether (1.06 M, 70.8 ml ≡ 75 mmol of PhLi). A further batch of red liquid containing the methoxyvinyl compound (32) was obtained.

The two batches of product were combined and distillation at approximately 72-74°at 0.1 mm Hg, using a Vigreux column, afforded the methoxyvinyl compound (32) (9.035 g). (The purity of the distillate

was estimated at approximately 93% w/w by nmr, with triphenylphosphine, triphenylphosphonium oxide and biphenyl impurities present. The mass spectrum of the distillate was also obtained and the molecular ion peaks of these impurities appeared at m/e 262, 278 and 154 respectively. The molecular ion peak of compound (32) appeared at m/e 141.) The product was then redistilled at reduced pressure (0.1 mm Hg) using a fractionating column (6 cm x 1 cm) filled with glass helices. The fraction distilling at 68-70°C was collected (7.912 g). (The purity of redistilled compound (32) was estimated at 98% w/w from nmr, with compound (32) consisting of a 1:2 mixture of the cis-(32a) and trans-(32b) isomers. The mass spectrum of the redistilled product showed peaks at m/e 154 and 141 due to the molecular ions peaks of biphenyl and compound (32), respectively.)

[Nmr spectrum ($CDCl_3$); cis-isomer (32a) - δ3.86 (2'-OMe), δ5.78 (d, $J_{1'H, 2'H}$=6.0Hz, 1'-H), δ6.38 (d, $J_{2'H, 1'H}$=6.0Hz, 2'-H), δ7.05 (d, $J_{4H, 3H}$=1.9Hz, 4-H), δ8.28 (m, 3-H); trans-isomer (32b) - δ3.68 (d, $J_{OMe, 1'H}$=0.3Hz, 2'-OMe), δ5.95 (d b, $J_{1'H, 2'H}$=13.2Hz, 1'-H), δ6.93 (d, $J_{4H, 3H}$=1.9Hz, 4-H), δ7.11 (d, $J_{2'H, 1'H}$=13.3Hz, 2'-H), δ8.28 (m, 3-H); biphenyl impurity - δ7.28-7.64(m)]

A solution of methyl fluorosulphonate (8.00 ml, 100 mmol) in methylene chloride (25 ml) was then added dropwise to a stirred solution of the redistilled methoxyvinyl compound (32) (containing biphenyl impurity) in methylene chloride (25ml) and the resulting solution was then stirred at room temperature for 5 minutes. The fluorosulphonate salt (33) separated from solution on the addition of a large excess of ether, and the ether was decanted off. The residual

solid was washed well with ether, the ether washings being decanted off. The residual solid was then taken up in acetonitrile (25 ml) and gradual addition of ether precipitated the fluorosulphonate salt. The 2-methyl-5-(2-methoxyvinyl)isothiazolium salt (33) was filtered, washed with ether and dried in vacuo over P_2O_5 (yield 13.577 g, 53%). A small portion of the product (ca 0.2 g) was recrystallised, as colourless prisms, from acetonitrile for characterisation, mp = 177-178°.

Found C, 33.18; H, 4.47; N, 5.70%

$C_7H_{10}O_4S_2NF$ requires C, 32.93; H, 3.95; N, 5.51%

[Nmr spectrum (d^6-dimethylsulphoxide) of bulk sample; cis-isomer (33a) - δ4.18 (s, 2'-OMe), δ4.20 (b, 2-Me), δ6.39 (d, $J_{1'H, 2'H}$=5.6Hz, 1'-H), δ7.42 (d, $J_{2'H, 1'H}$=5.6Hz, 2'-H), δ7.50 (d, $J_{4H, 3H}$=3.1Hz, 4-H), δ9.00 (d b, $J_{3H, 4H}$=3.0Hz, 3-H); trans-isomer (33b) - δ3.81 (s, 2'-OMe), δ4.15 (b, 2-Me), δ6.52 (d, $J_{1'H, 2'H}$=12.8Hz, 1'-H), δ7.62 (d, $J_{4H, 3H}$=3.1Hz, 4-H), δ8.00 (d, $J_{2'H, 1'H}$=12.8Hz, 2'-H), δ8.83 (d, $J_{3H, 4H}$=3.0Hz, 3-H). Ratio of cis/trans isomers = 1:2]

[UV spectrum, MeOH; λ_{max} (nm) 206, 256, 329 (log ε 3.86, 3.67, 4.28)]

1,6-Dimethyl-6a-thia-1,6-diazapentalene (29)

Aqueous methylamine (25 ml) was added to a solution of 2-methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate (33) (1.277 g, 5 mmol) in acetonitrile (50 ml) and the solution was allowed to stand at room temperature for 5 minutes. Water (250 ml) was then added and the resulting mixture was cooled in ice for 30 minutes. The mixture was then filtered and the residual brown solid was dried in vacuo over P_2O_5.

The brown solid was recrystallised from petroleum affording 1, 6-dimethyl-6a-thia-1, 6-diazapentalene (29) as pale yellow prisms (0.376 g). The mother liquors were evaporated and recrystallisation of the residue gave a further crop of compound (29) (0.093 g).

Total yield of 1, 6-dimethyl-6a-thia-1, 6-diazapentalene (29) (0.496 g, 61%), mp = 94-96° (lit.[39] 82-84° decomp.).

$M^{+\cdot}$ at m/e 154

(Nmr spectrum of product obtained here identical to nmr spectrum of a previously prepared sample of compound (29)[39].)

6-Methyl-1-oxa-6a-thia-6-azapentalene (34)

A solution of 2-methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate (33) (1.277 g, 5 mmol) in acetonitrile (50 ml) was added to an ice cold aqueous 0.5 M-sodium hydroxide solution (100 ml) and the resulting mixture was allowed to stand for 2 hours at room temperature. The mixture was then diluted with water and extracted twice with petroleum. The petroleum extracts were discarded. The aqueous mixture was then extracted twice with ether. The ether extracts were washed with water, dried (Na_2SO_4) and evaporated. The residual oil was extracted with boiling petroleum. The extracts were evaporated, at reduced pressure, to low volume and a yellow solid crystallised from solution. Filtration of the solution gave 6-methyl-1-oxa-6a-thia-6-azapentalene (0.077 g, 11%) as orange prisms, mp = 36-40° .

Found C, 51.33; H, 5.07; N, 9.87%

C_6H_7NSO requires C, 51.04; H, 5.00; N, 9.92%

[Nmr spectrum ($CDCl_3$); δ3.60 (3H, d, $J_{6Me, 5H}$=0.4Hz, 6-Me), δ6.35 (1H, d, $J_{3H, 2H}$=2.6Hz, 3-H), δ6.60 (1H, d, $J_{4H, 5H}$=3.6Hz, 4-H), δ7.66 (1H, dd, $J_{5H, 4H}$=3.6Hz, $J_{5H, 6Me}$=0.4Hz, 5-H), δ8.85 (1H, d, $J_{2H, 3H}$=2.6Hz, 2-H)]

M^+ at m/e 141

ν_{max} (KBr disc) 1530 (C=O) cm^{-1}

[UV spectrum, cyclohexane; λ_{max} (nm) 206, 235, 374 (log ε 3.97, 3.74, 4.13)]

6-Methyl-1, 6a-dithia-6-azapentalene (28)

Ice-cold aqueous 1M-sodium hydrogen sulphide (50 ml) was added to a solution of 2-methyl-5-(2-methoxyvinyl)isothiazolium fluorosulphonate (33) (1.277 g, 5mmol) in acetonitrile (50 ml) in an ice-bath. The resulting mixture was then diluted with water and extracted with benzene. The extracts were washed with water, dried (Na_2SO_4) and evaporated. Chromatography (alumina, Merck grade II-III, 30 x 2.7 cm) of the residue with benzene gave pale red eluates which afforded 1, 6, 6a-trithiapentalene (37) (0.022 g, 2.7%), mp = 111-112° (lit.[37] 112-113°).

M^+ at m/e 160

(Nmr spectrum of compound (37) isolated here identical to nmr spectrum of a previously prepared sample of compound (37)[37].)

Further elution with benzene gave pale yellow eluates which afforded 6-methyl-1, 6a-dithia-6-azapentalene (28) (0.182 g, 23%) as yellow needles from n-hexane, mp = 107.5-108.5° (lit.[47] 107-108°).

M^+ at m/e 157

(Nmr spectrum of compound (28) isolated here identical to nmr spectrum of a previously prepared sample of compound (28)[47].)

Further elution with ether gave orange eluates which afforded a red oil. The oil was extracted with boiling petroleum. The extracts were evaporated, at reduced pressure, to low volume and a red solid crystallised from solution. Filtration of the solution gave 5-methoxy-1-methylamino-penta-1,4-diene-3-thione (36) (0.067 g, 8.5%) as red prisms, mp = 53-55°.

Found C, 53.15; H, 6.98; N, 8.64%

$C_7H_{11}OSN$ requires C, 53.47; H, 7.05; N, 8.91%

[Nmr spectrum ($CDCl_3$); δ3.12 (3H, d, $J_{NMe, NH}$=5.2Hz, 1-NMe), δ3.70 (3H, 5-OMe), δ5.85 (1H, d, $J_{2H, 1H}$=7.8Hz, 2-H), δ6.04 (1H, d, $J_{4H, 5H}$=12.2Hz, 4-H), δ7.09 (1H, dd, $J_{1H, 2H}$=7.8Hz, $J_{1H, NH}$=13.9Hz, 1-H), δ7.64 (1H, d, $J_{5H, 4H}$=12.2Hz, 5-H), δ12.94 (1H, b, 1-NH)]

ν_{max} (KBr disc) 2930 (N-H) cm^{-1} M^+ at m/e 157

[UV spectrum, cyclohexane; λ_{max} (nm) 201, 335(sh), 349, 406 (log ε 4.09, 4.15, 4.16, 4.02)]

D Synthesis of 1, 6, 6a-Trithia-3-azapentalenes and 6, 6a-Dithia-1, 3-diazapentalenes from 5-Amino-1, 2-dithiole-3-thiones

5-Amino-4-carbomethoxy-1, 2-dithiole-3-thione (39a) was prepared by the method described by Gewald[151] and modified by Scattergood[152]. 5-Amino-4-phenyl-1, 2-dithiole-3-thione (39b) was prepared by the method of Scattergood[152].

(1) Preparation of 2, 5-Dimethylmercapto-1, 6, 6a-trithia-3-azapentalenes

General Procedure

Triethylamine (0.84 ml, 6 mmol) was added to a solution of the 5-amino-1, 2-dithiole-3-thione (5 mmol) in dimethylformamide (10 ml) at 50°. Carbon disulphide (0.62 ml, 10 mmol) was then added and the resulting solution was stirred for 10 minutes at 50°. The solution was then cooled to room temperature, methyl iodide (1.25 ml, 20 mmol) was added, and the solution was stirred at room temperature for 30 minutes. The solution was then diluted with water and the resulting mixture was extracted with benzene, the extracts being washed with water (x6), dried (Na_2SO_4) and evaporated. Chromatography (alumina 25 x 3.2 cm) of the residue with benzene gave yellow eluates which afforded the 1, 6, 6a-trithia-3-azapentalene.

4-Carbomethoxy-2, 5-dimethylmercapto-1, 6, 6a-trithia-3-azapentalene (43a)

The general procedure was used and 5-amino-4-carbomethoxy-1, 2-dithiole-3-thione (39a) (1.035 g, 5 mmol) gave 4-carbomethoxy-2, 5-dimethylmercapto-1, 6, 6a-trithia-3-azapentalene (43a) (1.398 g, 90%)

as orange needles from cyclohexane, mp = 108-110° .

Found C, 31.10; H, 3.07; N, 4.51%

$C_8H_9NO_2S_5$ requires C, 30.84; H, 2.91; N, 4.50%

[Nmr spectrum ($CDCl_3$); δ2.64 (6H, 2- and 5-SMe), δ3.97 (3H, 4-CO_2Me)]

M^+ at m/e 311

ν_{max} (KBr disc) 1715 (C=O) cm^{-1}

[UV spectrum, cyclohexane,; λ_{max} (nm) 230(sh), 255, 320, 355, 428 (log ε 4.37, 4.58, 4.26, 3.84, 4.03)]

2,5-Dimethylmercapto-4-phenyl-1,6,6a-trithia-3-azapentalene (43b)

The general procedure was used and 5-amino-4-phenyl-1,2-dithiole-3-thione (39b) (1.112 g, 5 mmol) gave 2,5-dimethylmercapto-4-phenyl-1,6,6a-trithia-3-azapentalene (43b) (1.149 g, 70%) as yellow needles from cyclohexane, mp = 163-164° .

Found C, 43.93; H, 3.28; N, 4.27%

$C_{12}H_{11}S_5N$ requires C, 43.74; H, 3.37; N, 4.25%

[Nmr spectrum ($CDCl_3$); δ2.32 (3H, 2- or 5-SMe), δ2.58 (3H, 2- or 5-SMe), δ7.34-7.44 (5H, m, 4-Ph)]

M^+ at m/e 329

[UV spectrum, cyclohexane, λ_{max} (nm) 196, 231, 254, 321, 354, 439 (log ε 4.39, 4.44, 4.55, 4.23, 3.86, 4.08)]

(2) 2,5-Dibenzylmercapto-4-carbomethoxy-1,6,6a-trithia-3-azapentalene (44)

Triethylamine (0.84 ml, 6 mmol) was added to a solution of 5-amino-4-carbomethoxy-1,2-dithiole-3-thione (39a) (1.035 g, 5 mmol)

in dimethylformamide (10 ml) at 50° . Carbon disulphide (0.62 ml, 10 mmol) was then added and the resulting solution was stirred for 10 minutes at 50° . Benzyl chloride (1.40 g, 12 mmol) was then added and the solution was stirred for 2 hours at 50°C before being diluted with water. The resulting mixture was extracted with benzene, the extracts being washed with water (x6), dried (Na_2SO_4) and evaporated. Chromatography (alumina 25 x 3.2 cm) of the residue with benzene gave orange eluates which afforded 2,5-dibenzylmercapto-4-carbomethoxy-1,6,6a-trithia-3-azapentalene (44) (1.866 g, 81%) as orange prisms from cyclohexane, mp = 129-130° .

Found C, 51.81; H, 3.74; N, 3.04%

$C_{20}H_{17}S_5NO_2$ requires C, 51.81; H, 3.70; N, 3.02%

[Nmr spectrum ($CDCl_3$); δ3.85 (3H, 4-CO_2Me), δ4.34 (2H, 2- or 5-S$\underline{C}H_2$Ph), δ4.50 (2H, 2- or 5-S$\underline{C}H_2$Ph), δ7.23-7.44 (10H, m, 2- and 5-SCH$_2\underline{Ph}$)]

M^+ at m/e 463

ν_{max} (KBr disc) 1710 (C=O) cm^{-1}

[UV spectrum, cyclohexane; λ_{max} (nm) 201, 228(sh), 260, 325, 359, 430 (log ε 4.07, 4.35, 4.69, 4.35, 3.88, 4.07)]

(3) Preparation of 2,5-Dimethylmercapto-6,6a-dithia-1,3-diazapentalenes and 2-Anilino-5-methylmercapto-1,6,6a-trithia-3-azapentalenes

General Procedure

Triethylamine (0.84 ml, 6 mmol) was added to a solution of the 5-amino-1,2-dithiole-3-thione (5 mmol) in dimethylformamide (10 ml). Phenylisothiocyanate (0.73 ml, 6 mmol) was then added and

the resulting solution was stirred at room temperature for 30 minutes, before diluting with water and extracting with benzene. The extracts were washed with water (x6), dried (Na_2SO_4) and evaporated. Subsequent procedure given for individual cases.

4-Carbomethoxy-2, 5-dimethylmercapto-6, 6a-dithia-1, 3-diazapentalene (50a) and 2-Anilino-4-carbomethoxy-5-methylmercapto-1, 6, 6a-trithia-3-azapentalene (47a)

The general procedure was used and 5-amino-4-carbomethoxy-1,2-dithiole-3-thione (39a) (1.035 g, 5 mmol) gave an orange residue on evaporation of the benzene extracts. Chromatography (alumina 20 x 3.2 cm) of the residue with benzene gave pale yellow eluates which afforded 4-carbomethoxy-2, 5-dimethylmercapto-6, 6a-dithia-1,3-diazapentalene (50a) (0.605 g, 33%) as pale yellow prisms from cyclohexane, mp = 110-112° .

Found C, 45.39; H, 3.89; N, 7.56%

$C_{14}H_{14}S_4N_2$ requires C, 45.38; H, 3.81; N, 7.56%

[Nmr spectrum ($CDCl_3$); δ2.60 (3H, 2- or 5-SMe), δ2.63 (3H, 2- or 5-SMe), δ3.98 (3H, 4-CO_2Me), δ7.20-7.46 (5H, m, 1-Ph)]

M^+ at m/e 370

ν_{max} (KBr disc) 1680 (C=O) cm^{-1}

[UV spectrum, cyclohexane; λ_{max} (nm) 205, 233, 269(sh), 319, 386 (log ε 4.54, 4.53, 4.32, 3.79, 4.11)]

Further elution with ether gave yellow eluates which afforded 2-anilino-4-carbomethoxy-5-methylmercapto-1, 6, 6a-trithia-3-azapentalene (47a) (0.915 g, 51%) as orange prisms from cyclohexane-benzene (4:1), mp = 134-135° .

Found C, 44.01; H, 3.43; N, 7.92%

$C_{13}H_{12}N_2O_2S_4$ requires C, 43.79; H, 3.39; N, 7.86%

[Nmr spectrum ($CDCl_3$); δ2.59 (3H, 5-SMe), δ3.94 (3H, 4-CO_2Me); δ7.06-7.55 (5H, m, 2-NHPh), δ8.39 (1H, b, 2-NHPh)]

M^+ at m/e 356

ν_{max} (KBr disc) 3360 (N-H) cm^{-1}, 1730 (C=O) cm^{-1}

[UV spectrum, cyclohexane; λ_{max} (nm) 197, 217(sh), 258, 311, 361, 413 (log ε 4.51, 4.40, 4.62, 4.32, 3.83, 4.10)]

2,5-Dimethylmercapto-4-phenyl-6,6a-dithia-1,3-diazapentalene (50b) and 2-Anilino-5-methylmercapto-4-phenyl-1,6,6a-trithia-3-azapentalene (47b)

The general procedure was used and 5-amino-4-phenyl-1,2-dithiole-3-thione (39b) (1.112 g, 5 mmol) gave a yellow residue on evaporation of the benzene extracts. Chromatography (alumina 30 x 3.2 cm) of the residue with petroleum-benzene (1:1) gave pale yellow eluates which afforded 2,5-dimethylmercapto-4-phenyl-6,6a-dithia-1,3-diazapentalene (50b) (0.291 g, 15%) as yellow needles from petroleum, mp = 119-121°.

Found C, 55.75; H, 4.15; N, 7.04%

$C_{18}H_{16}S_4N_2$ requires C, 55.64; H, 4.15; N, 7.21%

[Nmr spectrum, ($CDCl_3$); δ2.30 (3H, 2- or 5-SMe), δ2.54 (3H, 2- or 5-SMe), δ7.20-7.52 (10H, m, 1- and 4-Ph)]

[UV spectrum, cyclohexane; λ_{max} (nm) 203, 235, 317, 400 (log ε 4.60, 4.50, 3.88, 4.16)]

Further elution with benzene gave yellow eluates which afforded

2-anilino-5-methylmercapto-4-phenyl-1,6,6a-trithia-3-azapentalene (47b) (0.945 g, 51%) as yellow prisms from cyclohexane-benzene (1:1), mp = 219-220° .

Found C, 54.83; H, 3.85; N, 7.43%

$C_{17}H_{14}N_2S_4$ requires C, 54.52; H, 3.77; N, 7.48%

[Nmr spectrum, ($CDCl_3$); δ2.59 (3H, 5-SMe), δ7.06-7.56 (11H, m, 2-NHPh, 2-NHPh and 4-Ph)]

M^+ at m/e 374

ν_{max} (KBr disc) 3290 (N-H) cm^{-1}

[UV spectrum, cyclohexane; λ_{max} (nm) 198, 214(sh), 260, 315, 366, 421 (log ε 4.61, 4.50, 4.61, 4.28, 3.89, 4.16)]

E Protonation Studies of 1,6,6a-Trithiapentalenes and Pyrrolo[2,1-b]thiazole-thioaldehydes

3,4-Dimethyl-1,6,6a-trithiapentalene (51b) was prepared according to the procedure of Dingwall, Ingram, Reid and Symon[47]. Hydroxymethylene cycloheptanone and hydroxymethylene cyclooctanone were prepared by the method of reference 153.

3,5,6-Trimethyl- (61a), 5,6-dimethyl- (61b), 2,3,5,6-tetramethyl- (61c), 3,6-dimethyl- (61d) and 3-methyl-6-t-butylpyrrolo[2,1-b]thiazole-7-thiocarbaldehyde (61e) were prepared by the method of reference 46. 3,5,6-Trimethyl-[46] and 3,6-dimethylpyrrolo[2,1-b]thiazole[154] were prepared as described in the references cited. 6-Methylpyrrolo[2,1-b]-thiazole-5-[^{2}H]thiocarbaldehyde (75) was prepared by the method of reference 46.

6-Methyl- (77a), 2,6-dimethyl- (77b), 3,6-dimethyl- (77c), and 2,3,6-trimethylpyrrolo[2,1-b]thiazole-5-thiocarbaldehyde (77d) were prepared by the method of reference 46.

(1) Synthesis of 3,4-Disubstituted 1,6,6a-Trithiapentalenes

Preparation of 1,2-Dithiolium Salts (General Procedure)

Hydrogen disulphide (6 ml) was added to a solution of the diketone (100 mmol) and perchloric acid (12.5 ml, 150 mmol) in acetic acid (300 ml). The solution was then heated for 10 minutes at 60-65° and then cooled to room temperature. Ether was added to the point of incipient crystallisation and the mixture was filtered (cotton wool plug) to remove sulphur. Ether was then added gradually to the filtrate

until the salt began to crystallise and then a large excess of ether (ca 1 l) was added to complete precipitation. The 1,2-dithiolium salt was filtered, washed with ether, carbon disulphide and ether. The salt was then transferred to a conical flask, swirled with more ether, filtered, washed with ether, and dried in vacuo over KOH.

5,6,7,8-Tetrahydro-4H-cyclohepta[c]-1,2-dithiolium perchlorate (59c)

The general procedure was used and hydroxymethylene cycloheptanone (14.00 g, 100 mmol) gave 5,6,7,8-tetrahydro-4H-cyclohepta[c]-1,2-dithiolium perchlorate (59c) (22.347 g, 83%). A small portion of the product (ca 0.2 g) was recrystallised as colourless plates, from acetic acid for characterisation, mp = 118.5-119° .

Found C, 35.21; H, 4.32%

$C_8H_{11}S_2ClO_4$ requires C, 35.49; H, 4.10%

[Nmr spectrum (CF_3COOH); δ2.07 (6H, m, 5-, 6- and 7-CH_2), δ3.30 (2H, t, 4-CH_2), δ3.58 (2H, t, 8-CH_2), δ9.88 (1H, 3-H)]

[UV spectrum, methanol; λ_{max} (nm) 201, 304, 254 (log ε 3.42, 3.81, 3.74)]

4,5,6,7,8,9-Hexahydrocycloocta[c]-1,2-dithiolium perchlorate (59d)

The general procedure was used and hydroxymethylene cyclooctane (15.40 g, 100 mmol) gave 4,5,6,7,8,9-hexahydroxycycloocta[c]-1,2-dithiolium perchlorate (59d) (22.508 g, 79%). A small portion of the product (ca 0.2 g) was recrystallised, as colourless spars, from acetic acid for characterisation, mp = 93-94° .

Found C, 37.99; H, 4.72%

$C_9H_{13}S_2ClO_4$ requires C, 37.96; H, 4.60%

[Nmr spectrum (CF_3COOH); δ1.57 (4H, m, 6- and 7-CH_2), δ2.02 (4H, b, 5- and 8-CH_2), δ3.28 (2H, t, 4-CH_2), δ3.64 (2H, t, 9-CH_2), δ9.91 (1H, 3-H)]

[UV spectrum, methanol; λ_{max} (nm) 201, 258, 305 (log ε 3.46, 3.72, 3.84)]

Preparation of 3,4-Disubstituted 1,6,6a-Trithiapentalenes (General Procedure)

A solution of the 1,2-dithiolium salt (10 mmol) and dimethylthioformamide (2.1 ml, 25 mmol) in acetic anhydride (30 ml) was boiled for 5 minutes and then cooled to room temperature. The resulting Vilsmeier salt separated as an oil on the addition of a large excess of ether. The ether was decanted from the oil and the oil was then washed with ether. The ether washings and the ether-acetic anhydride solution were combined, treated with aqueous 1M-sodium hydroxide and set aside as they contained a small amount of trithiapentalene.

A solution of the residual Vilsmeier salt in acetonitrile (50 ml) was treated with aqueous 2M-sodium hydrogen sulphide (50 ml) and the resulting mixture was diluted with water and extracted with benzene. The extracts were washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 25 x 3.2 cm) of the residue with benzene-petroleum (1:1) gave dark red eluates which afforded the 1,6,6a-trithiapentalene.

The retained ether solution was used to extract the aqueous sodium hydrogen sulphide solution from the main reaction. The ether solution was then washed with water (x3), dried (Na_2SO_4) and evaporated.

Chromatography (alumina 25 x 1.4 cm) of the residue with benzene-petroleum (1:1) gave red eluates which afforded a further crop of 1, 6, 6a-trithiapentalene.

3, 4, 5, 6-Tetrahydrocyclohepta[c, d]-1, 6, 6a-trithiapentalene (51c)

The general procedure was used and 5, 6, 7, 8-tetrahydro-4H-cyclohepta[c]-1, 2-dithiolium perchlorate (59c) (2.700 g, 10 mmol) gave 3, 4, 5, 6-tetrahydrocyclohepta[c, d]-1, 6, 6a-trithiapentalene (51c) (1.376 g, 64%) as red prisms from cyclohexane, mp = 92-92.5°.

Found C, 50.30; H, 4.98%

$C_9H_{10}S_3$ requires C, 50.43; H, 4.70%

[Nmr spectrum ($CDCl_3$); δ2.00 (4H, m, 4- and 5-CH_2), δ3.16 (4H, m, 3- and 6-CH_2), δ8.76 (2H, s, 2- and 7- H)]

[UV spectrum, cyclohexane; λ_{max} (nm) 196, 233, 261, 495 (log ε 4.29, 4.30, 4.70, 3.69)]

4, 5, 6, 7-Tetrahydro-3H-cycloocta[c, d]-1, 6, 6a-trithiapentalene (51d)

The general procedure was used and 4, 5, 6, 7, 8, 9-hexahydrocycta-[c]-1, 2-dithiolium perchlorate (59d) (2.840 g, 10 mmol) gave 4, 5, 6, 7-tetrahydro-3H-cycloocta[c, d]-1, 6, 6a-trithiapentalene (51d) (1.608 g, 71%) as dark red spars from cyclohexane, mp = 125-126°.

Found C, 52.30; H, 5.44%

$C_{10}H_{12}S_3$ requires C, 52.59; H, 5.30%

[Nmr spectrum ($CDCl_3$); δ1.42 (2H, m, 5-CH_2), δ1.79 (4H, m, 4- and 6-CH_2), δ3.43 (4H, b, 3- and 7-CH_2), δ8.82 (2H, 2- and 8- H)]

[UV spectrum, cyclohexane, λ_{max} (nm) 193, 233, 262, 490 (log ε 4.28, 4.27, 4.70, 3.72)]

(2) Recovery of Pyrrolo[2,1-b]-thiazole-7-thioaldehydes from Trifluoroacetic Acid Solution

General Procedure

A solution of the thioaldehyde (2 mmol) in trifluoroacetic acid (5 ml) was allowed to stand at room temperature for a specified period of time. The solution was then poured onto water, made alkaline with sodium carbonate and the resulting mixture was extracted with benzene. The extracts were washed with water (x4), dried (Na_2SO_4) and evaporated, leaving the crude recovered thioaldehyde. Chromatography (alumina 4 x 3.6 cm) of the crude thioaldehyde with benzene gave orange eluates which afforded the pure recovered thioaldehyde.

A solution of 5,6-dimethylpyrrolo[2,1-b]thiazole-7-thiocarbaldehyde (61b) (0.390 g, 2 mmol) was allowed to stand for 8 days. 0.302 g (77%) of pure thioaldehyde was recovered. (The recovered thioaldehyde ran concurrently on tlc with an authentic sample of thioaldehyde (61b). The nmr spectrum of the recovered thioaldehyde was identical to the nmr spectrum of an authentic sample of thioaldehyde (61b).)

A solution of 2,3,5,6-tetramethylpyrrolo[2,1-b]thiazole-7-thiocarbaldehyde (61c) (0.446 g, 2 mmol) was allowed to stand for 21 days. 0.263 g (59%) of pure thioaldehyde was recovered. (The recovered thioaldehyde ran concurrently on tlc with an authentic sample of thioaldehyde (61c). The nmr spectrum of the recovered thioaldehyde was identical to the nmr spectrum of an authentic sample of thioaldehyde (61c).)

(3) Synthesis of Pyrrolo[2,1-b]thiazole Deuteriothioaldehydes

3,5,6-Trimethylpyrrolo[2,1-b]thiazole-7-[^{2}H]thiocarbaldehyde (67a)

Phosphoryl chloride (0.46 ml, 5.0 mmol) was added to a solution of [$^2H_7$]dimethylformamide (0.46 ml, 6 mmol) in 1,2-dichloroethane (4 ml) at 0°. After 10 minutes a solution of 3,5,6-trimethylpyrrolo-[2,1-b]thiazole (0.660 g, 4 mmol) in 1,2-dichloroethane (2 ml) was added and the deep red solution was kept at room temperature for 1 hour. The solution was then shaken with aqueous 2M-sodium hydrogen sulphide (40 ml), diluted with water, and extracted with benzene. The extracts were washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 25 x 2.2 cm) of the residue with benzene gave red eluates which afforded 3,5,6-trimethylpyrrolo[2,1-b]thiazole-7-[^{2}H]thiocarbaldehyde (67a) (0.719 g, 85%) as orange needles from benzene.

Found C, 57.34; H+D, 5.53; N, 6.66%

$C_{10}H_{10}S_2ND$ requires C, 57.10; H+D, 5.30; N, 6.66%

[Nmr spectrum ($CDCl_3$); δ2.28 (3H, q, 6-Me), δ2.48 (3H, q, 5-Me), δ2.61 (3H, d, $J_{3Me,2H}$=1.2 Hz, 3-Me), δ6.56 (1H, q, 2-H)]

3,6-Dimethylpyrrolo[2,1-b]thiazole-7-[^{2}H]thiocarbaldehyde (67b) and 3,6-Dimethylpyrrolo[2,1-b]thiazole-5-[^{2}H]thiocarbaldehyde (80)

Phosphoryl chloride (1.15 ml, 12.5 mmol) was added to a solution of [$^2H_7$]dimethylformamide (1.15 ml, 15 mmol) in 1,2-dichloroethane (10 ml) at 0°. After 10 minutes a solution of 3,6-dimethylpyrrolo[2,1-b]-thiazole (1.510 g, 10 mmol) in 1,2-dichloroethane (5 ml) was added and the deep red solution was kept at room temperature for 1 hour. The

solution was then shaken with aqueous 2M-sodium hydrogen sulphide (100 ml), diluted with water, and extracted with benzene. The extracts were washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 10 x 3.2 cm) of the residue with benzene gave red eluates which afforded a mixture of the thioaldehydes (67b) and (80). Recrystallisation of the mixture from cyclohexane-benzene (1:1) and then from cyclohexane-benzene (3:1) gave 3,6-dimethylpyrrolo[2,1-*b*]-thiazole-5-[^{2}H]thiocarbaldehyde (80) (0.505 g, 26%) as red prisms.

Found C, 55.35; H+D, 4.79; N, 7.14%

$C_9H_8S_2ND$ requires C, 55.05; H+D, 4.66; N, 7.04%

[Nmr spectrum ($CDCl_3$); δ2.64 (3H, d, $J_{6Me, 7H}$=0.8Hz, 6-Me), δ2.65 (3H, d, $J_{3Me, 2H}$=1.2Hz, 3-Me), δ6.40 (1H, q, 7-H), δ6.55 (1H, q, 2-H)]

The mother liquors contained a mixture of thioaldehydes (67b) and (80). Silica (8 g) was added to the mother liquors and the solvent was evaporated at reduced pressure leaving the thioaldehydes (67b) and (80) adsorbed on the silica. The dry adsorbed silica was then poured on to a dry column (silica 65 x 3 cm) and the column was eluted with benzene till the solvent reached the bottom of the column. The column was then cut into fractions as shown in the diagram opposite.

The individual fractions were extracted with boiling benzene, the extracts being filtered and examined by tlc. The extracts from fraction A contained impurities and were discarded.

The extracts from fractions B and C contained the 7-deuterio-thioaldehyde (67b) and were evaporated. Chromatography (alumina 8 x 2.3 cm) of the residue with benzene-acetone (199:1) gave yellow

eluates which afforded 3,6-dimethylpyrrolo[2,1-b]thiazole-7-[^{2}H]-thiocarbaldehyde (67b) (0.175 g, 9%) as yellow needles from cyclohexane.

Found C, 55.28; H+D, 4.68; N, 7.16%

$C_9H_8S_2ND$ requires C, 55.05; H+D, 4.66; N, 7.14%

[Nmr spectrum ($CDCl_3$); δ2.38 (3H, d, $J_{3Me, 2H}$=1.2Hz, 3-Me or 6-Me), δ2.43 (3H, d, $J_{6Me, 5H}$=1.2Hz, 6-Me or 3-Me), δ6.62 (1H, q, 2-H), δ6.95 (1H, q, 5-H)]

The extracts from fraction D contained a mixture of compounds (67b) and (80) and were discarded.

The extracts from fraction E contained the 5-deuteriothioaldehyde (80) and were evaporated. Chromatography (alumina 6 x 2.3 cm) of the residue with benzene gave red eluates which afforded a further crop of compound (80) (0.324 g) as red prisms from cyclohexane-benzene (3:1). (Total yield of compound (80), 0.829 g, 42%).

The extracts from fractions F and G contained slow moving impurities and were discarded.

(4) Synthesis of 5-Deuteriomethyl-6-methylpyrrolo[2,1-b]thiazole-7-thiocarbaldehyde

5-Deuteriomethyl-6-methylpyrrolo[2,1-b]thiazole (76)

Aluminium chloride (7.470 g, 56 mmol) was added as quickly as possible to a rapidly stirred solution of lithium aluminium deuteride (1.176 g, 28 mmol) in dry ether (200 ml). A solution of 6-methylpyrrolo-[2,1-b]thiazole-5[^{2}H]thiocarbaldehyde(75) in benzene (50 ml) was added dropwise to the mixture over 30 minutes and the mixture was then

stirred for a further 30 minutes. The mixture was then poured cautiously over crushed ice-sulphuric acid (600 g:1.6 ml), made alkaline with sodium carbonate, and extracted with ether. The extracts were washed with water, dried (Na_2SO_4) and evaporated. Distillation of the residual liquid at 90-95°/0.1 mm Hg gave 5-deuteriomethyl-6-methylpyrrolo[2,1-b]thiazole (76) (0.658 g, 53%) as a pale yellow liquid.

Found C, 62.66; H+D, 5.81; N, 9.03%

$C_8H_6D_3SN$ requires C, 62.69; H+D, 6.04; N, 9.08%

[Nmr spectrum ($CDCl_3$); δ2.53 (3H, 6-Me), δ5.95 (1H, b, 7-H), δ6.46 (1H, d, $J_{2H,3H}$=4.2Hz, 2-H), δ7.07 (1H, q, $J_{3H,2H}$=4.2Hz, $J_{3H,7H}$=0.7Hz, 3-H)]

5-Deuteriomethyl-6-methylpyrrolo[2,1-b]thiazole-7-thiocarbaldehyde (72)

Phosphoryl chloride (0.23 ml, 2.5 mmol) was added to a solution of dimethylformamide (0.23 ml, 3 mmol) in 1,2-dichloroethane (2 ml) at 0° . After 10 minutes a solution of 5-deuteriomethyl-6-methylpyrrolo-[2,1-b]thiazole (76) (0.308 g, 2 mmol) in 1,2-dichloroethane (1 ml) was added and the solution was kept at room temperature for 1 hour. The solution was then shaken with aqueous 2M-sodium hydrogen sulphide (20 ml), diluted with water and extracted with benzene. The extracts were washed with water (x3), dried (Na_2SO_4) and evaporated. Chromatography (alumina 12 x 2.5 cm) of the residue with benzene gave orange eluates which afforded 5-deuteriomethyl-6-methylpyrrolo[2,1-b]-thiazole-7-thiocarbaldehyde (72) (0.380 g, 95%) as yellow cubes from cyclohexane-benzene (1:1), mp = 163-165° .

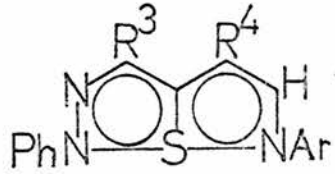
Found C, 54.50; H+D, 4.83; N, 6.95%

$C_9H_6D_3SN$ requires C, 54.51; H+D, 4.70; N, 7.06%

[Nmr spectrum ($CDCl_3$); δ2.28 (3H, 6-Me), δ7.04 (1H, d, $J_{2H, 3H}$=4.0Hz, 2-H), δ7.42 (1H, d, $J_{3H, 2H}$=4.0Hz, 3-H), δ10.63 (1H, 7-CHS)]

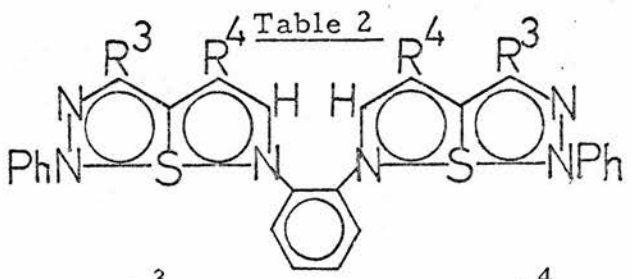
Solutions were in deuteriochloroform unless otherwise stated. Signals are singlets unless otherwise stated (d=doublet, t=triplet, q=quartet, dd=double doublet, b=broad peak, m=multiplet).

Table 1 (1,6-diaryl-6a-thia-1,2,6-triazapentalenes)



Compound	1-Ph	R^3		R^4	5-H	6-Ar
1a	7.00-7.68(m)	2.78		2.54(d) $J_{4Me,5H}$= 0.5Hz	7.98(q)	7.00-7.68(m)
1b	6.94-7.66(m)	3.00(t, α-CH_2)	2.05(q, β-CH_2)	2.76 (t, γ-CH_2)	8.12	6.94-7.66(m)
1c	6.84-7.60(m)	2.76		2.52(d) $J_{4Me,5H}$= 0.5Hz	7.90(q)	6.84-7.60(m, $C_6\underline{H}_4OMe$) 3.76 ($C_6H_4O\underline{Me}$)
1d	6.88-7.64(m)	3.04(t, α-CH_2)	2.08(q, β-CH_2)	2.79(t, γ-CH_2)	8.12	6.88-7.64(m, $C_6\underline{H}_4OMe$) 3.80 ($C_6H_4O\underline{Me}$)
1g	6.74-7.70(m)	2.82		2.62(d) $J_{4Me,5H}$= 0.6Hz	8.06(b)	6.74-7.70(m, $C_6\underline{H}_4NH_2$) 4.18 (b, $C_6H_4N\underline{H}_2$)
1h	6.71-7.56(m)	3.00(t, α-CH_2)	2.07(q, β-CH_2)	2.78(t, γ-CH_2)	8.20	6.71-7.56(m, $C_6\underline{H}_4NH_2$) 4.30 (b, $C_6H_4N\underline{H}_2$)
13a	6.90-7.70(m)	2.84(b)		2.61(d) $J_{4Me,5H}$= 0.5Hz	8.34(q)	6.90-7.70(m, $C_6\underline{H}_4$- and C$\underline{H}$=N) 2.84 (b, NMe_2)

Table 2

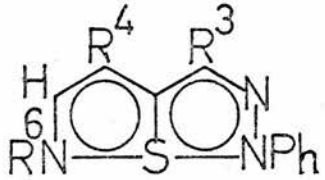


Compound	1-Ph and 6-Ar	R^3	R^4	5-H
12a	6.97-7.48(m)	2.42(d) $J_{4Me,5H}$=0.5Hz	2.67	7.90(q)
12b	6.94-7.42(m)	2.88(t, α-CH_2) 1.90(q, β-CH_2)	2.66(t, γ-CH_2)	8.10

Table 3 (6a-thia-1,2,6-triazapentalenes)

* - in d^6-dimethylsulphoxide

** - in d^6-dimethylsulphoxide at 100°C

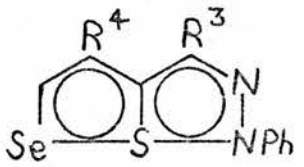


Compound	1-Ph	R^3	R^4	5-H	R^6
11*	7.40(b, o- and m-H) 7.00(b, p-H)	2.42(b) or 2.60(b)	2.42(b) or 2.60(b)	8.04(b)	11.70
1m*	6.91-7.64(m)	2.86(t, α-CH_2) 1.93(q, β-CH_2)	2.52(t, γ-CH_2)	8.01	11.60
1n	7.20-7.36(m, o- and m-H) 6.94-7.06(m, p-H)	2.62	2.36(b)	7.85(b)	4.10
1n*	7.35-7.40(m, o- and m-H) 6.96-7.14(m, p-H)	2.62	2.40(b)	8.08(b)	4.08

Table 3 (cont)

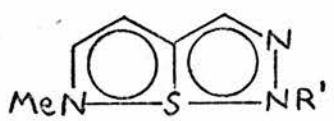
Compound	1-Ph	R^3	R^4	5-H	R^6
1o	7.30-7.37(m, o- and m-H) 6.90-7.04(m, p-H)	2.88(t, α-CH_2) 1.98(q, β-CH_2)	2.54(t, γ-CH_2)	7.88	4.06
1o*	7.30-7.36(m, o- and m-H) 6.90-7.10(m, p-H)	2.86(t, α-CH_2) 1.92(q, β-CH_2)	2.56(t, γ-CH_2)	8.05	4.00
1r**	7.31-7.36(m, o- and m-H) 6.90-7.04(m, p-H)	2.56	2.36	7.90	7.12(d, J=9.7Hz, o- or m-ArH) 8.11(d, J=9.7Hz, o- or m-ArH) 11.10(b, NH)
1s**	7.32-7.36(m, o- and m-H) 6.90-7.14(m, p-H)	2.84(t, α-CH_2) 1.93(q, β-CH_2)	2.58(t, γ-CH_2)	7.92	7.04(d, J=9.5Hz, o- or m-ArH) 8.16(d, J=9.5Hz, o- or m-ArH) 11.18(b, NH)

Table 4 (6a-Thia-6-selena-1,2-diazapentalenes)



Compound	1-Ph	R^4	R^3	2-H
19a	7.24-7.50 (m, m- and p-H) 7.74-7.85 (m, o-H)	2.94(d) $J_{3Me, 2H}$ = 0.8Hz	2.88	10.18(q)
19b	7.20-7.44 (m, m- and p-H) 7.70-7.84 (m, o-H)	3.06(t, α- and γ-CH_2)	2.05(q, β-CH_2)	10.02

Table 5 (6a-thia-1,2,6-triazapentalenes)



Compound	R^1	3-H	4-H	5-H	6-Me
27b	7.77(d, J=9.8Hz, o- or m-H) 8.23(d, J=9.8Hz, o- or m-H)	8.26	7.01(d) $J_{4H, 5H}$ = 3.6Hz	8.08(dd) $J_{5H, 4H}$ = 3.6Hz $J_{5H, 6Me}$ = 0.7Hz	3.72(d) $J_{6Me, 5H}$ = 0.7Hz
27c	3.70	8.02	6.64(d) $J_{4H, 5H}$ = 4.0Hz	7.90(d b)	3.54(b)

APPENDIX B: ULTRAVIOLET AND VISIBLE SPECTRAL DATA

Solutions were in cyclohexane (sh=shoulder, b = broad peak)

* - Qualitative spectrum

Table 1 (3,4-Disubstituted-6a-thia-1,2,6-triazapentalenes)

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
1a	203	4.36	1b	205	4.41
	251	4.14		250	4.18
	292	4.18		295	4.20
	476	4.34		488	4.35
1c	203	4.36	1d	203	4.43
	228	4.14		244	4.16
	292	4.22		295	4.23
	475	4.32		488	4.34
1e	204	4.34	1f	204	4.37
	284	4.20		283	4.16
	361	4.05		361	4.07
	513	4.41		530	4.43
1g	210	4.41	1h	210	4.46
	235(sh)	4.17		253(sh)	4.17
	288	4.10		289	4.14
	476	4.20		499	4.30
12a	205	4.58	12b	207	4.59
	245	4.43		247	4.41
	291	4.37		294	4.40
	470	4.57		482	4.55
13a	203	4.39			
	223(sh)	4.34			
	247	4.30			
	290(sh)	4.23			
	476	4.30			

Table 1 (cont)

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
1l	205	4.50	1m	205	4.39
	221(sh)	4.27		221(sh)	4.17
	277	4.18		278	3.98
	437	4.20		431	4.33
				452	4.31
1n	205	4.42	1o	202	4.41
	221(sh)	4.18		227(sh)	4.03
	277	4.09		280	4.02
	440	4.34		434	4.34
				453	4.34
1r*	199		1s	200	4.49
	220(sh)			225	4.20
	327			329	4.21
	373			376	4.24
	501			499	4.34
	517(sh)			527	4.31
1t*	195		1u*	191	
	248			250	
	287			289	
	463			459	
	477(sh)			479	

Table 2 (6a-Thia-6-selena-1,2-diazapentalenes)

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
19a	204	4.27	19b	204	4.32
	254	4.43		250	4.49
	281	4.12		279(sh)	4.12
	514	4.08		525	4.07

Table 3 (6a-thia-1,2,6-triazapentalenes)

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
27b	201	4.22	27c	202	4.00
	236	3.99		223	4.01
	344	3.78		283	2.41
	456	4.55		386	4.11

REFERENCES

1 F. Arndt, P. Nachtwey, and J. Pusch, Ber., 1925, 58, 1633

2 F. Arndt, R. Schwarz, C. Martius, and E. Aron, Rev. Fac. Sci. Univ. Instabul Ser. C, 1948, A13, 57; Chem. Abstracts, 1948, 42, 4178g

3 G. Traverso and M. Sanesi, Ann. Chim. (Rome), 1953, 43, 795

4 S. Bezzi, M. Mammi, and C. Garbuglio, Nature, 1958, 182, 247

5 S. Bezzi, C. Garbuglio, M. Mammi, and G. Traverso, Gazzetta, 1958, 88, 1226

6 G. Guillouzo, Bull. Soc. chim. France, 1958, 1316

7 N. Lozac'h, Adv. Heterocyclic Chem., 1971, 13, 161

8 E. Klingsberg, Quart. Rev., 1969, 23, 537

9 D.H. Reid, "Organic Compounds of Sulphur, Selenium and Tellurium", ed. D.H. Reid, The Chemical Society, London, 1970, Vol. 1, p. 231

10 R.J.S. Beer, ibid., 1972, Vol. 2, p. 497

11 R.J.S. Beer, ibid., 1974, Vol. 3, p. 494

12 M. Mammi, R. Bardi, C. Garbuglio, and S. Bezzi, Acta. Cryst., 1960, 13, 1048

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

14 A. Hordvik, ibid., 1966, 20, 1885

15 L. Pauling, "The Nature of the Chemical Bond", 3rd edn., Cornell Univ. Press, Ithaca, New York, 1960

16 D.W.J. Cruickshank, Acta Cryst., 1970, B26, 1260

17 A. Hordvik, O. Sjolset, and L.J. Saethre, Acta Chem. Scand, 1973, 27, 379

18 O. Hjellum and A. Hordvik, ibid., 1973, 27, 2666

19 A. Hordvik and L.J. Saethre, ibid., 1972, 26, 1729

20 A. Hordvik and K. Julshamn, ibid., 1971, 25, 1835

21 A. Hordvik, E. Sletten, and J. Sletten, ibid., 1969, 23, 1852

22 A. Hordvik, ibid., 1971, 25, 1583

23 P.L. Johnston and I.C. Paul, Chem. Comm., 1968, 863

24 B. Birknes, A. Hordvik, and L.J. Saethre, Acta Chem. Scand., 1972, 26, 2140

25 A. Hordvik, Israel J. Chem., 1972, 10, 239

26 L.K. Hansen, A. Hordvik, and L.J. Saethre, Chem. Comm., 1972, 222

27 M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, Nature, 1961, 192, 1282

28 A. Hordvik and K. Julshamn, Acta Chem. Scand., 1971, 25, 1895

29 A. Hordvik and K. Julshamn, ibid., 1971, 25, 2507

30 F.C. Leung and S.C. Nyburg, Canad. J. Chem., 1972, 50, 324

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

32 A. Hordvik and L. Milje, ibid., 1973, 27, 511

33 B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, J. Mol. Spec., 1958, 2, 361

34 P.L. Johnstone, K.I.G. Reid, and J.C. Paul, J. Chem. Soc. (B), 1971, 946

35 A. Hordvik, unpublished data

36 G. Pfister-Guillouzo and N. Lozac'h, Bull. Soc. chim. France, 1964, 3254

37 J.G. Dingwall, S. McKenzie, and D.H. Reid, J. Chem. Soc. (C), 1968, 2543

38 J.G. Dingwall, Ph.D. Thesis, University of St. Andrews, 1968

39 A.S. Ingram, D.H. Reid, and J.D. Symon, J.C.S. Perkin I, 1974, 242

40 D.H. Reid, J. Chem. Soc. (C), 1971, 3187

41 R.M. Christie, Ph.D. Thesis, University of St. Andrews, 1974

42 R.J.S. Beer and A.J. Poole, Tetrahedron Letters, 1972, 1835

43 H. Behringer and J. Falkenberg, Chem. Ber., 1969, 102, 1580

44 D. Paquer, M. Perrier, and J. Vialle, Bull. Soc. chim. France, 1970, 4517

45 S. McKenzie and D.H. Reid, J. Chem. Soc. (C), 1970, 145

46 R.K. Mackie, S. McKenzie, D.H. Reid, and R.G. Webster, J.C.S. Perkin I, 1973, 657

47 J.G. Dingwall, A.S. Ingram, D.H. Reid, and J.D. Symon, J.C.S. Perkin I, 1973, 2351

48 D.H. Reid and R.G. Webster, J.C.S. Perkin I, 1972, 1447

49 R. Pinel, Y. Mollier, and N. Lozac'h, Bull. Soc. chim. France, 1966, 3187

50 D.T. Clark, D. Kilcast, and D.H. Reid, Chem. Comm., 1971, 638

51 D.T. Clark, Int. J. Sulphur Chem., 1972, C, 7, 11

52 B.J. Lindberg, ibid., 1972, C, 7, 35

53 R.A.W. Johnston and S.D. Ward, Theor. Chim. Acta, 1969, 14, 420

54 A. Grandin and J. Vialle, Bull. Soc. chim. France, 1967, 1851

55 H. Behringer and D. Weber, Chem. Ber., 1964, 97, 2567

56 E. Klingsberg, J. Org. Chem., 1968, 33, 2915

57 F. Gerson, R. Gleiter, J. Heinzer, and H. Behringer, Angew. Chem. Internat. Edn., 1970, 9, 306

58 Q. Sherc and K. Hedberg, J. Amer. Chem. Soc., 1974, 96, 289

59 G. Giacometti and R. Rigatti, J. Chem. Phys., 1959, 30, 1633

60 G. Pfister-Guillouzo and N. Lozac'h, Bull. Soc. chim. France, 1963, 153

61 K. Maeda, Bull. Chem. Soc. Japan, 1960, 33, 1466

62 K. Maeda, ibid., 1961, 34, 785

63 K. Maeda, ibid., 1961, 34, 1166

64 R.A.W. Johnstone and S.D. Ward, Theor. Chim. Acta, 1969, 14, 420

65 R. Gleiter and R. Hoffmann, Tetrahedron, 1968, 24, 5899

66 R. Daudel and O. Chalvet, J. Chem. Phys., 1956, 53, 943

67 R.J. Hach and R.E. Rundle, J.Amer. Chem. Soc., 1951, 73, 4321

68 G.S. Pimentel, J. Chem. Phys., 1951, 12, 187

69 R. Mooney-Slater, Acta Cryst., 1959, 12, 187

70 T. Migchelsen and A. Vos, ibid., 1967, 23, 796

71 T. Bernstein and F.H. Herbstein, ibid., 1968, B24, 1640

72 M. Stavaux and N. Lozac'h, Bull. Soc. chim. France, 1967, 2082

73 G. Traverso, Ann. Chim. (Rome), 1954, 44, 1018

74 G. Traverso, Ann. Chim. (Rome), 1955, 45, 687

75 H. Behringer, M. Ruff and R. Weidenmann, Chem. Ber., 1964, 97, 1732

76 D. Leaver, W.A.H. Robertson, and D.M. McKinnon, J. Chem. Soc., 1962, 5104

77 G. Traverso, Ann. Chim. (Rome), 1956, 46, 821

78 G. Traverso, Chem. Ber., 1958, 91, 1224

79 J.G. Dingwall, D.H. Reid, and J.D. Symon, J. Chem. Soc. (C), 1970, 2412

80 F. Arndt, P. Nachtwey, and E. Scholz, Chem. Ber., 1924, 57, 1903

81 E. Klingsberg, J. Amer. Chem. Soc., 1963, 85, 3244

82 O. Coulibaly and Y. Mollier, Bull. Soc. chim. France, 1969, 3208

83 E.I.G. Brown, D. Leaver, and D.M. McKinnon, J. Chem. Soc. (C), 1970, 1202

84 D.T. Clark and D. Kilcast, Tetrahedron, 1971, 4367

85 R.J.S. Beer, D. Cartwright, and D. Harris, Tetrahedron Letters, 1967, 953

86 R.J.S. Beer, D. Cartwright, R.J. Gait, R.A.W. Johnstone, and S.D. Ward, Chem. Comm., 1968, 688

87 R.J.S. Beer, D. Cartwright, R.J. Gait and D. Harris, J. Chem. Soc. (C), 1971, 963

88 J. Bignebat and H. Quiniou, Compt. rend., 1968, 267, C, 180

89 J. Bignebat and H. Quiniou, ibid., 1969, 269, C, 1129

90 J. Bignebat and H. Quiniou, Bull. Soc. chim. France, 1972, 645

91 J.G. Dingwall, D.H. Reid, and K. Wade, J. Chem. Soc. (C), 1969, 913

92 G. Duguay, D.H. Reid, K.O. Wade, and R.G. Webster, J. Chem. Soc. (C), 1971, 2829

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

94 R.J.S. Beer and R.J. Gait, Chem. Comm., 1970, 328

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

96 R.M. Christie, A.S. Ingram, D.H. Reid, and R.G. Webster, Chem. Comm., 1973, 92

97 R.J.S. Beer, R.P. Carr, D. Cartwright, D. Harris, and R.A. Slater J.C.S. (C), 1968, 2440

98 M. Stavaux and N. Lozac'h, Bull. Soc. chim. France, 1968, 2077

99 J.G. Dingwall and D.H. Reid, Chem. Comm., 1968, 863

100 R.M. Christie and D.H. Reid, J.C.S. Perkin I , 1976, 228

101 F.E. King and D.G.I. Felton, J. Chem. Soc., 1949, 274

102 M. Perrier and J. Vialle, Bull. Soc. chim. France, 1971, 4591

103 A. Grandin and J. Vialle, ibid., 1967, 1851

104 G. Lang and J. Vialle, ibid., 1967, 2865

105 H. Behringer and D. Bender, Chem. Ber., 1967, 100, 4027

106 J.L. Derocque and J. Vialle, Bull. Soc. chim. France, 1967, 3079

107 J.L. Derocque, M. Perrier, and J. Vialle, ibid., 1968, 2062

108 D. Wobig, Annalen, 1975, 1018

109 A. Schoberl and A. Wagner, in "Methodeu der Organischen Chemie" (ed. E. Muller, Houben, Weyl, Berlin), 9, 762

110 R.G. Webster, Ph.D. Thesis, University of St. Andrews, 1974

111 R.N. Hurd and G. De La Mater, Chem. Rev., 1961, 61, 45

112 N.V. Sidgwick, "The Organic Chemistry of Nitrogen", 3rd Edn., page 248

113 A.W. Hofmann, Annalen, 1868, 145, 360

114 H. Klinger, Chem. Ber., 1878, 10, 1023

115 E. Baumann and E. Fromm., ibid., 1889, 22, 2600

116 J.F. Suyrer, Rec. Trav. Chim., 1905, 24, 377

117 F.O. Chattaway and E.G. Kellet, J. Chem. Soc., 1930, 1359

118 O. Hassell and H. Viervoll, Acta Chem. Scand., 1947, 1, 149

119 N.F. Moerman and E.H. Wibenga, Z. Krist., 1937, 97, 323

120 K.E. Calderbank and R.J.W. Le Fevre, J. Chem. Soc., 1949, 199

121 K. Hayaski, J. Chem. Soc. Japan, 1953, 74, 386

122 K. Hayaski, ibid., 1955, 76, 284

123 E. Baumann and E. Fromm., Chem. Ber., 1891, 24, 1431

124 E. Campaigne and W. Budde, Proc. Indiana Acad. Sci., 1948, 58, 111

125 J.A. Stanfield and L.B. Reynolds Jr., J. Amer. Chem. Soc., 1952, 74, 2878

126 R.U. Lemieux, R.K. Kullnig, H.J. Bernstein, and W.G. Schneider, ibid., 1958, 80, 6098

127 E. Campaigne, N.F. Chamberlain, and B.E. Edwards, J. Org. Chem., 1962, 27, 135

128 E. Campaigne and M. Georgiadis, ibid., 1963, 28, 1044

129 E. Campaigne and M. Georgiadis, J. Heterocyclic Chem., 1969, 6, 339

130 R.B. Woodward et al, J. Amer. Chem. Soc., 1960, 82, 3800

131 S. McKenzie, Ph.D. Thesis, University of St. Andrews, 1966

132 M. Fraser, A. Melera, B.B. Molloy, and D.H. Reid, J. Chem. Soc., 1962, 3288

133 D.H. Reid, unpublished data

134 J.L. Bolland, Quart. Rev., 1949, 3, 1

135 U.S. Patent 2,816,116

136 U.S. Patent 2,653,910

137 U.S. Patent 2,995,569

138 U.S. Patent 2,763,908

139 U.S. Patent 2,971,909

140 U.S. Patent 3,621,030

141 U.S. Patent 3,816,312

142 Belgian Patent 823,391

143 R.G. Webster, M.Sc. Thesis, University of St. Andrews, 1972

144 P. Sykes and H. Ullah, J.C.S. Perkin I , 1972, 2305

145 G. Wittig and M. Schlosser, Ber., 1961, 94, 1373

146 R. Förster, F. Lange, D. Drossbach,and W. Seidel, Z. anorg. Chem., 1923, 128, 245

147 F. Feher and W. Laue, Z. anorg. Chem., 1956, 288, 103; F. Feher, W. Laue, and G. Winkhaus, Z. anorg. Chem., 1956, 288, 113

148 R. Willstätter and T. Wirth, Ber., 1909, 42, 1920

149 G.R. Pettit and L.R. Garson, Canad. J. Chem., 1965, 43, 2640

150 K. Ziegler and H. Colonius, Annalen, 1930, 479, 135; H. Gilman E.A. Zoellner,and W.M. Selby, J. Amer. Chem. Soc., 1932, 54, 1957

151 K. Gewald, J. Prakt. Chem., 1966, 31, 214

152 R. Scattergood, unpublished data

153 V. Prelog, L. Ruzicka,and O. Metzler, Helvetica Chem. Acta, 1947, 30, 1883

154 B.B. Molloy, D.H. Reid,and F.S. Skelton, J. Chem. Soc., 1965, 65