ASPECTS OF THE REACTIVITY OF 1,6,6aλ^4-TRITHIAPENTALENES AND RELATED HYPERVALENT SYSTEMS WITH ELECTROPHILES

being a Thesis presented by
David Burns McLeary, B.Sc.,
to the University of St. Andrews,
in application for the degree of
Doctor of Philosophy.

November, 1984.

To My Mother and Father.

DECLARATION

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

November, 1984.

D. B. McLeary

CERTIFICATE

I hereby declare that David Burns McLeary has spent eleven terms at research work under my supervision, has fulfilled the conditions of the Resolution of the University Court, 1967, No. 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

November, 1984.

Director of Research

UNIVERSITY CAREER

I entered the University of St. Andrews in October, 1973, and subsequently graduated with the degree of B.Sc., with Upper Second Class Honours, in Chemistry in June,1977.

In October, 1977, I was awarded a University of St. Andrews Research Studentship, and from then until July, 1980, I carried out research at the Department of Chemistry, University of St. Andrews, under the supervision of Professor D. H. Reid. The results of my work during that period are embodied in this thesis.

ACKNOWLEGEMENTS

I wish to express my sincere gratitude to Professor D. H. Reid for his advice, guidance and continued interest throughout the course of this work.

I am most grateful to Professor Lord Tedder and Professor P. A. H. Wyatt for making available the excellent research facilities of the Department of Chemistry, University of St. Andrews.

I wish to thank the technical staff of the Department of Chemistry, University of St. Andrews, for the invaluable assistance which they provided.

Finally, I must thank the University of St. Andrews for awarding the Research Studentship which made this work possible.

EXPLANATORY NOTE

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

Part 1 is a review of the relevant background literature.

Part 2 is a discussion of the results obtained.

Part 3 is a description of the experimental procedures employed to obtain the results discussed in Part 2, and is complementary to Part 2.

Where reference is made to the chemical literature, this is denoted by a number in superscript form, the key to which can be found at the end of this thesis.

The structural formulae which are presented for the purpose of illustration are assigned Arabic numerals. These numerals correspond to the numbers which have been assigned to the appropriate compounds in the text. The structural formulae keys to Parts 1 and 2 are independent. The key to Part 2 is the same as that of Part 3.

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SUMMARY

The reaction of 5-substituted-1,2-dithiole-3-thiones with arenediazonium tetrafluoroborates was investigated.

4,5-Dimethyl-1,2-dithiole-3-thione reacted with benzenediazonium tetrafluoroborate to give 4-methyl-1-phenyl-5-phenylthio-6,6aλ^4-dithia-1,2-diazapentalene.

p-Nitrobenzenediazonium tetrafluoroborate reacted with the same thione to give 4-methyl-1-(*p*-nitrophenyl)-5-(*p*′-nitrophenylthio)-6,6aλ^4-dithia-1,2-diazapentalene. With *p*-methoxybenzenediazonium tetrafluoroborate, 4,5-dimethyl-1,2-dithiole-3-thione gave 4-methyl-1-(*p*-methoxyphenyl)-5-(*p*′-methoxyphenylthio)-6,6aλ^4-dithia-1,2-diazapentalene. 4,5,6,7-Tetrahydrobenzo[d]-1,2-dithiole-3-thione and *p*-methoxybenzenediazonium tetrafluoroborate gave 1-(*p*-methoxyphenyl)-5-(*p*′-methoxyphenylthio)-3,4-propano-6,6aλ^4-dithia-1,2-diazapentalene.

5-Methyl-1,2-dithiole-3-thione reacted with benzenediazonium tetrafluoroborate to give 1-phenyl-5-phenylthio-6,6aλ^4-dithia-1,2-diazapentalene, 3-carbomethoxy-1,6-diphenyl-6aλ^4-thia-1,2,5,6-tetraazapentalene, and a compound believed to be phenyl 1,6-diphenyl-4-phenylazo-6aλ^4-thia-1,2,5,6-tetraazapentalene-3-dithiocarboxylate.

The same thione and *p*-methoxybenzenediazonium tetrafluoroborate gave 1-(*p*-methoxyphenyl)-5-(*p*′-methoxyphenylthio)-6,6aλ^4-dithia-1,2-diazapentalene, *p*-methoxyphenyl 1,6-di(*p*′-methoxyphenyl)-6aλ^4-thia-1,2,5,6-tetraazapentalene-3-dithiocarboxylate, and 3-carbomethoxy-

1,6-di(p-methoxyphenyl)-6aλ^4-thia-1,2,5,6-tetraazapentalene.

In general, the reaction of 5-substituted-1,2-dithiole-3-thiones with arenediazonium tetrafluoroborates in the presence of added pyridine afforded higher yields of the corresponding 6,6aλ^4-dithia-1,2-diazapentalene. Exceptionally, 5-methyl-1,2-dithiole-3-thione reacted with benzenediazonium tetrafluoroborate in the presence of pyridine to give only phenyl 1,6-diphenyl-6aλ^4-thia-1,2,5,6-tetraazapentalene-3-dithiocarboxylate and 3-carbomethoxy-1,6-diphenyl-6aλ^4-thia-1,2,5,6-tetraazapentalene.

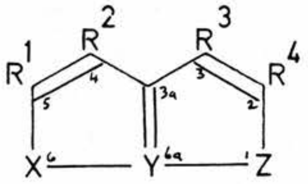
The successful reaction of 5-_tert_-butyl-1,2-dithiole-3-thione and 5-phenyl-1,2-dithiole-3-thione with arenediazonium tetrafluoroborates gave the corresponding 3-arylthio-1,2-dithiolylium tetrafluoroborates.

The formation of metal complexes of several triheterapentalene systems was investigated. Pentacarbonylchromium(0), molybdenum(0) and tungsten(0) complexes of 1-oxa-6,6aλ^4-dithia-2-azapentalenes, 6,6aλ^4-dithia-1,2-diazapentalenes, and 6,6aλ^4-dithia-1-azapentalenes were synthesised. Attempts to prepare the tungsten pentacarbonyl complex of 5-_tert_-butyl-1-oxa-6,6aλ^4-dithiapentalene were unsuccessful.

Group VI A metal pentacarbonyl derivatives of substituted 1,2-dithiole-3-thiones were also prepared.

FOREWORD

1,6,6aλ^4-Triheterapentalenes are a class of heterocyclic compounds based on structure (I), in which X and Z are NR, O, S or Se, and Y is S, Se or Te.



(I)

Many other aza analogues of (I) arise when one or more of the ring carbon atoms at positions 2, 3, 4, and 5 are replaced by nitrogen atoms.

The first triheterapentalene was synthesised by Arndt, Nachtwey and Pusch[1] in 1925. They prepared 2,5-dimethyl-1,6,6aλ^4-trithiapentalene ((I), X=Y=Z=S, $R^1=R^4=CH_3$, $R^2=R^3=H$) from heptane-2,4,6-trione and phosphorus pentasulphide, but at that time they incorrectly assigned a 1,2-dithiepine structure to the compound. The true structure was not established until 1958, when Mammi, Bezzi and Garbuglio[2] examined Arndt's compound by X-ray diffraction. Their data showed the molecule to be planar, with the three sulphur atoms in a straight line, and spaced 2.36 Å apart, a distance which is much longer than the normal sulphur-sulphur single-bond length (2.08 Å).

Since these results were announced, much attention has been given to understanding the unusual structures displayed by 1,6,6aλ^4-trithiapentalenes and their analogues. Several theories of bonding have been proposed to account for the unusual geometry of this class of heterocycles. The most widely accepted theory invokes the concept of a four-electron three-centre bond to hold the heteroatoms together. The central heteroatom contributes two electrons to this bond, while the lateral atoms contribute one electron each. 1,6,6aλ^4-triheterapentalenes also possess a 10π-electron system.

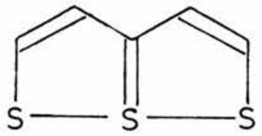
Many syntheses of triheterapentalenes are now available, and these have enabled the chemical reactivity of the heterocycles to be studied. The electrophilic substitution reactions of triheterapentalenes have received most attention. With this type of reaction, electrophilic attack usually occurs at ring position C(3) or C(4). The product is determined by both the nature of the attacking electrophile and the substitution pattern of the triheterapentalene. In the case of 1,6,6aλ^4-trithiapentalenes, there is also some evidence to suggest that electrophilic attack at the lateral sulphur atoms, S(1) and S(6), can occur as a competing reaction.

The object of the work reported in Parts 2 and 3 of this thesis has been to explore the scope and mechanism of electrophilic substitution reactions involving heteroatoms (1) and (6) of triheterapentalenes. Eventually, studies of this kind should lead to a clearer understanding of the chemical reactivity of these heterocycles.

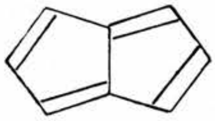
Reviews of the chemistry of triheterapentalenes have been written by Lozac'h[3,4], Klingsberg[5], Reid[6], Beer[7-9], Leaver and Davis[10,11]. The structure, bonding and reactivity of these compounds will be discussed in detail in Part 1 of this thesis.

NOTE ON NOMENCLATURE

The heterocyclic compounds discussed in this thesis can be named in a variety of ways. For example, compound (II) has been known previously as: 6a-thiathiophthen, thiothiophthen, meribicyclo-3,5-epidithiopenta-2,4-dienthial and 1,2-dithiolo[b]-1,2-dithiole.

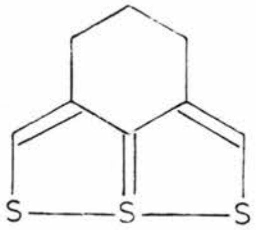


(II)



(III)

In the interests of consistency and clarity in this thesis, all compounds related to structure (I) will be named in accordance with the system proposed by Lozac'h[3]. Nomenclature using this system is based on the assumption that compound (II) and related structures can be derived from pentalene (III) by the use of replacement nomenclature. Thus, compound (IV), which under the more rigorous fusion system of nomenclature would be named 6,7-dihydro-5*H*-2,2aλ^4,3-trithiacyclopent[cd]indene, will be named 3,4-propano-1,6,6aλ^4-trithiapentalene.



(IV)

Also for reasons of clarity, the metal complexes of 1,6,6aλ^4-trithiapentalenes and related compounds discussed in this thesis have been numbered in the same way as the corresponding 1,6,6aλ^4-triheterapentalenes.

INTRODUCTION

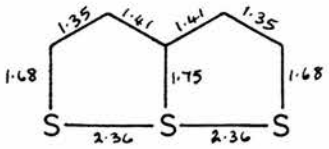
A.

STRUCTURAL STUDIES OF $1,6,6a\lambda^4$-TRIHETERAPENTALENES

Many of the techniques for structure analysis have been used to elucidate the structures of $1,6,6a\lambda^4$-triheterapentalenes. Studies involving X-ray crystallography and nmr spectroscopy have been particularly informative.

1. X-Ray Crystallography

$1,6,6a\lambda^4$-Trithiapentalene (1)[12] crystal structure data show that the molecule is planar, with the three sulphur atoms adopting a collinear arrangement, and possesses C_{2v} symmetry along the C(3a)-S(6a) bond. The observed S-S bond lengths (2.363 Å) are ca. 10 per cent longer than the average interatomic distance of two-electron, covalent sulphur-sulphur single bonds[13] (2.08 Å), but are considerably shorter than the sum of the Van der Waals' radii for two sulphur atoms[14] (3.70 Å). These data suggest that significant bonding interactions occur between the two lateral sulphur atoms and the central sulphur atom, but that the bond orders are less than unity.



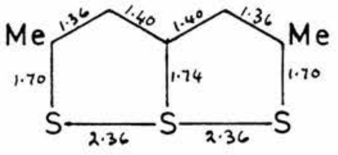
(1)

Note: for reasons of clarity, the double bonds of structures (1) to (20) have been omitted.

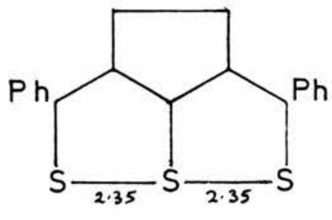
The C(2)-S(1) and C(5)-S(6) bond lengths (1.684 Å) fall between those of a carbon-sulphur single bond[14] (1.81 Å) and carbon-sulphur double bond[14] (1.61 Å), and partial double bond character is indicated. In contrast, the C(3a)-S(6a) bond length (1.75 Å) is only slightly shorter than a normal carbon-sulphur single bond. The remaining bond lengths in the trithiapentalene skeleton are similar to those of the corresponding bonds in naphthalene[15] which also possesses a 10π-electron system.

Symmetrically substituted trithiapentalenes may or may not exhibit equal sulphur-sulphur bond lengths and C_{2v} symmetry. Examples of molecules which possess C_{2v} symmetry are (2)[2,16], (3)[17] and (4)[18]. The molecular dimensions of the 2,5-dimethyl compound (2) are similar to those of the parent molecule (1).

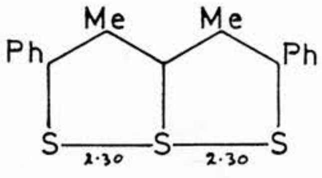
The unequal sulphur-sulphur bond lengths found in some trithiapentalenes are due to the influence of inter- and intramolecular crystal forces. Symmetrically substituted molecules with unequal sulphur bond lengths are (5)[19], (6)[20] and (7)[21]. The 2,5-diphenyl compound (5) has nearly equal S-S bond lengths, the slight distorsion being caused by weak intermolecular effects. The two phenyl groups of compound (5), like those of many other trithiapentalenes, are twisted out of the basal plane of the molecule. The S-S bond lengths in the 3,4-diphenyl compound (7) are markedly unequal. The combined influences of steric clash of the bulky phenyl substituents and intermolecular effects are thought to be responsible for this inequality.


Me
1.36
1.40
1.40
1.36
Me
1.70
1.74
1.70
S
S
S
2.36
2.36

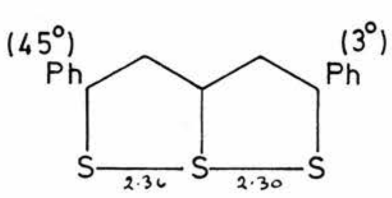
(2)


Ph
Ph
S
S
S
2.35
2.35

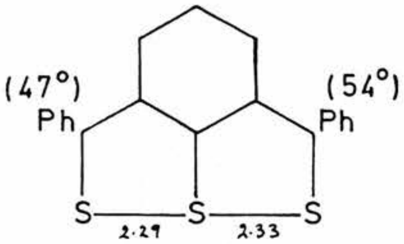
(3)


Me
Me
Ph
Ph
S
S
S
2.30
2.30

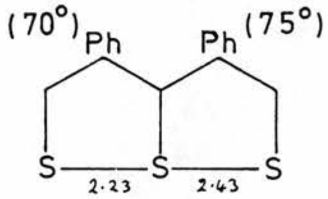
(4)


(45°)
Ph
(3°)
Ph
S
S
S
2.36
2.30

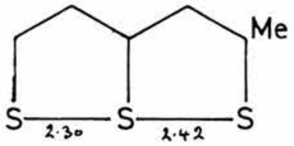
(5)


(47°)
Ph
(54°)
Ph
S
S
S
2.29
2.33

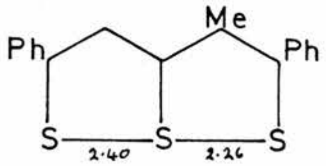
(6)


(70°)
Ph
Ph
(75°)
S
S
S
2.23
2.43

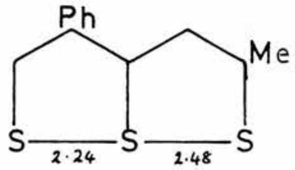
(7)


Me
S
S
S
2.30
2.42

(8)

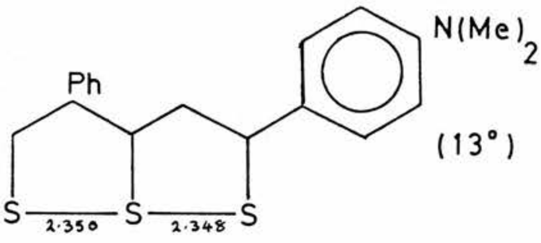

Me
Ph
Ph
S
S
S
2.40
2.26

(9)


Ph
Me
S
S
S
2.24
2.48

(10)

Unsymmetrically substituted trithiapentalenes commonly possess unequal S-S bond lengths, e.g. compounds (8)[22], (9)[23] and (10)[24]. However, the electronic effects exerted by substituents may cause the bond lengths to become equal. For example, 2-*p*-dimethylaminophenyl-4-phenyl-1,6,6aλ^4-trithiapentalene (11), a molecule with a completely unsymmetrical substitution pattern, is believed[25] to have almost equal S-S bond lengths for this reason.

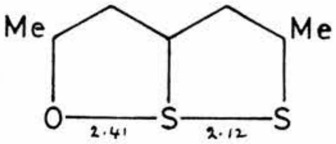


(11)

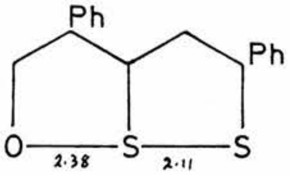
Although the individual S-S bond lengths found in trithiapentalenes vary by up to 0.4 Å, the total S(1)-S(6) interatomic distance remains constant at ca. 4.7 Å.

X-ray crystallographic studies of many other triheterapentalene systems have confirmed the bicyclic planar nature of these heterocycles.

Oxadithiapentalenes usually exhibit strong S-S and weak S-O bonding interactions. Thus, compounds (12)[26] and (13)[27] display S-S bond lengths (ca. 2.1 Å) close to the covalent single bond value (2.08 Å)[13]. The S-O bond length (ca. 2.4 Å) falls between the covalent S-O single bond length (1.70 Å)[14] and the sum of the Van der Waals' radii for a sulphur and an oxygen atom (3.2 Å)[14]. The molecules are therefore considered to be bicyclic.

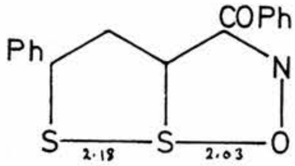


(12)

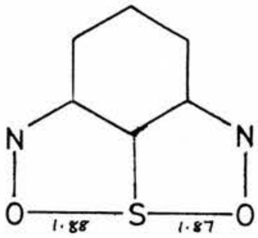


(13)

Oxadithiaazapentalene (14)[25] and dioxathiadiazapentalene (15)[29] possess considerably shorter S-O bond lengths than those found in compounds (12) and (13), which suggests that these are also bicyclic structures.

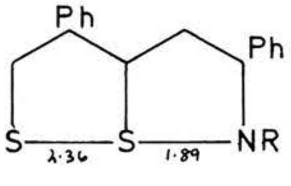


(14)



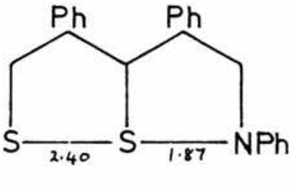
(15)

Dithiaazapentalenes (16)[30] and (17)[31] display S-S bond lengths similar to those found in 1,6,6aλ^4-trithiapentalene (1). The S-N bond lengths are greater than those of two electron, covalent S-N single bonds (1.74 Å)[14], but are significantly less than the sum of the Van der Waals' radii for a sulphur and nitrogen atom (3.35 Å)[14]. These data support the formulation of dithiaazapentalenes as bicyclic structures, involving four-electron three-centre bonding.



(16)

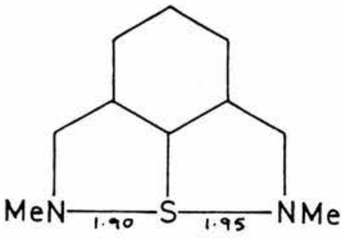
R = 3-QUINOLYL



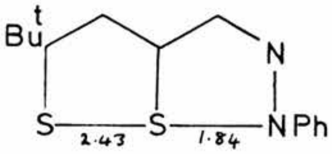
(17)

Thiadiazapentalene (18)[32] does not exhibit two equal S-N bond lengths, presumably because of strain induced by the propano bridge and intermolecular forces. However, the average S-N bond length (1.92 Å), like the average S-S bond length found in 1,6,6aλ^4-trithiapentalene (1), is approximately 10 per cent longer than the normal single-bond length, which suggests the molecule is bicyclic.

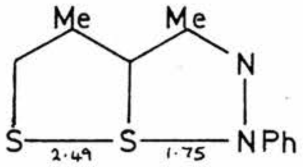
6,6aλ^4-dithia-1,2-diazapentalenes (19)[33] and (20)[34] have S-S bonds which are longer and therefore weaker than those of 1,6,6aλ^4-trithiapentalene (1), but the S-N bonds are shorter than those found in compounds (17) and (18). This suggests that compounds are to be regarded as bicyclic and not as 3-phenylazomethylene-1,2-dithioles (21).



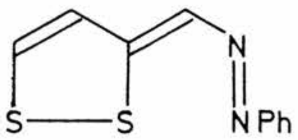
(18)



(19)



(20)

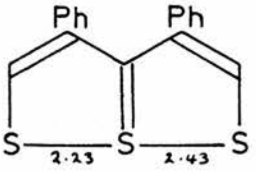


(21)

A comprehensive review of the results from numerous X-ray crystallographic studies of triheterapentalenes has been published by Hordvik and Saethre[35].

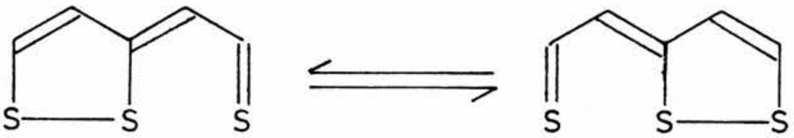
2. NMR Spectroscopy

Several studies of 1,6,6aλ^4-trithiapentalenes[36-38] have been performed using the nmr method. In all cases, the spectra of symmetrical trithiapentalenes show equivalence of ring protons or identical substituents at the pairs of sites C(2), C(5) and C(3), C(4). This indicates that in solution, where intermolecular effects are averaged out, these compounds possess C_{2v} symmetry and equal S-S bond lengths. Even trithiapentalenes, e.g. (22)[39], which have unequal S-S bond distances in the solid state, show this symmetry in solution.



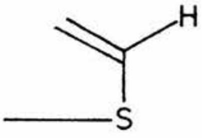
(22)

^{1}H nmr studies of trithiapentalenes have not yet established whether the apparent symmetry is real or time-averaged. Valence tautomers, (23) and (24), interconverting more rapidly than the nmr time scale, could give rise to time-averaged C_{2v} symmetry[40].



(23) (24)

Dingwall, McKenzie and Reid[37] have provided evidence for the existence of the real-time bicyclic structure. They have found that the chemical shift of thioformyl protons in heterocyclic thioaldehydes[41,42] is usually in the range δ 10.4 - 11.2. Even when the thioformyl group is in the polarised form $=CH-S^-$, the proton chemical shift does not occur at field values higher than δ 10.2. As the chemical shift for H-2 in trithiapentalenes is usually found at field values higher than δ 9.3, this is consistent with H-2 being in an environment more like (25) than (26).



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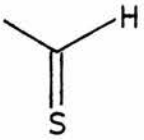
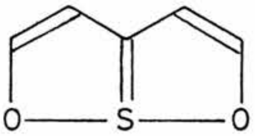


(26)

Observations that the ring protons in trithiapentalenes are more deshielded than the corresponding protons in oxadithiapentalenes[36] and thiophene[3] has been taken as evidence that trithiapentalenes have the greater ring currents and aromaticity[43].

^{1}H nmr studies of other symmetrically substituted triheterapentalene systems, (27)[44], (28)[45], (29)[46] and (30)[47], have shown these to exhibit real or time-averaged C_{2v} symmetry in solution.



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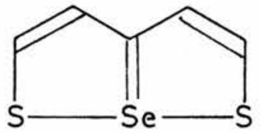

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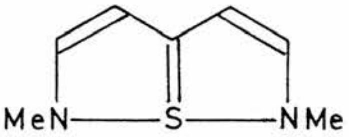

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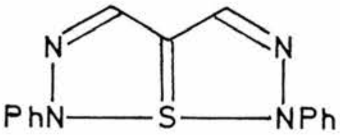


(30)

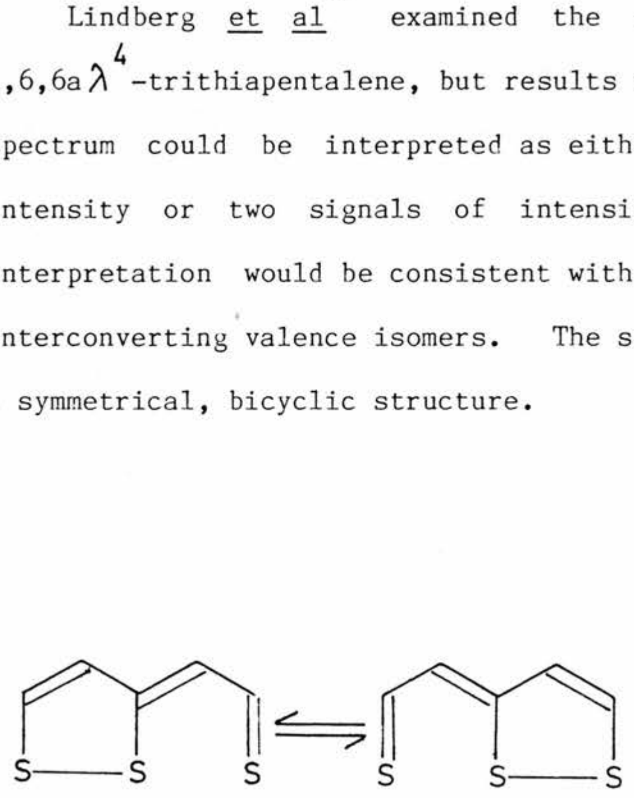
Low temperature (-60°C) ^{1}H nmr studies of many triheterapentalene systems[44,45,49,50] have failed to detect the presence of interconverting valence tautomeric forms such as (23) and (24). However, this does not preclude the possibility that very rapid isomerisation may occur at these low temperatures.

In agreement with ^{1}H nmr findings, the ^{13}C nmr spectra of symmetrically substituted trithiapentalenes[51,52] indicate C_{2v} symmetry within the nmr time scale.

3. Photoelectron Spectroscopy

Several groups of workers have studied the structure of 1,6,6aλ^4-trithiapentalenes using the electron spectroscopy for chemical analysis (ESCA) method.

Lindberg *et al*[53] examined the solid state structure of 1,6,6aλ^4-trithiapentalene, but results were inconclusive. The ESCA spectrum could be interpreted as either three signals of equal intensity or two signals of intensity ratio 2:1. The first interpretation would be consistent with the presence of two rapidly interconverting valence isomers. The second interpretation favours a symmetrical, bicyclic structure.



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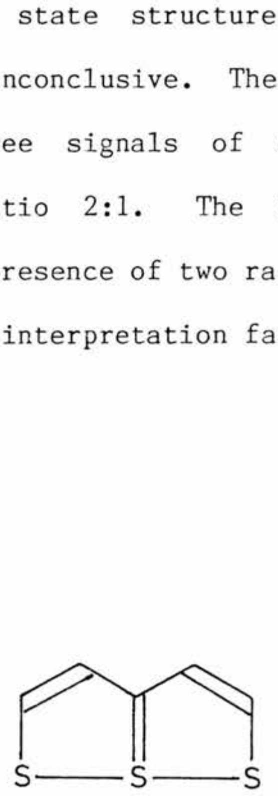
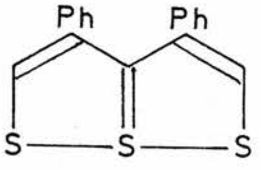


(31)

In a more sophisticated solid-state study, Clark, Kilcast and Reid[54] measured the sulphur molecular core binding energies of various trithiapentalenes and interpreted the results using self-consistent field molecular orbital calculations. Two types of sulphur atom in the ratio of 2:1 were found in 1,6,6aλ^4-trithiapentalene (31) and 2,5-dimethyl-1,6,6aλ^4-trithiapentalene (32). This suggested that both molecules possess symmetrical structures. The sulphur molecular core binding energies for the 3,4-diphenyl (22) and 2-methyl (33) derivatives indicated that each compound contained three types of sulphur atom. Thus, these compounds have unsymmetrical geometry for the bicyclic nucleus. Clark and co-workers' findings are entirely consistent with the X-ray crystallographic data, (cf. structures (1)[12], (2)[2,16], (7)[21] and (8)[22]).



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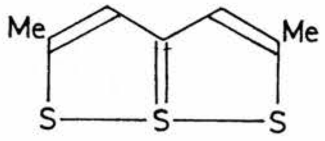

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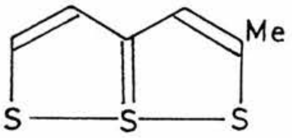
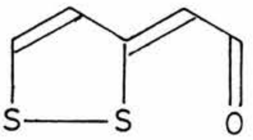


(33)

Gas-phase ESCA studies of the 1,6,6aλ^4-trithiapentalene structure[55] and of symmetrical 1,6-dioxa-6aλ^4-thia-2,5-diazapentalene and its 6aλ^4-selena and 6aλ^4-tellura analogues[56] are in agreement with Clark's findings.

4. Infra-Red Spectroscopy

Infra-red spectroscopy has been most useful in correctly identifying the structures of oxadithiapentalenes. This class of compounds may be represented by ketonic structures (34) or bicyclic structures (35).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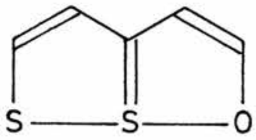
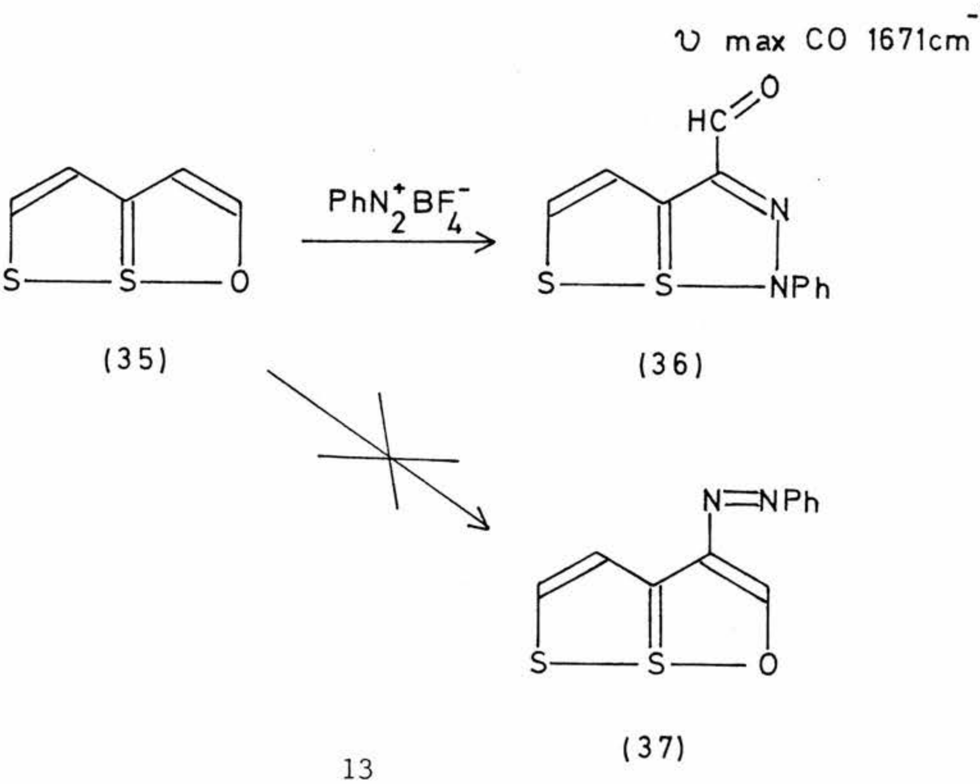

(35)

The absence of any C=O absorption in the 1620–1750 cm^{-1} region of the infra-red spectra of these compounds supports the correctness of structure (35). Festal and Mollier[57] have used ^{18}O isotopic labelling experiments to demonstrate that the C–O vibrations of (35) lie at lower frequency, in the 1500–1610 cm^{-1} region.

Infra-red spectroscopy has also proved useful in establishing that rearrangements resulting in the formation of exocyclic carbonyl groups sometimes occur when triheterapentalenes, for example (35), react with electrophiles[58].



5. Miscellaneous Methods

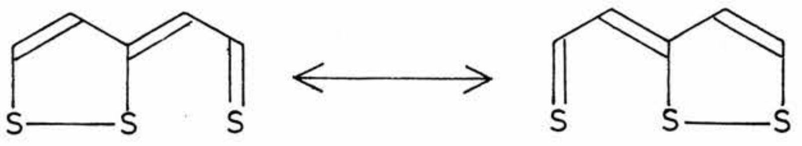
Dipole moment measurements[3,4] and ultra-violet, visible[4], and microwave spectroscopy[59] have been used to study the structures of triheterapentalenes. In general, these methods are of little value for this purpose.

B. BONDING IN 1,6,6aλ^4-TRIHETERAPENTALENES

Since the structure of Arndt's compound was correctly identified in 1958[2], considerable attention has been given to the structure and bonding of triheterapentalenes.

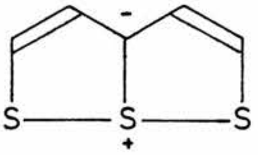
Any acceptable theory of bonding in triheterapentalenes must explain why the molecules are planar, with the three heteroatoms collinear. The sulphur-sulphur bond distances, which lie between the sum of the Van der Waals' radii (ca. 3.7 Å) and the covalent radii (ca. 2.08 Å) for two sulphur atoms, implying a bond order of less than one, must also be rationalised.

Several theories[2,48,60,62-72] have been proposed to account for these observations. The term "single bond-no bond resonance" was suggested by Bezzi[2], who invoked the concept of resonance hybrid of canonical forms (23) and (24) to describe the bonding in 1,6,6aλ^4-trithiapentalenes. However, this model is not satisfactory because it fails to account properly for the observed bond lengths[13] and aromaticity[43].



(23) (24)

A sulphonium ylid structure (34) which satisfies common valence theory and the octet rule at sulphur has also been suggested[60]. The



(34)

weakness of this model is that charge redistribution indicates that electrophilic attack should occur at the C(2) and C(5) positions. Experimental data do not support this finding[61].

Other theories of bonding require expansion of the valence shell on the central sulphur atom to include the use of d-orbitals[62-72].

The question of d-orbital participation in the bonding of trithiapentalenes is not without controversy[72]. Numerous theoretical calculations of various degrees of sophistication have been attempted to resolve this question. Early extended Hückel studies[66,67] gave best agreement with observed results when 3d-orbital functions were included in calculations. Hansen, Hordvik and Saethre[68] have carried out CNDO/2 calculations on 1,6,6aλ^4-trithiapentalene and its 2- and 3-methyl and 2- and 3-phenyl derivatives. Results consistent with X-ray data were obtained when allowance was made for d-orbital participation in bonding.

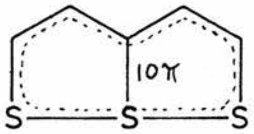
In contrast, more recent <u>ab initio</u> studies by Clark[69], and Palmer and Findlay[70,71] oppose this view. These workers have found that calculations using the ground state wave functions of trithiapentalenes show no appreciable d-orbital involvement in bonding.

These conflicting results indicate the shortcomings of theoretical calculations. Either they do not vary any or only a single geometrical parameter or their result indicates an imperfect parameterisation.

Gleiter and Hoffmann[66] have made a notable contribution towards understanding the bonding in trithiapentalenes and other triheterapentalene systems. These workers consider that sigma bonding between the three sulphur atoms can arise from the combination of three p-orbitals, one from each atom, to give three molecular orbitals. Four electrons - two from the central sulphur atom and one each from the lateral sulphur atoms - occupy these orbitals. In the ground state, the bonding orbital, in which electron density is spread over all three sulphur atoms, and non-bonding orbital, in which electron density is located mainly on the lateral atoms, are both doubly occupied. The anti-bonding orbital remains vacant. This type of bonding effectively means that three atoms are bonded together by two electrons, which is consistent with the unusually long sulphur-sulphur bond lengths found in these molecules.

Further stabilisation of the three-centre bonding system results from the formation of a delocalised 10π-electron system in the trithiapentalene molecule. The central sulphur atom and each carbon atom each contribute one electron and the lateral sulphur atoms each provide two electrons to this π system. The stabilisation engendered by this type of π-bonding is not great because the equilibrium distance for the three-centre bond occurs where $p\pi - p\pi$ orbital overlap is slight[6]. Thus, using the Gleiter and Hoffmann model, 1,6,6aλ^4-trithiapentalene may be described by either formula (35) or (36).

(35)



(36)

The bonding in all known triheterapentalenes can be explained successfully using this concept of four-electron three-centre bonding. Examples of this type of bonding are also found in inorganic chemistry[73], e.g. (I_3^-)[74] and $(SeCN)_3^-$[75]. Individual bond lengths in the three-centre sequences of these ions are found[75] to be approximately 10 per cent longer than the single-bond length (cf. trithiapentalenes in Section A).

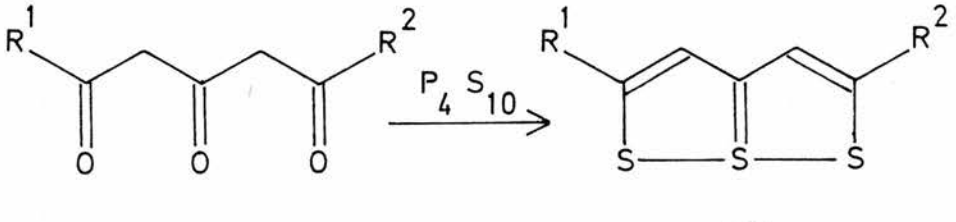
C. SYNTHESIS OF 1,6,6aλ^4-TRIHETERAPENTALENES

Many syntheses of triheterapentalenes are now available. This section describes the more important synthetic routes to the 1,6,6aλ^4-trithiapentalenes and their oxa and aza analogues, which are relevant to the work embodied in this thesis.

1. Synthesis of 1,6,6aλ^4-Trithiapentalenes

(a) From 1,3,5-Triketones

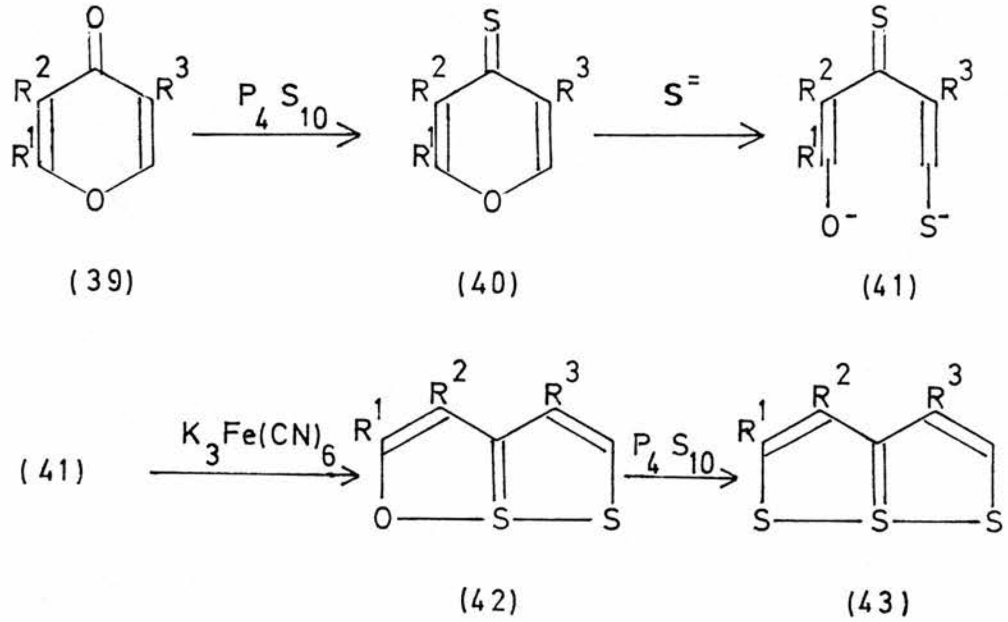
1,6,6aλ^4-Trithiapentalenes are obtained directly by the reaction of 1,3,5-triketones (37) with tetraphosphorus decasulphide. This reaction has been used extensively to prepare 2,5-disubstituted trithiapentalenes (38)[1,76,77], although Behringer[78] reports that yields rarely exceed 30 per cent.



(37) (38)

(b) From 4H-Pyran-4-ones and Related Compounds

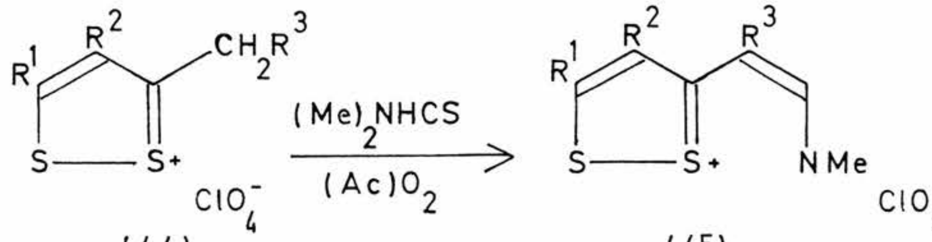
Ring opening of 4H-pyran-4-thione (40), prepared from 4H-pyran-4-one (39) and tetraphosphorus decasulphide, by sodium sulphide in dipolar aprotic solvents, followed by potassium ferricyanide oxidation of the resulting dianion (41) leads to the formation of oxadithiapentalenes (42), which can be thionated to give trithiapentalenes (43)[79].



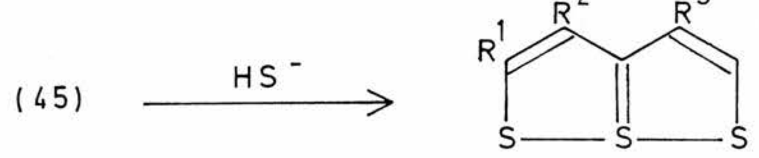
Sulphide ion ring opening of 4<u>H</u>-thiopyran-4-thiones, followed by oxidation, yields trithiapentalenes directly[80].

(c) From 1,2-Dithiolylium Salts

3-methyl(ene)-1,2-dithiolylium salts (44) condense with dimethylthioformamide in boiling acetic anhydride to give 3-(2-dimethylaminovinyl)-1,2-dithiolylium (Vilsmeier) salts (45)[37]. The salts react readily with sodium hydrogen sulphide to give 1,6,6aλ^4-trithiapentalenes (43).



(44) (45)



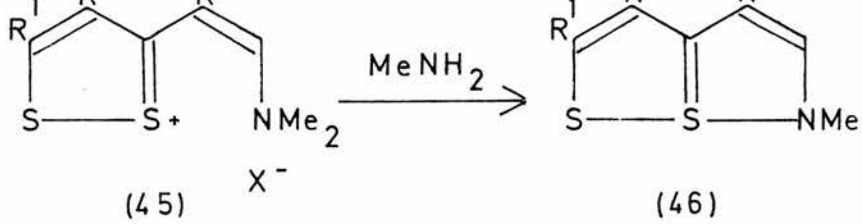
(43)

Salts of type (45) have been prepared by other workers[81,82].

2. Synthesis of Aza Analogues of 1,6,6aλ^4-Trithiapentalenes

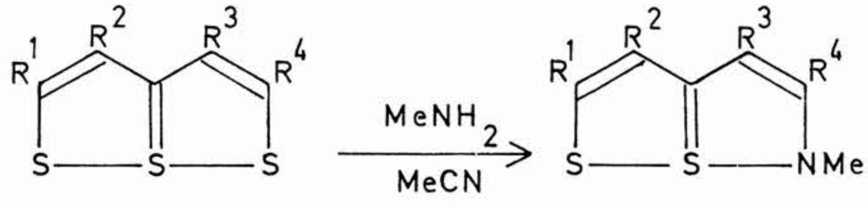
(a) Triheterapentalenes Containing One Nitrogen Atom

Reid and co-workers[83] have devised two noteworthy syntheses of 1,6aλ^4-dithia-6-azapentalenes. Reaction of 3-(2-dimethylaminovinyl)-1,2-dithiolylium salts (45)[37] with methylamine gave the expected dithiaazapentalenes (46) in good yield.



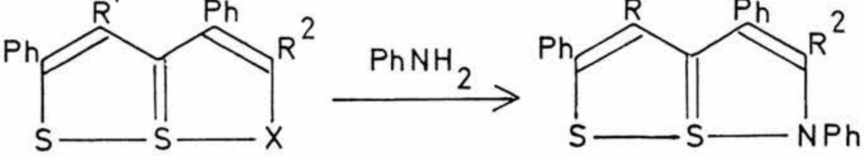
(45) (46)

1,6,6a λ^4-trithiapentalenes (47) in acetonitrile were found to react with ethanolic methylamine to give 1-methyl-6,6a λ^4-dithia-1-azapentalenes (46) directly[83].



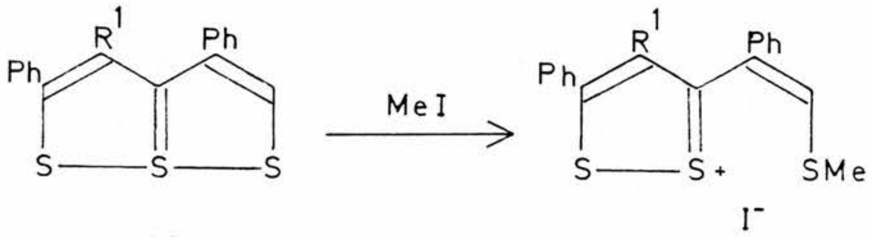
(47) (46)

Klingsberg[84] has shown that compounds (48, X = S,O; R^1 = Ph,H; R^2 = H) will react with aniline to give 1-phenyl-dithiaazapentalenes (49).

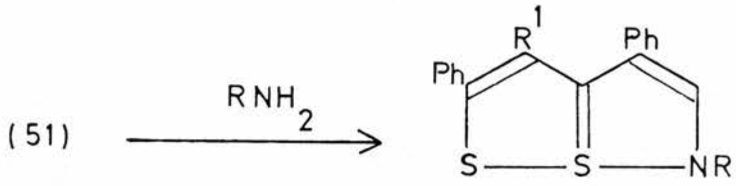


(48) (49)

S-Alkylation of trithiapentalenes (50, R^1 = H, Ph) results in the formation of dithiolylium salts (51) which react with primary amines to yield dithiaazapentalenes (52)[84].

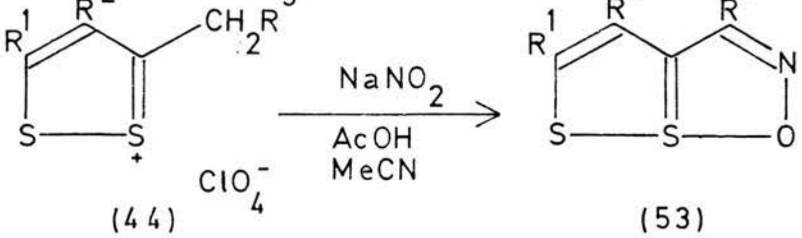


(50) (51)



(52)

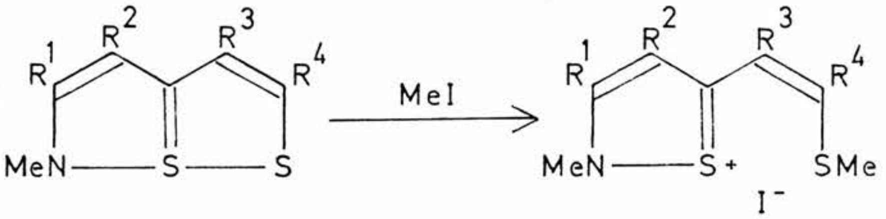
The 3-alkyl(ene) group of compound (44) is acidic[85] and will react with sodium nitrite in acetonitrile and acetic acid to give 1-oxa-6,6a λ^4-dithia-2-azapentalenes (53) in excellent yield[56].



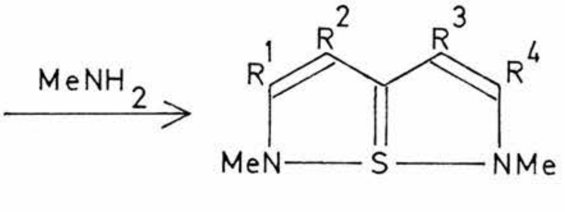
(44) (53)

(b) Triheterapentalenes Containing Two Nitrogen Atoms

1-Methyl-6,6aλ^4-dithia-1-azapentalenes (46) react with methyl iodide to yield isothiazolium iodides (54) which react with methylamine to give symmetrical 6aλ^4-thia-1,6-diazapentalenes (55)[46].



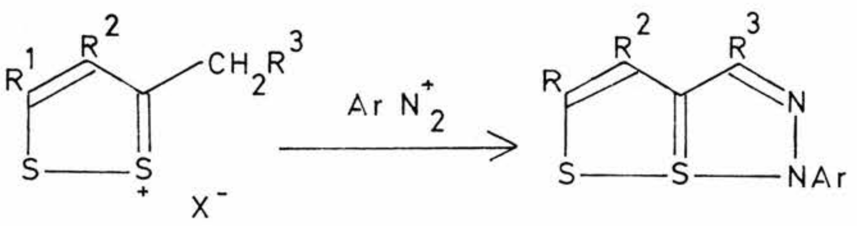
(46) (54)



(54)

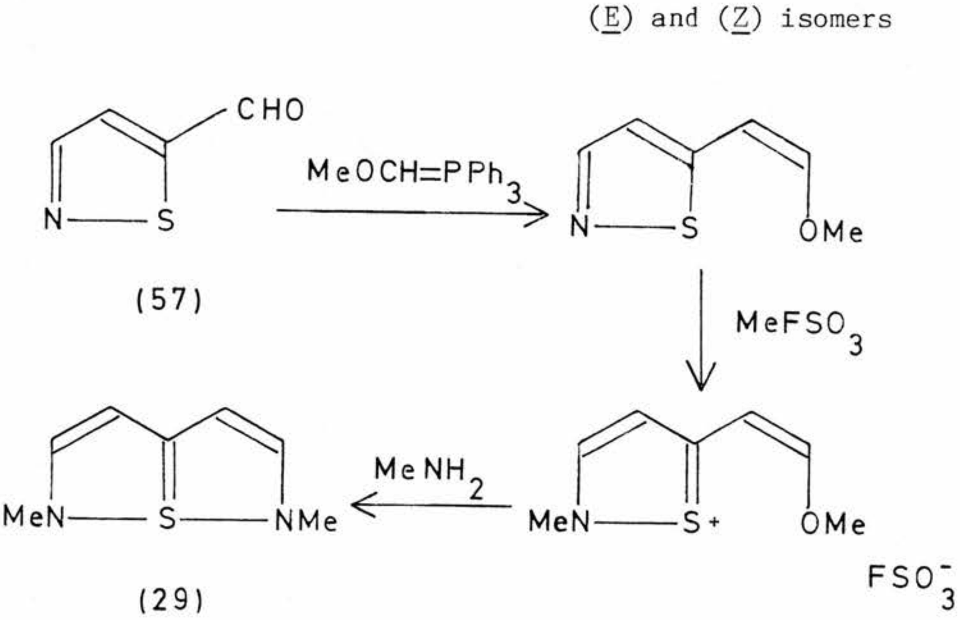
(55)

3-Methyl(ene)-1,2-dithiolylium salts (44) react with arenediazonium tetrafluoroborates to give 1-aryl-6,6aλ^4-dithia-1,2-diazapentalenes (56)[88].



(44) (56)

Both (*E*)- and (*Z*)-5-(2-methoxyvinyl)isothiazole isomers result from the Wittig reaction of isothiazole-5-carbaldehyde (57) and methoxymethylenetriphenylphosphorane[89]. Methylation of the isomers, followed by reaction with methylamine, gave 1,6-dimethyl-$6a\lambda^4$-thia-1,6-diazapentalene (29) (Scheme 1).

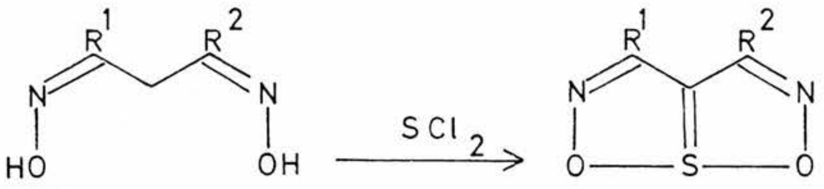


(57)

(29)

Scheme 1

A remarkably simple synthesis of dioxadiazapentalenes (59) from the reaction between dioximes of 1,3-diketones (58) and sulphur dichloride has been described by Vialle[90,91].

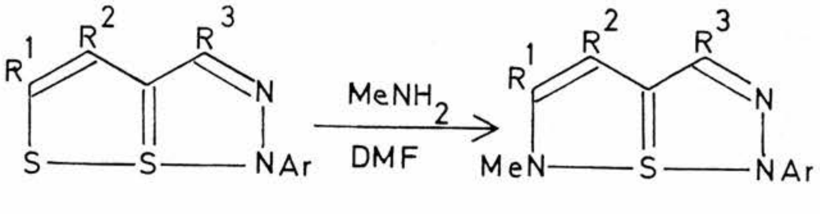


(58)

(59)

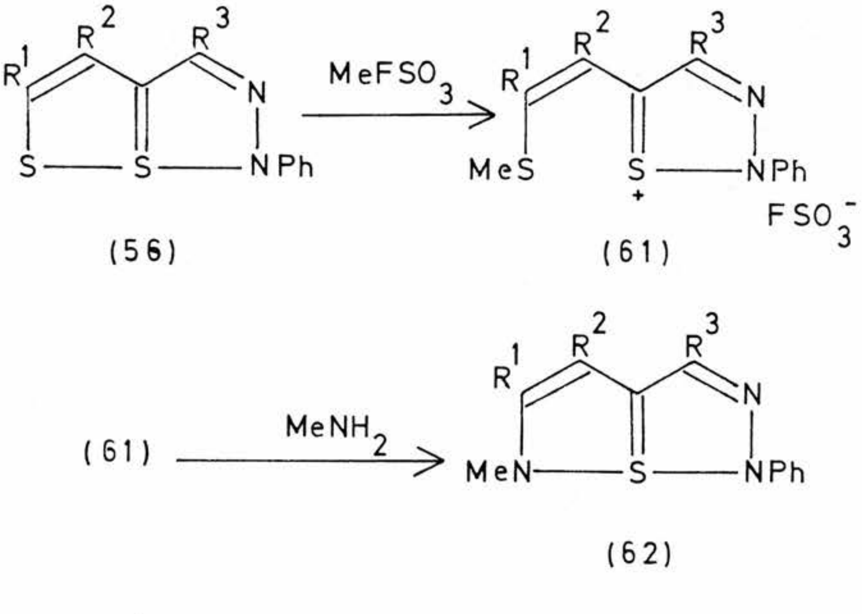
(c) Triheterapentalenes Containing Three Nitrogen Atoms

$6a\lambda^4$-Thia-1,2,6-triazapentalenes (60) have been synthesised[92] by the reaction of 1-aryl-6,$6a\lambda^4$-dithia-1,2-diazapentalenes (56) in dimethylformamide with ethanolic methylamine.

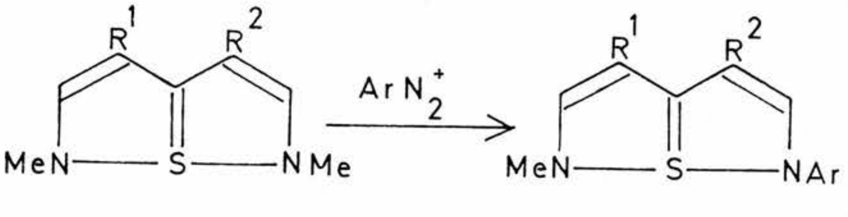


(56) (60)

Methylation of dithiadiazapentalenes (56) by methyl fluorosulphonate takes place at sulphur atom S(1) to give 1,2,3-thiadiazolium fluorosulphonates (61). These fluorosulphonates react with methylamine to give 1-phenyl-6-methyl-6a λ^4-thia-1,2,6-triazapentalenes (62)[92].

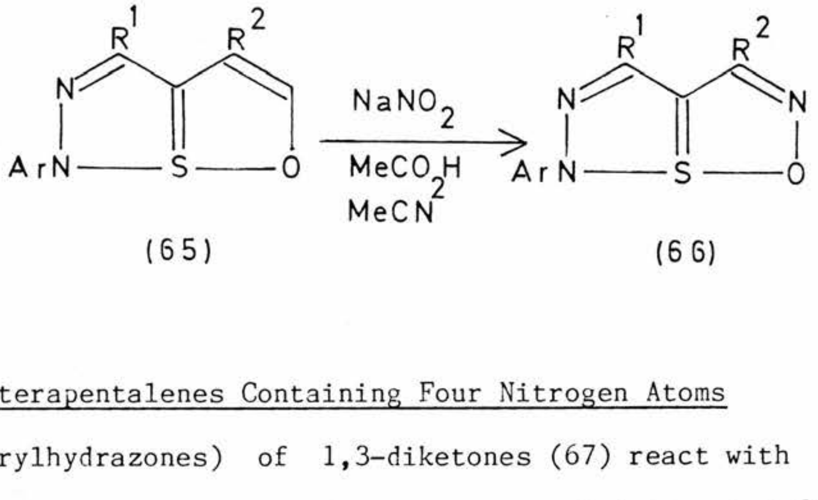


3,4-Dialkyl-6a λ^4-thia-1,6-diazapentalenes (63) couple with arenediazonium tetrafluoroborates to form isothiazolium intermediates which eliminate a methyliminomethyl group to give thiatriazapentalenes (64)[92].



(63) (64)

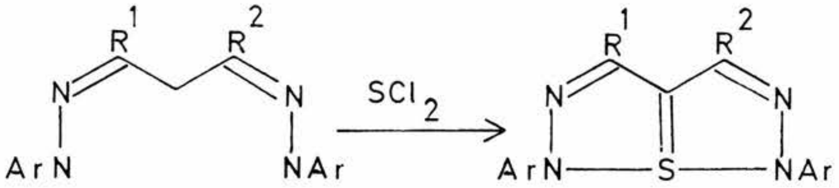
Oxathiadiazapentalenes (65, $R^1=R^2$=alkyl) undergo nitrosodeformylation when treated with sodium nitrite in acetic acid and acetonitrile. The resulting oxathiatriazapentalenes (66) are obtained in excellent yield[93].



(65) (66)

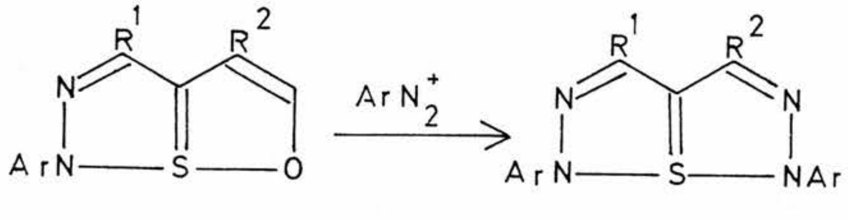
(d) Triheterapentalenes Containing Four Nitrogen Atoms

Bis(arylhydrazones) of 1,3-diketones (67) react with sulphur dichloride or disulphur dichloride to give 1,6-diaryl-6aλ^4-thia-1,2,5,6-tetraazapentalenes (68)[94].



(67) (68)

Thiatetraazapentalenes (68) are also obtained by reaction of 3,4-dialkyl-1-aryl-6-oxa-6aλ^4-thia-1,2-diazapentalenes (65) with arenediazonium tetrafluoroborates and accompanying deformylation[47].

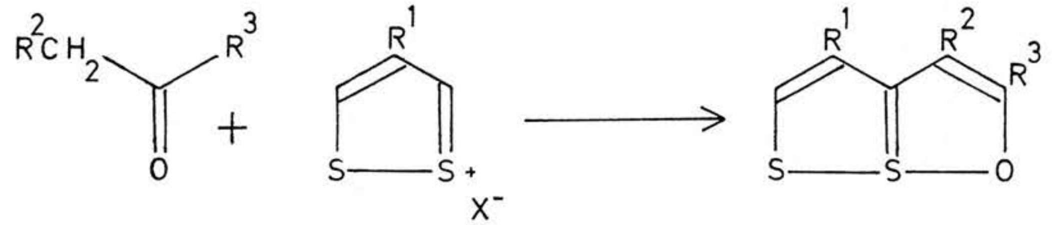


(65) (68)

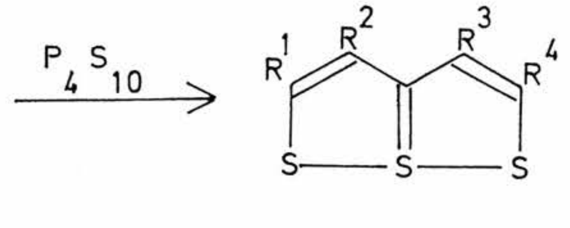
Synthesis of Oxygen Analogues of 1,6,6aλ^4-Trithiapentalenes

(a) Triheterapentalenes Containing One Oxygen Atom

1,2-Dithiolylium cations (69) which are not substituted at either ring carbon atoms (3) or (5) react with active methyl(ene) compounds, e.g. ketones, to yield substituted oxadithiapentalenes (70)[95,96]. Reaction of compounds (70) with tetraphosphorus decasulphide yields the corresponding trithiapentalenes (47).

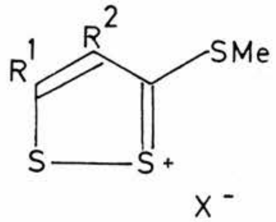


(69) (70)

(70) 

(47)

1,2-Dithiolylium cations, e.g. compounds (71) and (72), which have potentially good leaving groups at ring position 3 also react with active methylene compounds to give 1-oxa-6,6aλ^4-dithiapentalenes[3,82,97].



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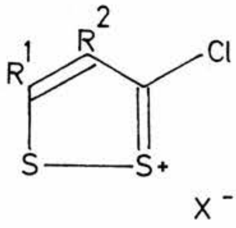
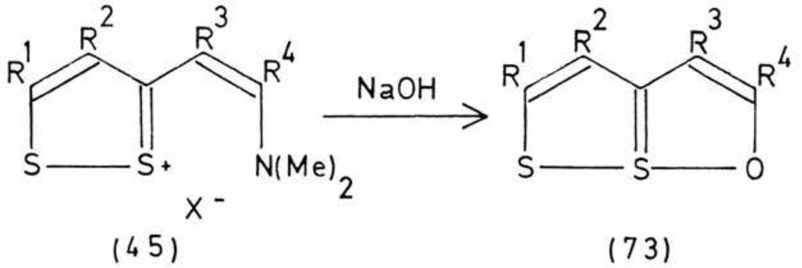
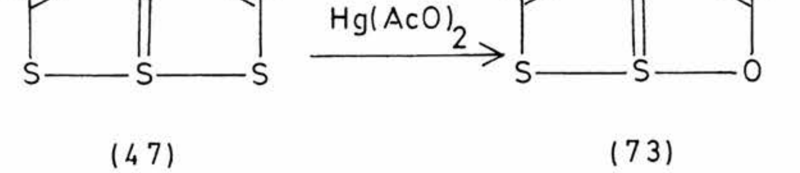


(72)

1-Oxa-6,6aλ^4-dithiapentalenes have been synthesised from the reaction of Vilsmeier salts (45) and sodium hydroxide[37].



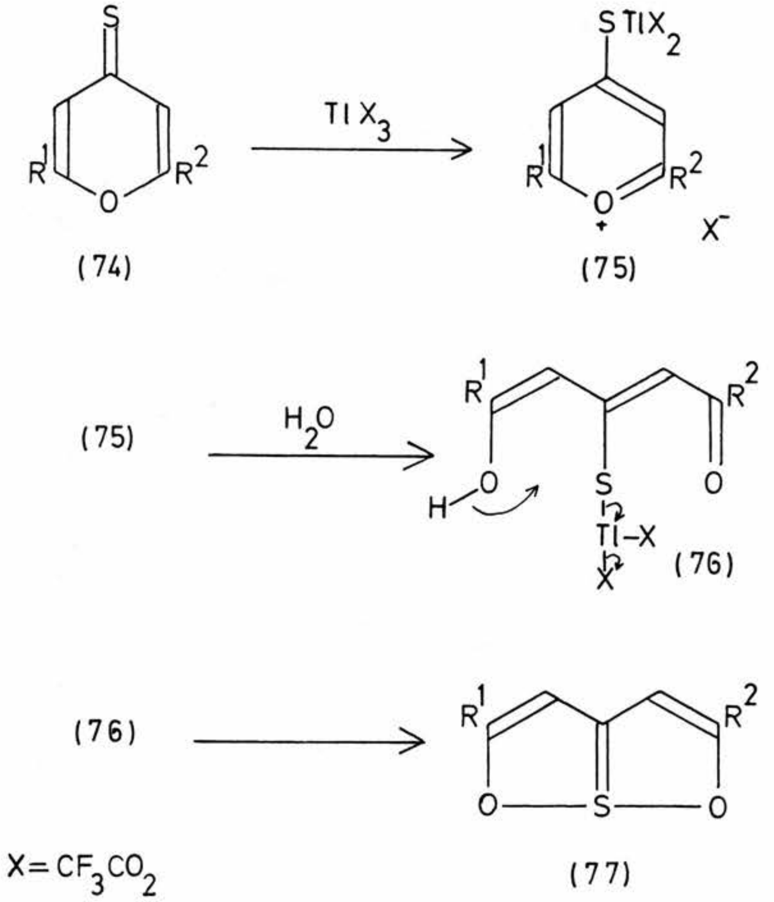
Treatment of trithiapentalenes (47) with mercury (II) acetate results in replacement of a lateral sulphur atom by an oxygen atom to give oxadithiapentalenes (73)[87,95].



(b) Triheterapentalenes Containing Two Oxygen Atoms

1,6-dioxa-6aλ^4-thiapentalenes (77) are conveniently synthesised by the reaction of pyran-4-thione (74) and thallium (III) trifluoroacetate in acetonitrile[44]. On treating the resulting salt (75) with water, instantaneous ring opening and loss of thallium (III) trifluoroacetate occur, with concomitant sulphur-oxygen bond formation to give dioxathiapentalenes (77) (Scheme 2).

Scheme 2



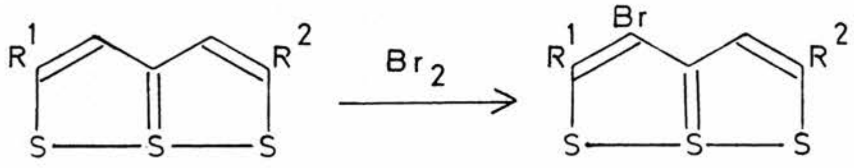
D. REACTIONS OF 1,6,6a λ^4-TRIHETERAPENTALENES WITH ELECTROPHILES

Although the structure and bonding of triheterapentalenes has been extensively investigated, the chemical reactivity of this class of compounds has, until relatively recently, received much less attention. Some of the more important reactions of triheterapentalenes with electrophiles are described in this Section.

1. 1,6,6a λ^4-Trithiapentalenes

(a) Halogenation

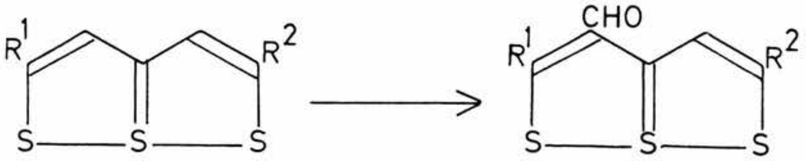
Beer and co-workers[98,99] have found that the 2,5-disubstituted trithiapentalenes (38) were monobrominated under mild conditions to give the corresponding 3-bromo-trithiapentalenes (78)



(38) (78)

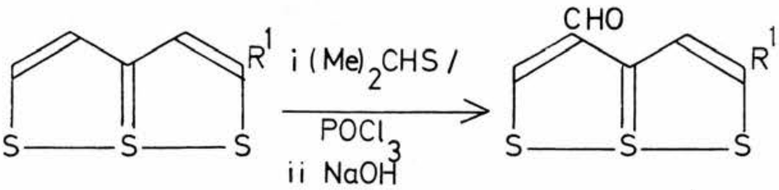
(b) Formylation

Bignebat and Quiniou[100] have shown that 2,5-disubstituted trithiapentalenes (38) are formylated at the more reactive 3-position.



(38) (79)

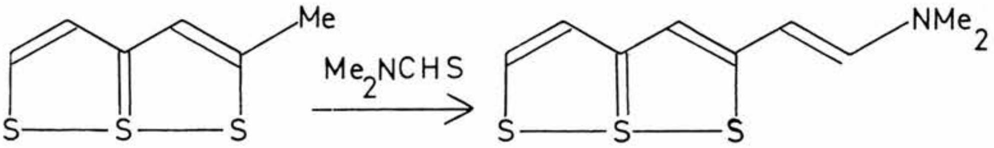
In a more thorough investigation of the formylation reaction, Reid[87] has studied the reactivity of the 2(5)- and the 3(4)-positions of simple trithiapentalenes. Treatment of the parent compound (31) with N,N-dimethylthioformamide and phosphoryl chloride, followed by solvolysis with aqueous sodium hydroxide, gave the 3-formyl derivative (80)



(31)

(80) $R^1 = H$
(81) $R^1 = Bu^t$

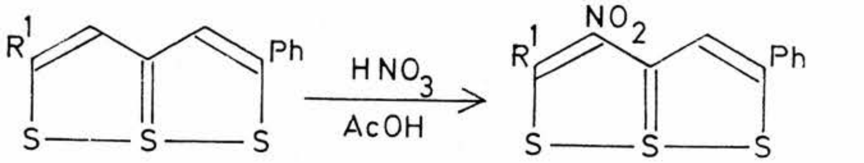
Treatment of the 2-tert-butyl-1,6,6aλ^4-trithiapentalene gave formylation at the 4-position (81). This was attributed to the steric bulk of the tert-butyl group. Attempts to formylate compound (33) resulted in the formation of enamine (82) by condensation of dimethylthioformamide with a methyl substituent.



(33) (82)

(c) Nitration and Nitrosation

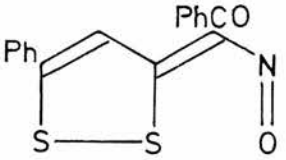
2-Methylthio-5-phenyl-1,6,6aλ^4-trithiapentalene (83) was nitrated by concentrated nitric acid in hot acetic acid[61]. Not unexpectedly, the 3-nitro product (85) was obtained in poor yield.



(83) R^1=MeS (85) R^1=MeS

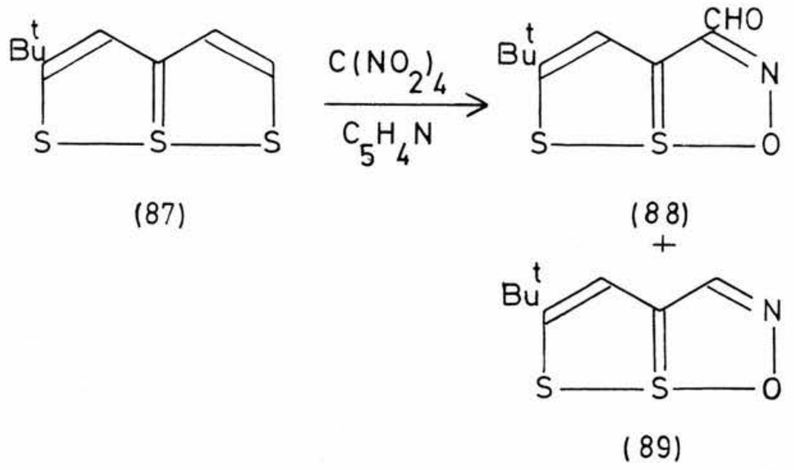
(84) R^1=Ph

Attempts to nitrate the symmetrical 2,5-diphenyl compound (84) using the HNO_3/CH_3CO_2H reagent did not give the expected product, however, the nitroso-ketone (86) was formed by rearrangement.



(86)

Reid and co-workers[86] have observed similar nitrosations when attempts were made to nitrate trithiapentalenes using tetranitromethane/pyridine. Compound (87) reacted under these conditions to give the aldehyde (88), by partial oxidative desulphurisation and nitrosation, and the 1-oxa-6,6aλ^4-dithia-2-azapentalene (89) in the ratio 5:1.



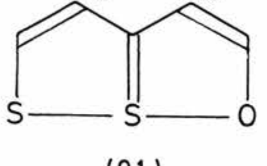
(87)

(88)

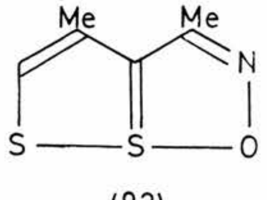
(89)

A similar product ratio was obtained from the nitration of 2-phenyl-1,6,6aλ^4-trithiapentalene. The major products from both reactions were formulated as aldehydes on the basis of strong carbonyl absorptions at ca. 1670 cm^{-1} in the infra-red spectra.

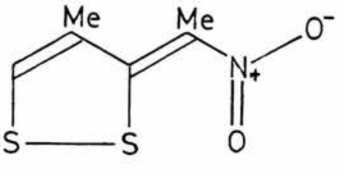
3,4-disubstituted trithiapentalenes were found to give three products when treated with tetranitromethane. 3,4-Dimethyl-1,6,6aλ^4-trithiapentalene (90) gave 3,4-dimethyl-1-oxa-6,6aλ^4-dithiapentalene (91), 3,4-dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (92) and 4-methyl-3-(1-nitroethylidene)-3*H*-1,2-dithiole (93).



(91)



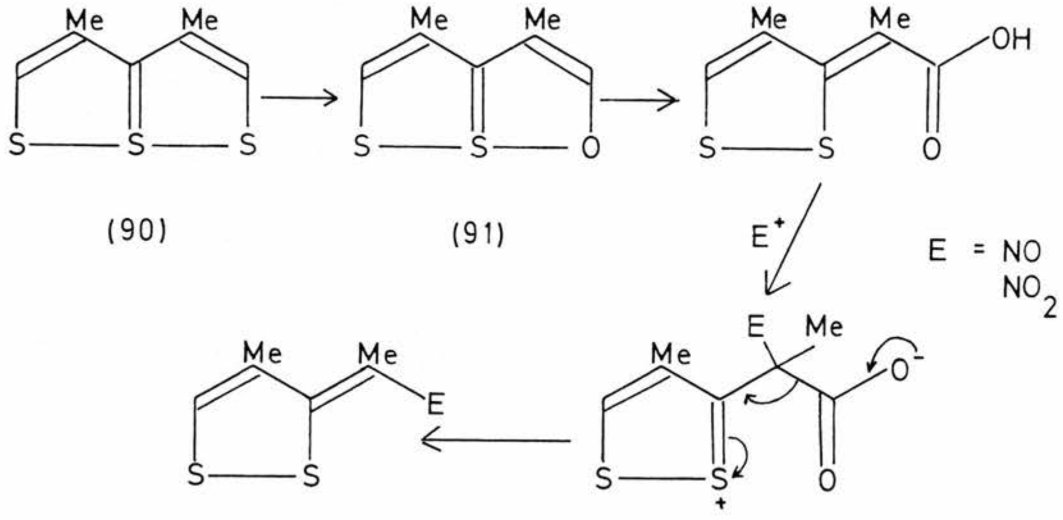
(92)



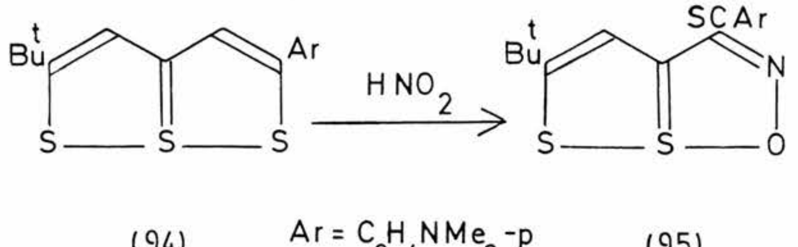
(93)

This product distribution was rationalised on the basis of a reaction sequence (Scheme 3) in which the starting compound (90) underwent oxidative desulphurisation to give compound (91). Further oxidation of compound (91) to the carboxylic acid followed by nitroso- or nitro-decarboxylation leads to compounds (92) or (93), respectively.

Scheme 3



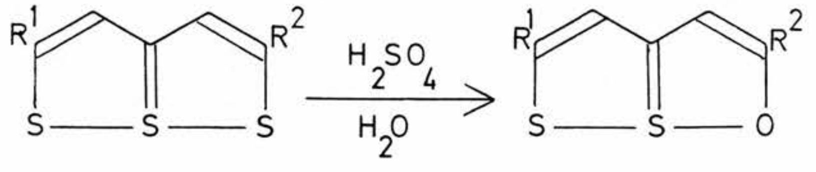
Nitrosation of 1,6,6aλ^4-trithiapentalenes by nitrous acid occurs with difficulty unless the heterocycle is activated by strongly electron-releasing substituents[101]. As in the case of nitration, reaction occurs with rearrangement of the three-centre bonded sequence. Trithiapentalene (94) forms the thioamide (95) in 97 per cent yield.



(94) Ar = $C_6H_4NMe_2$-p (95)

(d) Protonation

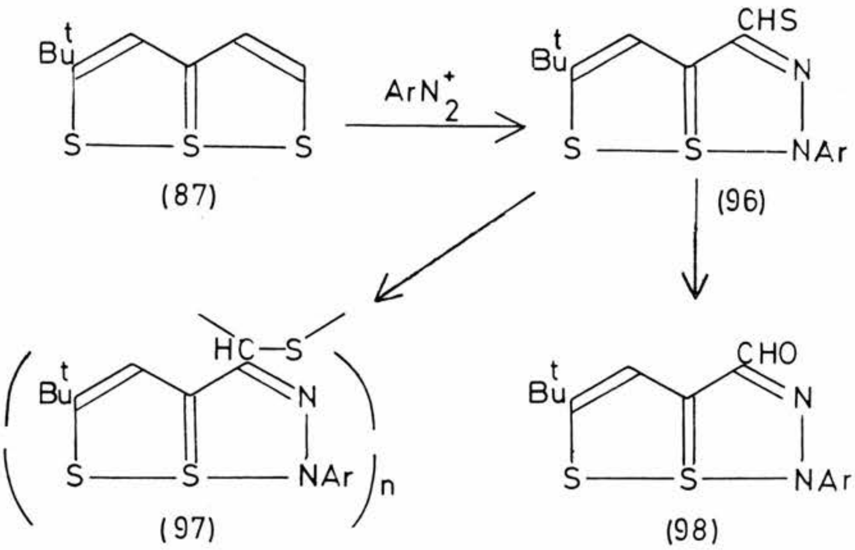
Leaver[82] and others[102] have observed that trithiapentalenes (38) are converted to the corresponding oxadithiapentalenes (77) by the action of concentrated mineral acids.



(38) (77)

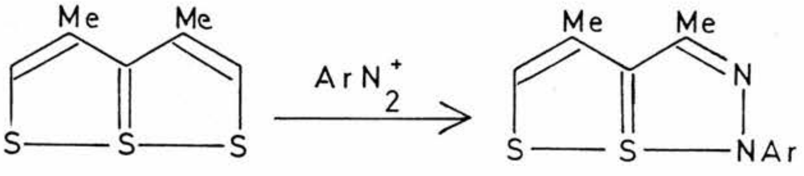
(e) Diazo Coupling

1,6,6aλ^4-trithiapentalenes undergo rearrangement during substitution reactions with arenediazonium tetrafluoroborates[103]. Trithiapentalene (87) reacted with p-nitrobenzenediazonium tetrafluoroborate in aqueous acetonitrile to give the intermediate (96). The intermediate could not be isolated but partly underwent polymerisation to give compound (97) and partly hydrolysed to the aldehyde (98).



(87) (96) (97) (98)

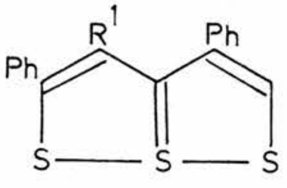
The reaction of p-nitrobenzenediazonium tetrafluoroborate with trithiapentalene (90) in which the reactive 3- and 4-positions are blocked, occurred by dethioformylation to give the dithiadiazapentalene (99).



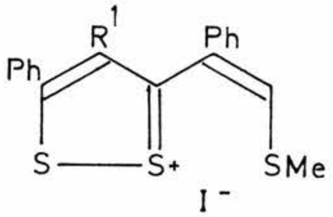
(90) (99)

(f) Alkylation

Klingsberg[84] has demonstrated that methyl iodide will react with 1,6,6a λ^4-trithiapentalenes (50,R^1=H,Ph) to give dithiolylium iodides (51).



(50)



(51)

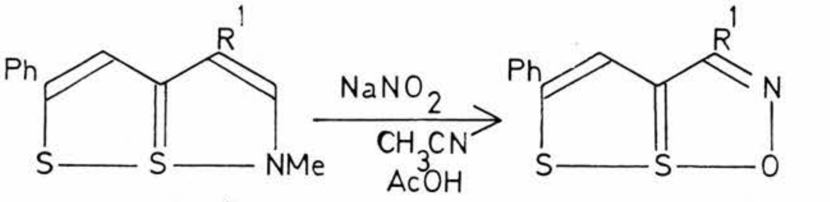
2,5-dimethyl- (32) and 2,5-diphenyl- (84) trithiapentalenes are less reactive than compounds (50) but undergo S-alkylation upon treatment with triethyloxonium tetrafluoroborate[49].

2. 6,6a λ^4-Dithia-1-azapentalenes

(a) Nitrosation

Reid[101] has observed that nitrosation of dithiaazapentalenes (100,101) occurs with hydrolysis [(100) ⟶ (102)] or with elimination of a methyliminomethyl group [(101) ⟶ (103)] to give 1-oxa-

6,6aλ^4-dithia-2-azapentalenes (102,103).

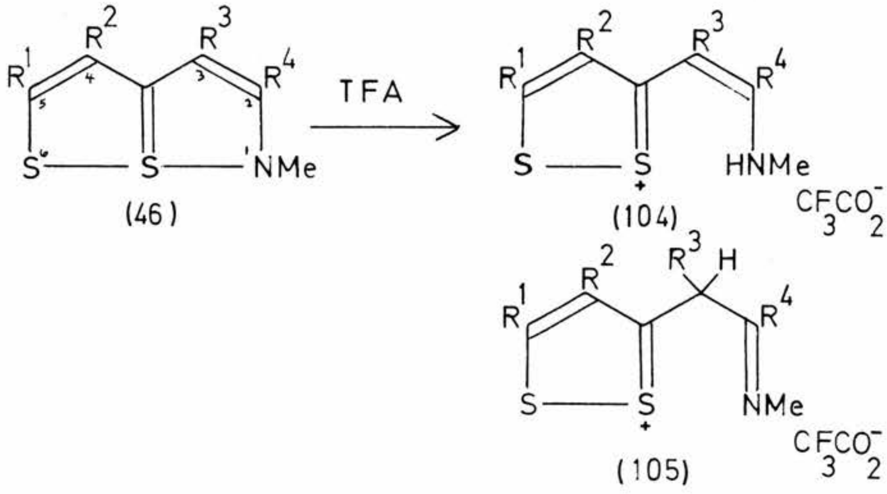


(100) R^1=H
(101) R^1=Me

(102) R^1= CHO
(103) R^1= Me

(b) Protonation

Compounds (46) are basic and may be protonated at sites N(1), S(6) or C(3). However, ^1H nmr spectral studies[83] show that protonation in trifluoroacetic acid occurs mainly at the nitrogen atom, N(1), to give dithiolylium salts (104). Small amounts of the C(3)-protonation product (105) were also observed.



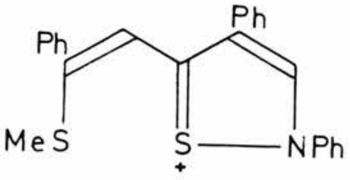
(46)

(104)

(105)

(c) Alkylation

Klingsberg[84] has shown that compound (49, $R^1=R^2=H$) reacts with methyl iodide to give the S-methylated derivative (106). Reid and co-workers[46] have shown that this is a general reaction of 1-methyl-6,6aλ^4-dithia-1-azapentalenes.

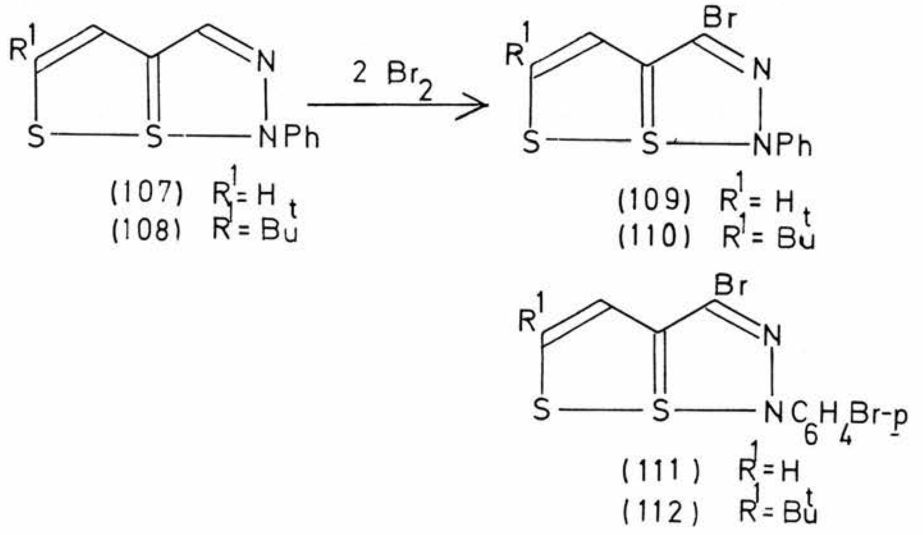


(106) I$^-$

3. 1-Aryl-6,6aλ^4-dithia-1,2-diazapentalenes

(a) Halogenation

Bromination of dithiadiazapentalenes (107,108)[104] occurs mainly at C(3) to give the monobromo derivative (109, 110), however, small quantities of the dibromo compounds (111, 112) are also obtained.



(107) R^1 = H

(108) R^1 = Bu^t

(109) R^1 = H

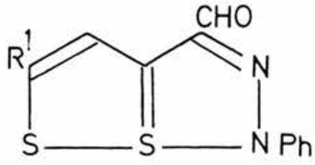
(110) R^1 = Bu^t

(111) R^1 = H

(112) R^1 = Bu^t

(b) Formylation

1-Phenyl-6,6aλ^4-dithia-1,2-diazapentalenes do not readily undergo Vilsmeier formylation[104]. Compound (113, R = Bu^t) was obtained in modest yield, but the unsubstituted compound (114, R^1=H) was only obtained in low yield. In general, a p-nitro substituent on the benzene ring lowered the yield of aldehyde.



(113) $R^1 = Bu^t$

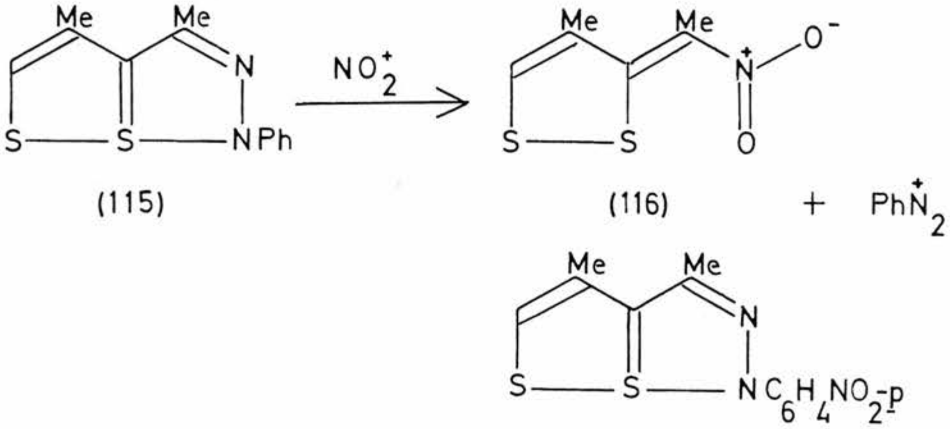
(114) $R^1 = H$

(c) Nitration and Nitrosation

The action of concentrated nitric acid on 6,6aλ^4-dithia-1,2-diazapentalenes which are not substituted at position 3, yields the corresponding 3-nitro derivatives as the major products[104]. Nitration of the benzene ring also occurs to a small extent.

Nitration of dithiadiazapentalenes, e.g. (115), which are substituted at position 3 occurs by nitro-dediazoniation to give 3-nitromethylene-1,2-dithiole (116).

Some nitration of the benzene ring also occurred to give compound (117).

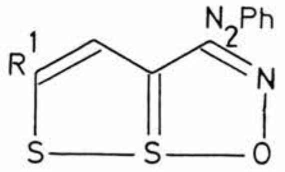


(115)

(116) + $Ph\overset{+}{N}_2$

(117)

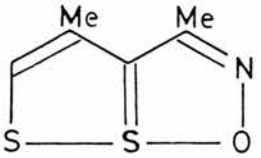
Reaction of dithiadiazapentalenes (107, 108) with sodium nitrite in acetic acid/acetonitrile occurs with rearrangement to give 3-phenylazo-1-oxa-6,6aλ^4-dithia-2-azapentalenes (118, 119).



(118) $R^1 = H$
(119) $R^1 = Bu^t$

Structures (118) and (119) are preferred to the alternative isomeric 3-nitroso-compounds because no $n \rightarrow \pi^*$ ultra-violet spectral absorptions of the N=O group were detected.

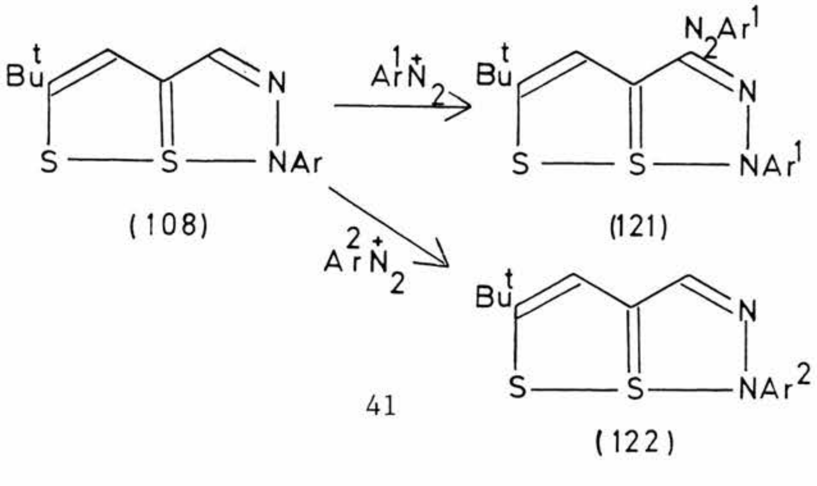
Nitrosation of 3,4-dimethyl compound (115) resulted in nitroso-dediazoniation to give the oxadithiaazapentalene (120) as the major product.



(120)

(d) Diazo-Coupling

6,6aλ^4-Dithia-1,2-diazapentalene (108) couples with arenediazonium tetrafluoroborates via an exchange reaction[88,104]. The product may be a 3-arylazo compound (121) or dithiadiazapentalene (122) depending on the relative electrophilicities of the aryl groups.

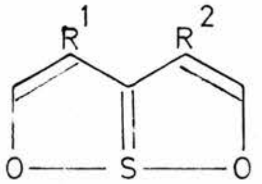


4. 1,6-Dioxa-6aλ^4-thiapentalenes

In general, this type of triheterapentalene system was found to undergo substitution with weak electrophiles. Strong electrophiles were found to destroy the system.

(a) Halogenation

Bromination of the dioxathiapentalene (27), using excess bromine, gave the 3,4-dibromo compound (123)[105].



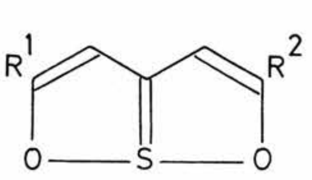
	R^1	R^2
(27)	H	H
(123)	Br	Br
(124)	I	I
(125)	I	H

When less than two equivalents of bromine were used, the 3,4-dibromo compound and starting material were obtained.

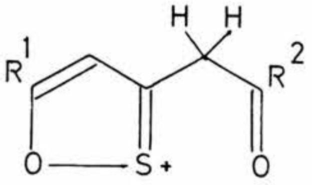
Iodination of compound (27) by elemental iodine/silver acetate was a more selective reaction, giving the 3,4-diiodo- (124) or 3-iodo- (125) dioxathiapentalene, depending on the reagent/substrate stoichiometry.

(b) Protonation

The unusual 1,2-oxathiolylium cations (127), (128) and (129), result from C(3)- and *O*-protonation of 1,6-dioxa-6aλ^4-thiapentalenes (27) and (126)[106]. The degree of protonation and relative amount of each species depends on the heterocycle and the nature of the protonating medium.



(27) $R^1 = R^2 = H$
(126) $R^1 = R^2 = Me$



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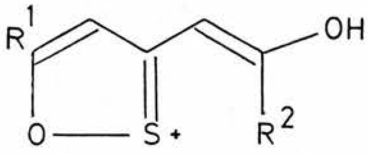
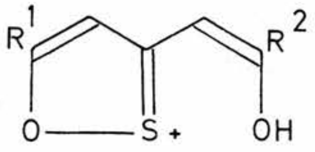


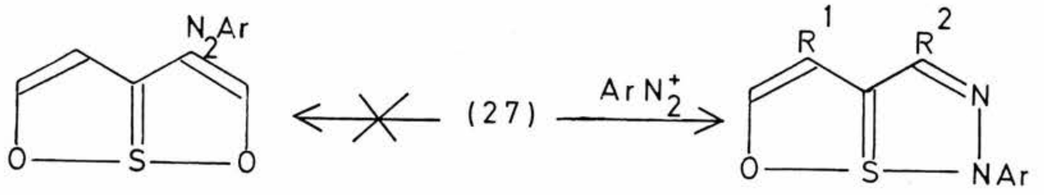
(128)



(129)

(c) <u>Diazo-Coupling</u>

1,6-dioxa-6a-thiapentalene (27) couples with p-nitrobenzenediazonium tetrafluoroborate to give not the 3-arylazo compound (130), but the 3-formyl compound (131) by rearrangement[103,105].

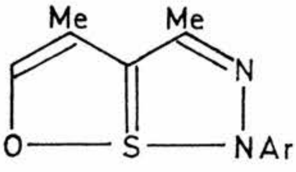


(130)

(131) R^1= H R^2= CHO

Structure (131) was preferred on the basis of infra-red and ^1H nmr spectral data.

3,4-Dialkyl-oxathiadiazapentalenes, e.g. (132), couple with arenediazonium tetrafluoroborates to give tetraaza derivatives (68)[47].



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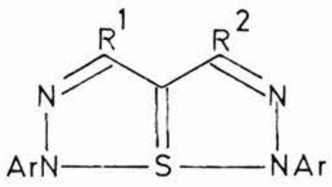


(68)

(d) Reactions with other Electrophiles

1,6-dioxa-6aλ^4-thiapentalene (27) could not be nitrated using concentrated HNO_3, $CuNO_3$/AcOH, or tetranitromethane[105].

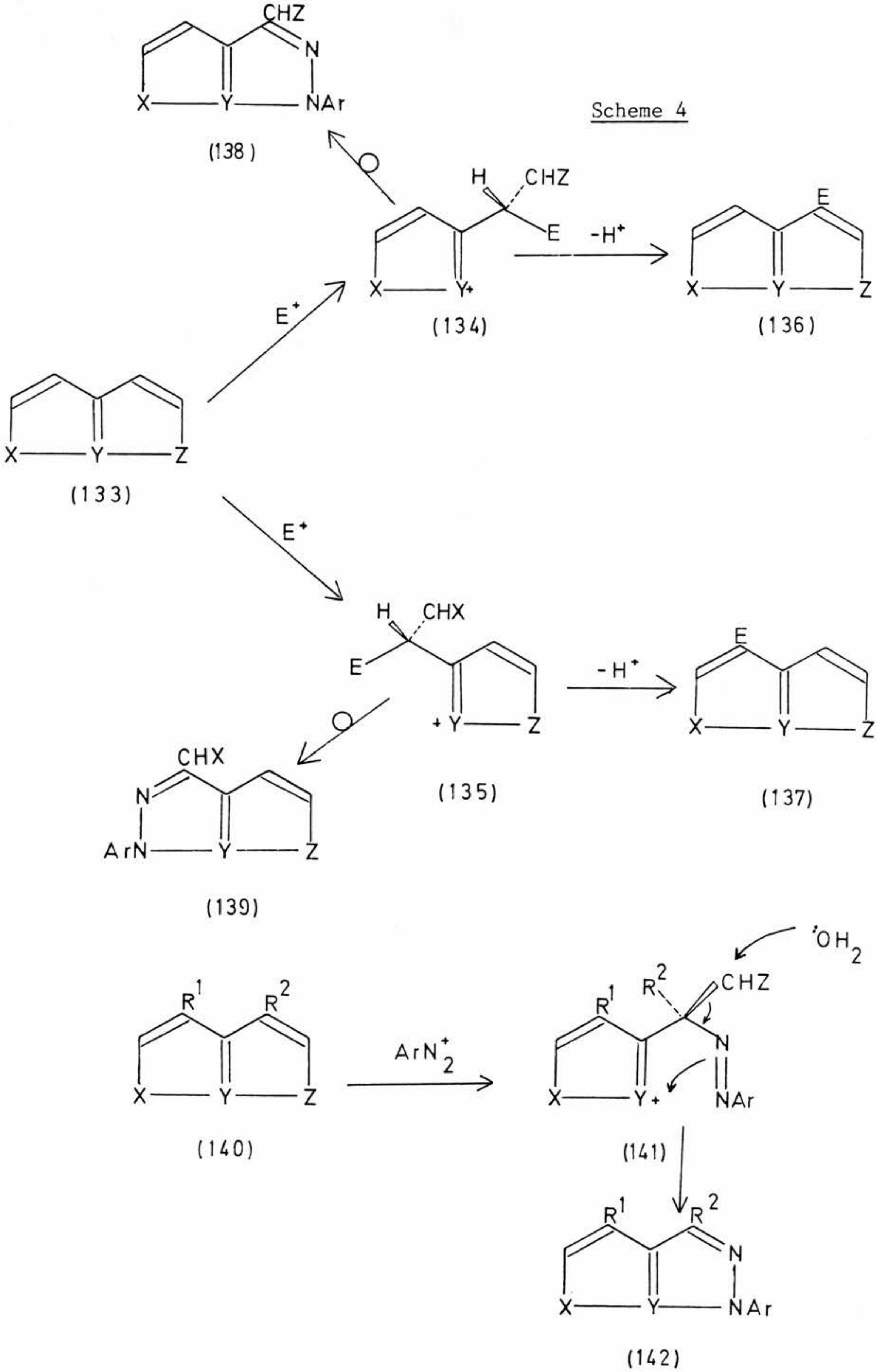
5. A Unifying Mechanism for the Reactions of 1,6,6aλ^4-Triheterapentalenes with Electrophiles

Reid[101] has shown that the behaviour of trithiapentalenes towards electrophiles may be explained in terms of the following mechanism (Scheme 4).

Addition of an electrophile (E^+) at position 3 or 4 of the trithiapentalene (133) results in the formation of the 6π-electron intermediate (134) or (135). Rotation about the C(3a)-C(3) or C(3a)-C(4) single bond permits the electrophile to approach atom Y. If the electrophile is monoatomic (e.g. $\overset{+}{Br}$) or is a group (e.g. CH=$\overset{+}{N}$Me) which is unable to form a stable three-centre bonding sequence, elimination of a proton occurs from the intermediate to give the expected substitution product (136) or (137).

Where the electrophile (E^+) is a group (e.g. $\overset{+}{N}\equiv$NAr) which contains a heteroatom capable of bonding to atom Y, the final reaction product will be determined by the relative strengths of the three-centre bonding interactions which may be formed. If the

Scheme 4


CHZ
N
NAr
X
Y
(138)
H
CHZ
E
-H⁺
(134)
(136)
E⁺
Y+
Z
(133)
E⁺
H
CHX
E
- H⁺
+Y
(135)
(137)
CHX
N
ArN
(139)
R1
R2
ArN2+
(140)
OH2
(141)
(142)

original bonding interaction [(133), X-Y-Z] is stronger than the new interaction [(134), X-Y-N; (135), N-Y-Z] then the product will be the 3(4)-substituted derivative (136) or (137). If the new bonding interaction is stronger, rearrangement, followed by elimination of a proton, occurs. Thus, (134) gives (138) and (135) gives (139). The CHZ group of (138) and CHX group of (139) may undergo further reaction, e.g. hydrolysis.

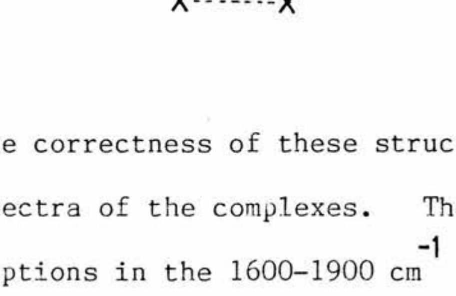
In the electrophilic substitution reactions of triheterapentalenes (140), which are blocked at the 3(4)-positions, the group (CHZ) not involved in the three-centre bonding sequence is eliminated, probably through nucleophilic attack by water on intermediates of type (141).

The mechanisms proposed by Reid provide a satisfactory rationalisation for the many electrophilic substitution reactions of triheterapentalenes.

E. METAL COMPLEXES OF 1,6,6aλ^4-TRIHETERAPENTALENES

The propensity of triheterapentalenes to form metal complexes has received very little attention. Of those complexes which have been described in the literature, almost all are derivatives of the trithiapentalene system.

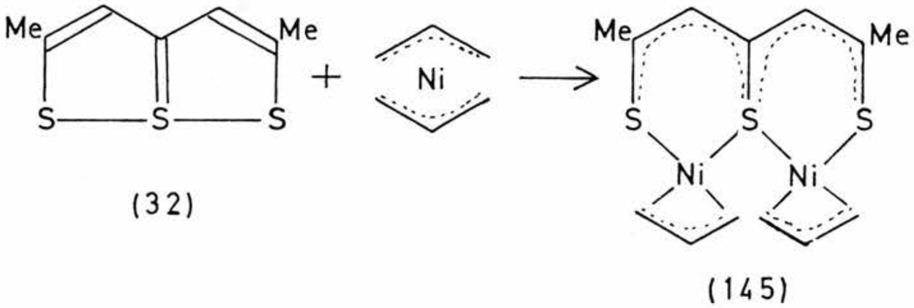
Furuhashi[107] has described attempts to prepare cobalt chelates by grinding hydrated cobalt (II) chloride or bromide with 2,5-dimethyl-1,6,6aλ^4-trithiapentalene (32). The expected chelates were not formed but, on the evidence of elemental analysis, compounds of formula Co $(C_7H_{10}SO_2)_2X_2$ (X=Cl or Br) were obtained. Both complexes produced ^1H nmr spectra, showing the presence of two types of hydrogen atom, and had measured magnetic moments of approximately 4.6 Bohr Magnetons. This evidence led Furuhashi to propose tetrahedral structures (143) and (144) for the complexes.



(143) X=Cl
(144) X=Br

Support for the correctness of these structures was obtained from the infra-red spectra of the complexes. These spectra showed strong carbonyl absorptions in the 1600-1900 cm^{-1} region. Infra-red analysis was also used to deduce the nature of the metal-sulphur bonding in the complexes. However, Furuhashi's conclusion that only a weak metal-sulphur bond existed, was made by comparing the position and intensity of the C=S absorption of 2,5-dimethyltrithiapentalene (32) with those of the complexes. As compound (32) does not produce a characteristic absorption due to C=S stretching or bending, the evidence for this conclusion appears invalid.

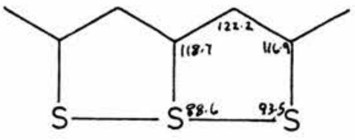
The mechanism leading to the formation of these complexes probably involves hydrolytic desulphurisation and reduction stages. Bogdanović, Kruger and Kuzmin[108] have synthesised bis(η^3-allylnickel)-2,4,6-heptanetrithionediate (145) by reacting 2,5-dimethyltrithiapentalene (32) with bis(η^3-allylnickel) or (η^3-allylnickel) chloride in tetrahydrofuran at 0°C.



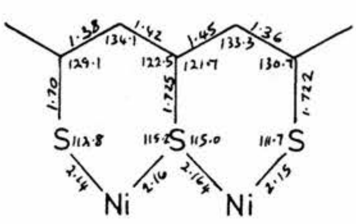
(32)

(145)

An X-ray crystal structure analysis of complex (145) showed the presence of bonding interactions between the ligand sulphur atoms and the nickel atoms, which possessed square planar coordination geometry. Large interatomic distances (ca. 3.35 Å) between adjacent sulphur atoms indicated that complex formation had destroyed sulphur-sulphur bonding[35]. The distance (3.91 Å) between nickel atoms implied the absence of metal-metal bonding. Complexation was found to increase the internal bond angles at C(2) and C(5), and C(3) and C(6), of the trithiapentalene by approximately 12°, otherwise, the bond geometry was unperturbed (146)[cf. (2)].

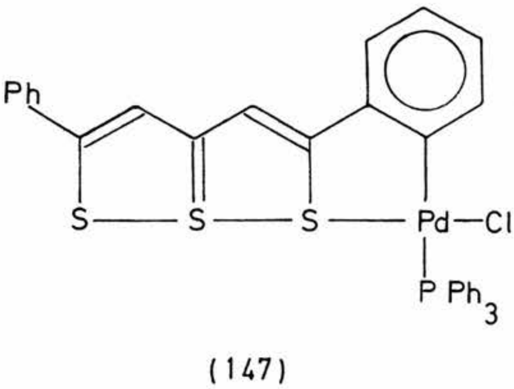


(2)

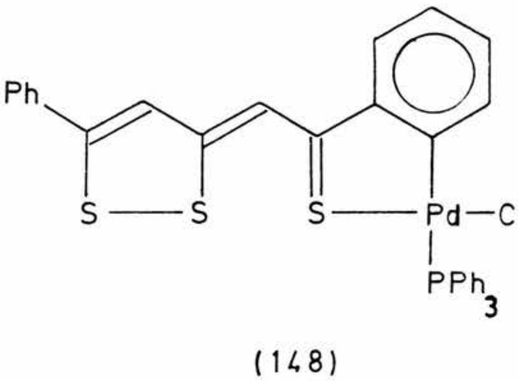


(146)

Bogdanovíc and co-workers[109] have found that 2,5-diphenyltrithiapentalene (84) reacts with palladium (II) chloride in boiling benzene/methanol to give a violet-coloured, air-stable solid. An X-ray crystal structure determination of the triphenylphosphine adduct of the product revealed the occurrence of an <u>ortho</u>-palladation reaction involving one of the phenyl substituents and one of the lateral sulphur atoms of the trithiapentalene. The product was therefore either the tricyclic species (147) or the bicyclic structure (148).

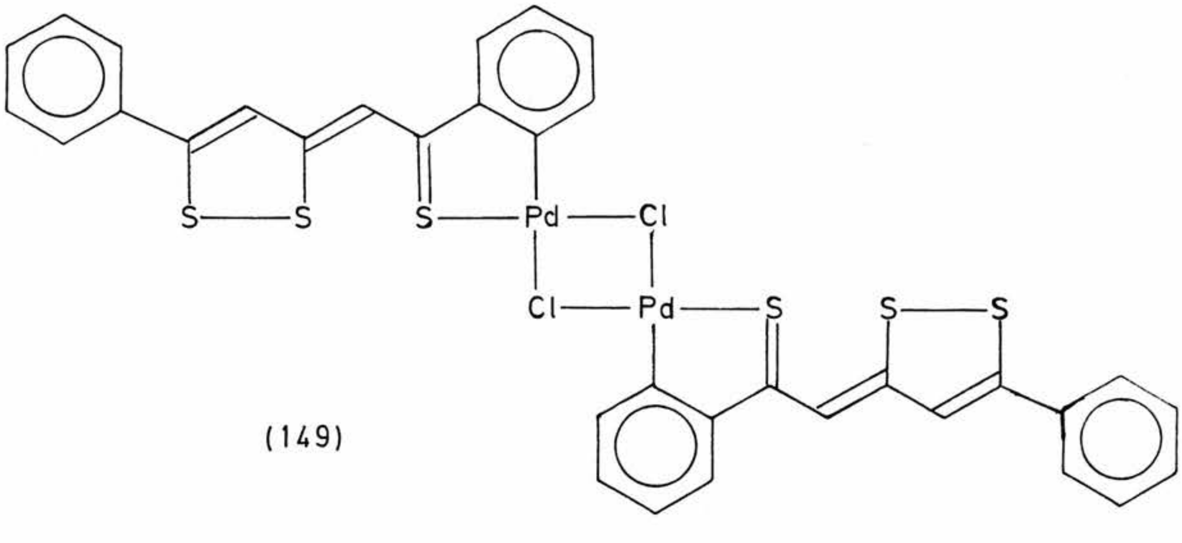


(147)



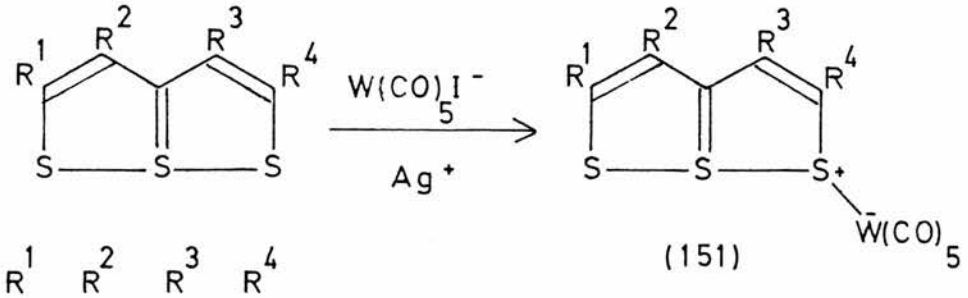
(148)

Bond length measurements suggested that the palladation reaction destroyed the original three-centre bonding system of the trithiapentalene (84). The interatomic distance (2.06 Å) between sulphur atoms S(1) and S(6a) showed the formation of a true two-electron, covalent bond between these atoms[13]. The S(6a)....S(6) interatomic distance (2.795 Å), although less than the sum of the Van der Waals' radii of two sulphur atoms (3.7 Å)[14], indicated that negligible bonding occurred. The observed loss of ligand planarity was consistent with these findings. The structure of the adduct was therefore assigned to be (148). The direct product of the <u>ortho</u>-palladation reaction was the dimer (149).



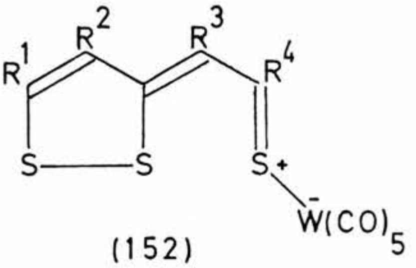
(149)

A recent publication by Reid and Pogorzelec[110] is of particular relevance to work embodied in this thesis. These authors reacted 1,6,6aλ^4-trithiapentalenes (32), (87) and (150) in the presence of the product obtained from tetraethylammonium iodopentacarbonyltungstate(0) and silver nitrate to form complexes which could have either structures (151) or (152).



(151)

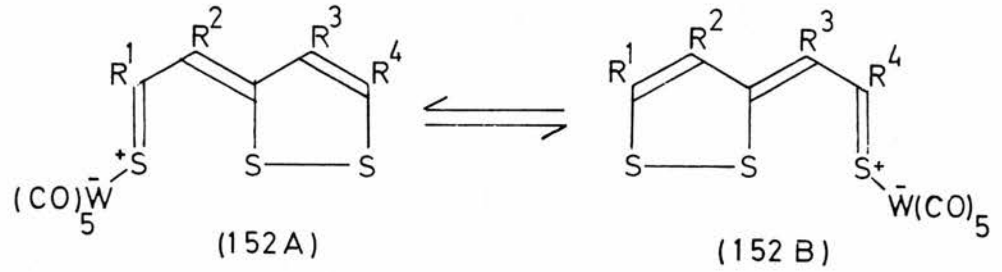
	R^1	R^2	R^3	R^4
(150)	H	$-(CH_2)_3-$		H
(32)	Me	H	H	Me
(87)	t-Bu	H	H	H



(152)

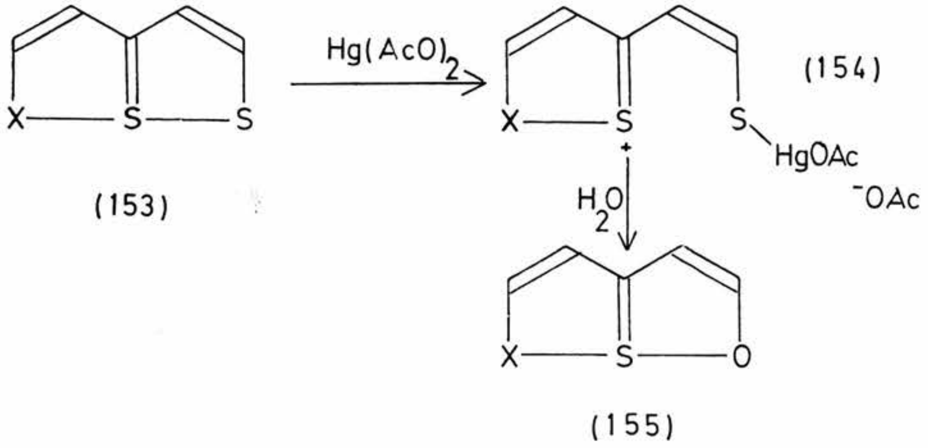
A single crystal X-ray study by Glidewell[111] *et al* has confirmed that these complexes do in fact have the thioaldehyde structure (152). Disruption of the three-centre bonding sequence resulted in a S(6)-S(6a) bond distance (2.75 Å) far greater than those found in trithiapentalenes (ca. 2.20-2.50 Å)[35]. The S(1)-S(6) interatomic distance (2.08 Å) was typical of that for two-electron covalent sulphur-sulphur bonds[18].

The tungsten complexes of symmetrically substituted trithiapentalenes (32) and (150) were found to display fluxional behaviour in solution. At -10°C, the ^1H nmr spectrum of complex obtained from (150) showed a singlet at δ 8.18 and at δ 9.46, attributable to the 2-H and 5-H proton, respectively. These signals broadened and collapsed as the temperature was increased. Coalescence occurred at 34°C, and at 60°C a sharp singlet was evident at δ 8.79. This behaviour was reversed by cooling. The coalescence temperature and line shape were independent of the concentration of the complex over the range 0.075 - 0.4M. The free energy change for the exchange process was calculated to be 14.7 kcal mol^{-1} at the coalescence temperature. As the ^1H nmr spectrum of complex obtained from (87) was temperature invariant in the region -20°C - 60°C, and tungsten complexes were not formed by 2,5-di-<u>tert</u>-butyl-1,6,6aλ^4-trithiapentalene, the ligand exchange process was concluded to be an intramolecular [Scheme 5. (152A) $\rightleftharpoons$ (152B)] rather than an intermolecular process.



Scheme 5

Organomercury intermediates are involved in the desulphurisation of dithiapentalenes (153, X=S,O,NR)[3]. The initial reaction step, acetoxymercuration of the lateral sulphur atom, occurs to give the complex (154). Subsequent hydrolysis of this dithiolylium cation generates the oxadithiapentalene (155).

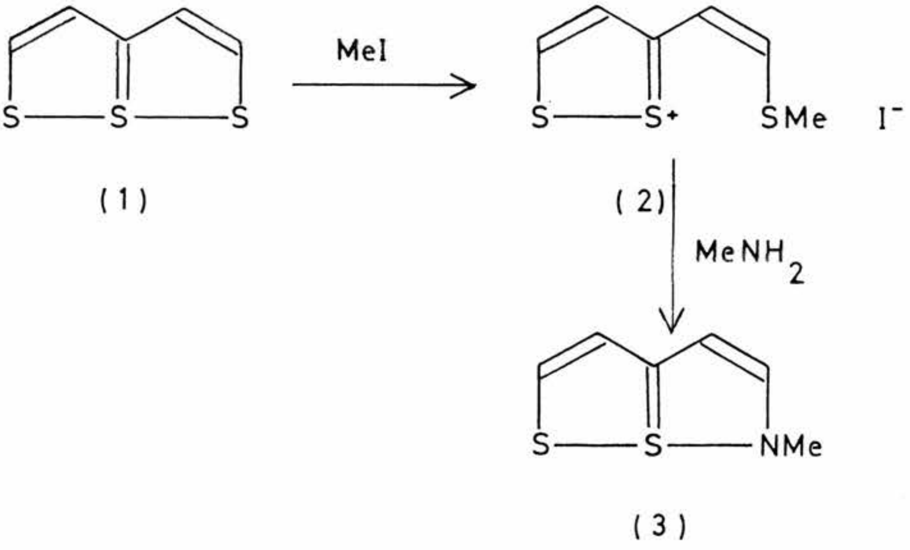


DISCUSSION

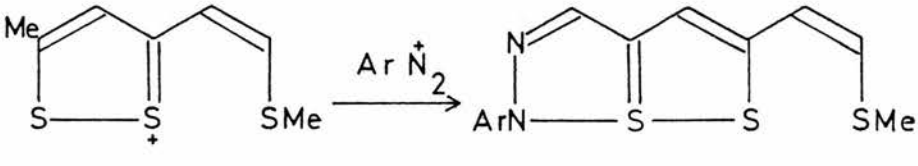
A. THE REACTION OF 5-SUBSTITUTED-1,2-DITHIOLE-3-THIONES WITH ARENEDIAZONIUM TETRAFLUOROBORATES

In Part One of this thesis, it was shown that electrophilic substitution reactions of 1,6,6aλ^4-triheterapentalenes usually proceed by reaction at ring sites C(3) or C(4). However, under certain conditions, an alternative reaction involving electrophilic attack at the heteroatoms at positions 1 and 6 may occur. This alternative reaction pathway is commonly encountered when attempts are made to alkylate triheterapentalenes (see Part One, Section C). The products formed by this type of reaction are useful intermediates (Scheme 1). Many workers, including Reid[46], Behringer[49] and Klingsberg[84], have shown that nucleophilic displacement of the alkylated group from the intermediate salt, e.g. compound (2), can result in the formation of a triheterapentalene (3) containing a modified heteroatom sequence.

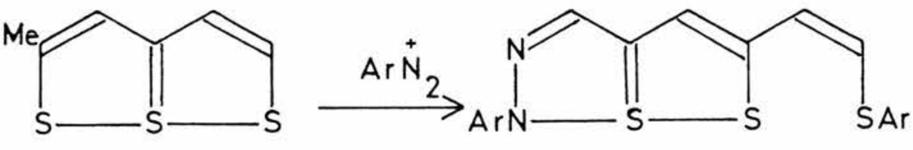
Scheme 1



In the case of 1,6,6aλ^4-trithiapentalenes (1), alkylation leads to intermediates (2) which may be considered as derivatives of 1,2-dithiolylium salts. Recognition of this has led Reid and Wolfe-Murray[112] to suggest that intermediates of this type, when formed from trithiapentalenes bearing a methyl(ene) substituent at position 2, may be regarded as analogues of 3-methyl(ene)-1,2-dithiolylium salts. These analogues should therefore be capable of reacting with electrophilic groups (e.g. $\overset{+}{\mathrm{N}}\mathrm{O}$) to form new three-centre bonded systems. In this way, the methylated adduct (4) of 2-methyl-1,6,6aλ^4-trithiapentalene is expected to react with arenediazonium tetrafluoroborates to yield substituted 6,6aλ^4-dithia-1,2-diazapentalenes (5). Work by Wolfe-Murray[113] has confirmed the correctness of this suggestion. Moreover, it was also demonstrated that 2-methyl-1,6,6aλ^4-trithiapentalene (6) itself will react with excess arenediazonium tetrafluoroborate to give dithiadiaza-



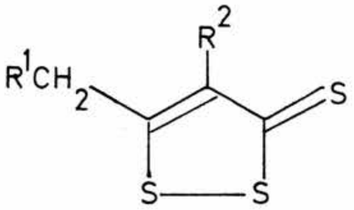
(4) (5)



(6) (7)

pentalenes (7) directly. This reaction is of considerable interest because it represents a new synthesis of 5-substituted dithiadiazapentalenes by a mechanism which probably involves electrophilic attack by an arene cation at a lateral sulphur atom.

As one of the objectives of the work reported in this thesis was to explore the nature of electrophilic reactions involving heteroatoms (1) and (6) of triheterapentalenes, it was decided to investigate the reaction of arenediazonium salts and 2-alkyltrithiapentalenes in detail. The aims of this study were to provide evidence for the proposed mechanism and to extend the scope of the synthesis. For convenience, the reactions of 5-substituted-1,2-dithiole-3-thiones (8), which are the lower vinylogues of trithiapentalenes and consequently yield simpler products, were studied.

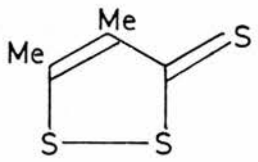


(8)

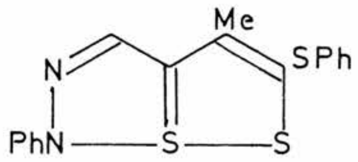
1. The Reaction of 4,5-Dimethyl-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate

4,5-Dimethyl-1,2-dithiole-3-thione (9), in methanol, reacted rapidly with benzenediazonium tetrafluoroborate. The reaction was accompanied by evolution of nitrogen gas. Two major products were obtained. These were purified by chromatography. A yellow compound was isolated and identified as the starting thione (9) on the basis of its ^{1}H nmr spectrum, melting point and tlc behaviour. The weight of thione recovered represented 54% of the starting amount.

A red compound was also isolated and was assigned the dithiadiazapentalene structure (10), which was consistent with the analytical data for the compound. Product (10) was obtained in disappointing yield (7.2%).



(9)

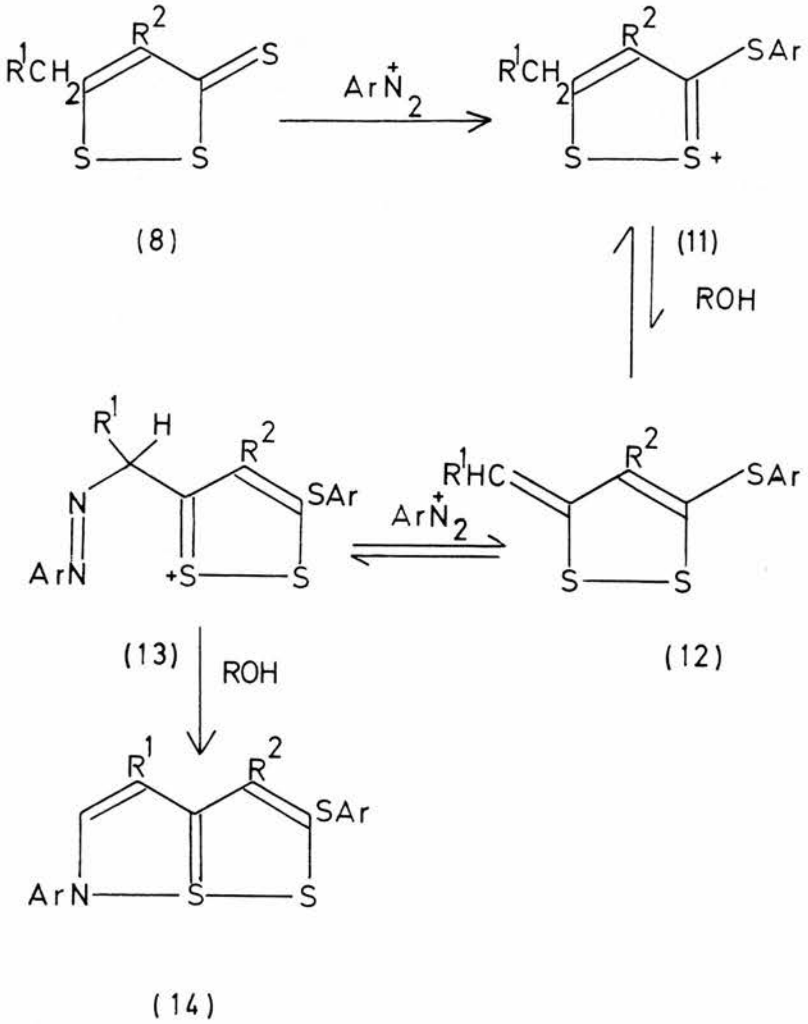


(10)

The formation of this dithiadiazapentalene, and others which will be discussed subsequently, can be accounted for in terms of the following mechanism (Scheme 2). It is proposed that 1,2-dithiole-3-thiones (8) initially react with arenediazonium tetrafluoroborates to give the corresponding 3-arylthio-1,2-dithiolylium cations (11). The precise mechanism of this step is not known, but it may be considered[114,115] as a nucleophilic substitution reaction involving loss of nitrogen from the arenediazonium salt and formation of the S-arylation product. The hydrogen atoms of the 5-methyl substituent of the dithiolylium cation (11) are expected to be acidic[85] and may be removed by the solvent (methanol). Solvent-assisted deprotonation of this type leads to the formation of the corresponding 5-methylene-1,2-dithiole (12). The weakly basic nature of methanol suggests that the equilibrium for this step will lie in favour of the cation (11). Once formed, however, the intermediate (12) will undergo rapid reaction with additional arenediazonium salt to yield a dithiolylium intermediate (13). This intermediate will also undergo solvent-assisted deprotonation to give, finally, the dithiadiazapentalene (14).

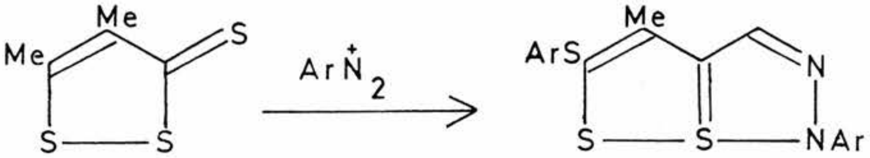
Reid and Christie[88] have suggested a similar mechanism to explain the formation of 6,6aλ^4-dithia- and 6,6aλ^4-diselena-1,2-diazapentalenes from 3-methyl(ene)-1,2-dithiolylium perchlorates and arenediazonium salts. These workers noted that the use of hydrogen-bonding solvents results in the best product yields. The proposed mechanism is consistent with this observation.

Scheme 2



2. The Reaction of 4,5 Dimethyl-1,2-dithiole-3-thione with p-Nitrobenzenediazonium Tetrafluoroborate

4,5-Dimethyl-1,2-dithiole-3-thione (9) reacted with *p*-nitrobenzenediazonium tetrafluoroborate to give the dithiadiazapentalene (15), which had low solubility in common polar organic solvents.



(9) (15)

$Ar = \underline{p}\text{-}O_2NC_6H_4$—

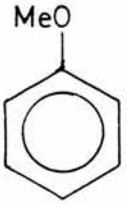
The yield of compound (15) (89%) was much greater than the yield of dithiadiazapentalene (10). As the thione used was the same in each case, the different product yields were attributed to the different reactivities of the arenediazonium salts used. An electron-withdrawing *p*-nitro substituent attached to the benzene ring was expected to enhance the electrophilicity of the arenediazonium cation, making it the more reactive arylating agent. Thus, greater yields of dithiadiazapentalene were expected when using the *p*-nitrobenzenediazonium salt. Additionally, *p*-nitrophenyl substituents, because of their electron withdrawing effect, were also expected to deactivate the dithiadiazapentalene nucleus (15) towards further electrophilic substitution reactions[116].

Thione (9) appeared to be completely consumed in this reaction.

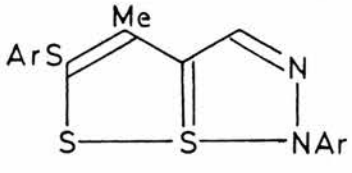
3. The Reaction of 4,5-Dimethyl-1,2-dithiole-3-thione with *p*-Methoxybenzenediazonium Tetrafluoroborate

Three products were identified from the reaction of 4,5-dimethyl-1,2-dithiole-3-thione (9) with *p*-methoxybenzenediazonium tetrafluoroborate. The starting thione was recovered as a yellow oil which would not crystallise as expected. Examination of the oil by mass spectrometry, showed that, in addition to the thione, a compound giving a molecular ion at m/e 108 was also present. Comparative tlc confirmed that this was methoxybenzene (16). This could arise from decomposition of *p*-methoxybenzenediazonium tetrafluoroborate, followed by reaction with the solvent (methanol)[117].

The dithiadiazapentalene (17) was obtained in modest yield (32%).



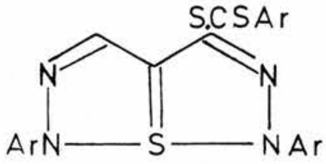
(16)



(17)

Ar = *p*-MeOC_6H_4—

This yield was higher than expected from previous results obtained using thione (9) and benzenediazonium tetrafluoroborate. *p*-Methoxybenzenediazonium tetrafluoroborate is a much weaker electrophile than the benzenediazonium salt and would therefore be expected to give the lower yield of product. The anomaly may be explained if the more reactive benzenediazonium cation reacted with compound (10) to give higher substitution products, such as the tetraaza compound (18), thereby effectively reducing the amount of dithiadiazapentalene formed. This line of argument suggests that the reactive p-nitrobenzenediazonium tetrafluoroborate and thione (9) should lead to the formation of significant amounts of higher substitution products. However, deactivation of the dithiadiazapentalene nucleus by the p-nitrophenyl groups is expected to prevent further substitution occurring in this case.

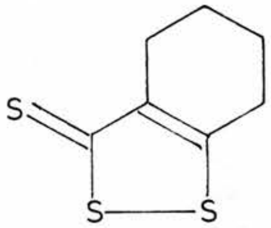


(18)

4. The Reaction of 4,5,6,7-Tetrahydrobenzo[d]-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate

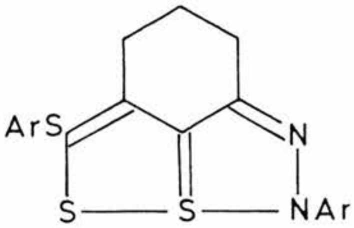
4,5,6,7-Tetrahydrobenzo[d]-1,2-dithiole-3-thione (19) appeared to react readily with p-methoxybenzenediazonium tetrafluoroborate. Only a small amount of thione (1.2%) was recovered from the reaction. A small quantity of a slower-running orange material was also isolated from the reaction products. The product was identified as p,p′-dimethoxyazobenzene (20) on the basis of analytical data. This compound probably arose from ths reductive coupling and partial dediazoniation of two p-methoxybenzenediazonium cations[118].

The red-coloured dithiadiazapentalene (21) was isolated in 38% yield. This yield was identical to that obtained when thione (9) was reacted with p-methoxybenzenediazonium tetrafluoroborate and suggested that thiones (9) and (19) possessed similar reactivity. However, the small amount of recovered thione (19) indicated that some material may have been lost in by-product formation.


(19)

ArN═NAr

(20)

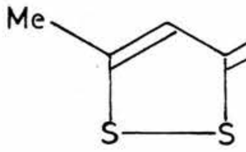

Ar = p-MeOC$_6$H$_4$— (21)

5. The Reaction of 5-Methyl-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate

Five products were isolated from the reaction of 5-methyl-1,2-dithiole-3-thione (22) with benzenediazonium tetrafluoroborate. Diphenyl disulphide (23) (90 mg) was obtained and identified by mass spectrometry and melting point behaviour. This product probably resulted from the oxidative coupling of thiophenol. The origin of this thiophenol was not clear, but it was thought not to arise from the decomposition of thione (22), as this compound was found to be stable in other diazo-coupling reactions.

A small quantity (16%) of 5-methyl-1,2-dithiole-3-thione (22) was recovered. The thione was identified by its ^{1}H nmr and mass spectrum and comparative tlc behaviour.

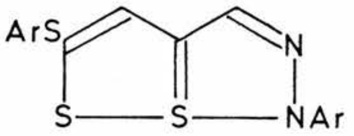
The dithiadiazapentalene (24) was obtained in low yield (5%). This yield was less than expected in view of the yield of dithiadiazapentalene obtained by reacting thione (9) with benzenediazonium tetrafluoroborate.



(22)

ArS—SAr

(23)

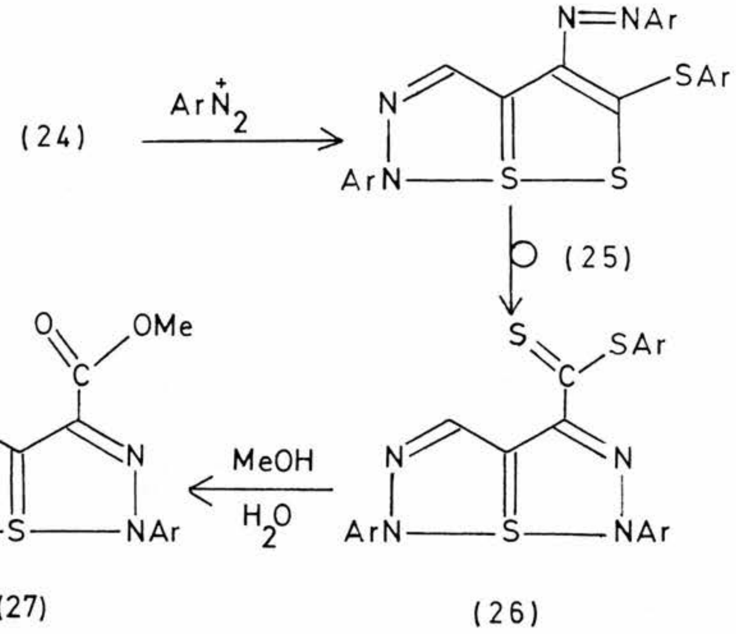


Ar = C_6H_5—

(24)

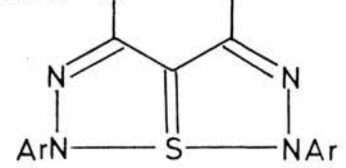
The low yield was partly explained by the subsequent isolation of substitution products derived from dithiadiazapentalene (24). The methyl ester (27) was isolated in 3.2% yield. This ester results from the electrophilic attack of a benzenediazonium cation at position C(4) of compound (24) (Scheme 3). The intermediate (25) formed by this process can rearrange and subsequently eliminate a proton to give the new three-centre bonded N-S-N sequence of compound (26). Hydrolysis of the thiocarbonyl group [C=S⟶C=O] and transesterification of the arylthio group by methanol will then result in the formation of the ester (27). This transesterification reaction is probably the source of thiophenol, which leads to the formation of compound (23).

Scheme 3



The formulation of compound (27) as an ester rather than a phenylazo derivative is based on the infra-red spectrum of the compound. The spectrum shows a strong carbonyl absorption at 1705 cm^{-1}, which falls in the region typical for esters. The simple ^1H nmr spectral pattern of the aromatic protons also provides some, though not conclusive, proof for structure (27).

A small quantity (6 mg) of a polar, purple compound was also isolated from the reaction. Insufficent material was available for a full analysis of the compound. However, mass spectral data suggested that the compound gave a molecular ion at m/e 536. Using this evidence, the compound was tentatively identified as the azo derivative (28).



(28)

$Ar=C_6H_5$

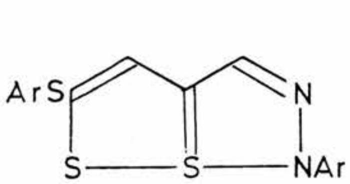
Compound (28) is expected to arise from the electrophilic attack of a benzenediazonium cation at ring position C(4) of intermediate (26). No rearrangement occurs in this instance because the starting and rearranged compounds would be identical. Elimination of a proton results in the reformation of the bicyclic nucleus.

The isolation of the higher substitution products (26) and (27) from this reaction clearly indicates that dithiadiazapentalenes which are not alkyl-substituted at positions 3 or 4, are very susceptible to further electrophilic attack. The results also suggest that the C(4)-position of compound (24) is less reactive than the C(3)-position in this type of reaction.

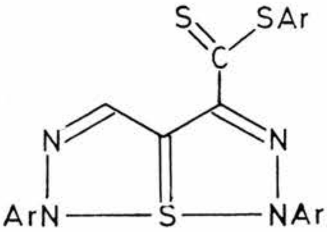
6. The Reaction of 5-Methyl-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate

5-Methyl-1,2-dithiole-3-thione (22) reacted with *p*-methoxybenzenediazonium tetrafluoroborate to give three products. The expected coupling product, dithiadiazapentalene (29), was obtained in low yield (8.2%). This suggested that, as in the previous reaction, the formation of higher substitution products had occurred. The isolation of a polar orange compound, which was subsequently identified as the methyl ester (31), confirmed this view. Structure (31) was assigned on the basis of the analytical data for this compound. The presence of a strong C=O absorption at 1689 cm^{-1} in the infra-red spectrum of this compound was the most compelling evidence in support of the proposed structure. This methyl ester was expected to arise from dithiadiazapentalene (29) by a mechanism similar to that which resulted in the formation of methyl ester (27) from compound (24).

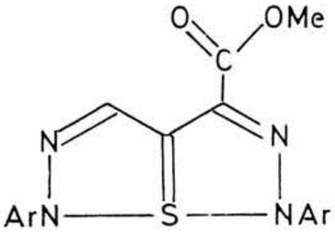
Another higher substitution product was also isolated from this reaction. This compound was identified as the dithioester (30). A dithioester of this type was proposed as an intermediate leading to the formation of the methyl ester (27), and doubtless is involved in the formation of compound (31). Detection of the dithioester is good evidence for the correctness of the mechanistic pathway proposed in Scheme 3.



(29)



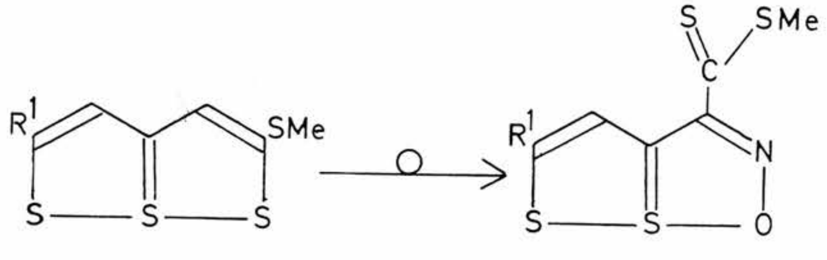
(30)



(31)

Ar = p-MeOC$_6$H$_4$–

Rearrangements similar to that which results in the transformation (29) ⟶ (30) have been observed by Christie, Ingram and Reid[101] during the nitrosation of 2-methylthio-trithiapentalenes (32, R^1 = Ph or Bu^t). In both the nitrosation and diazo-coupling



(32)

(33)

reactions, the driving force for the rearrangement process is the formation of the more stable three-centre bond.

That even the weakly electrophilic p-methoxybenzenediazonium cation will undergo further reaction with compound (29) is an indication of the ease with which dithiadiazapentalenes which are not substituted at positions 3 or 4 will participate in electrophilic substitution reactions.

B. REACTIONS OF 5-SUBSTITUTED-1,2-DITHIOLE-3-THIONES WITH ARENEDIAZONIUM TETRAFLUOROBORATES IN THE PRESENCE OF PYRIDINE

In Section A, a mechanism was proposed (Scheme 2) to account for the various features of the reaction leading to the formation of dithiadiazapentalenes. It was suggested that the solvent played a key role in this mechanism, acting to deprotonate the dithiolylium cation (11) and the arylazo intermediate (13). If this mechanism is correct, use of a stronger base than the solvent (methanol) employed previously should effect more efficient deprotonation of the intermediates (11) and (13). This in turn should lead to higher yields of dithiadiazapentalenes. In view of the somewhat disappointing yields experienced in the reactions discussed in Section A, it was decided to study the reactions of arenediazonium tetrafluoroborates and 5-substituted-1,2-dithiole-3-thiones in the presence of a stronger base. The tertiary base pyridine was used in these reactions.

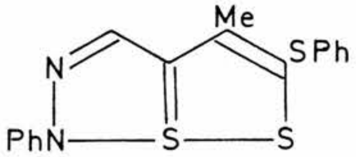
1. The Reaction of 4,5-Dimethyl-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate in the Presence of Pyridine

4,5-Dimethyl-1,2-dithiole-3-thione (9), in methanol, containing 5% pyridine, reacted rapidly with benzenediazonium tetrafluoroborate. Much nitrogen gas was evolved from the reaction. Purification of the reaction mixture by chromatography gave two products. Diphenyl disulphide (23) (0.1 g) was identified by its mass spectrum.

The dithiadiazapentalene (10) was the other reaction product.

Compound (10) was obtained in 37.6% yield. This represented an almost five-fold increase over the yield of product obtained when pyridine was not used. The result was entirely consistent with the proposed mechanism (Scheme 2) and clearly established the important role of the base in this reaction.

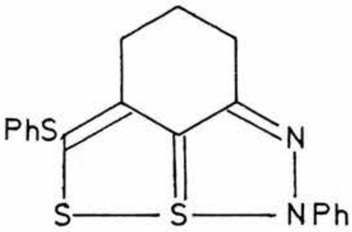
Unreacted thione (9) was not detected.



(10)

2. The Reaction of 4,5,6,7-Tetrahydrobenzo[d]-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate in the Presence of Pyridine

The reaction of 4,5,6,7-tetrahydrobenzo[d]-1,2-dithiole-3-thione (19) with benzenediazonium tetrafluoroborate gave rise to a small quantity of diphenyl disulphide (23) (90 mg) which was identified by mass spectrometry. The major product was the dithiadiazapentalene (34), which was obtained in 51.8% yield. The reaction in the absence of pyridine has been previously reported by Briggs[119]. The yield was reported to be 20.0%. Thus, as in the reaction of 4,5-dimethyl-1,2-dithiole-3-thione, the addition of a stronger base than methanol also improves the yield of product.



(34)

3. The Reaction of 4,5-Dimethyl-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate in the Presence of Pyridine

The expected dithiadiazapentalene (17) was obtained in 18% yield from the reaction of thione (9) and p-methoxybenzenediazonium tetrafluoroborate. This yield of product was less than half that found for the reaction conducted in the absence of pyridine. As unreacted thione was not detected amongst the products, it was hard to explain this result. Premature decompositon of the arenediazonium salt or further reaction of compound (17) may account for the low yield, although neither of these appear to be entirely satisfactory explanations.

4. The Reaction of 4,5,6,7-Tetrahydrobenzo[d]-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate in the Presence of Pyridine

Two products were obtained from the reaction of thione (19) and p-methoxybenzenediazonium tetrafluoroborate. A small amount of p,p′-dimethoxyazobenzene (20) (2.3%) was isolated, and identified by its mass spectrum. Starting thione was not found in the reaction mixture.

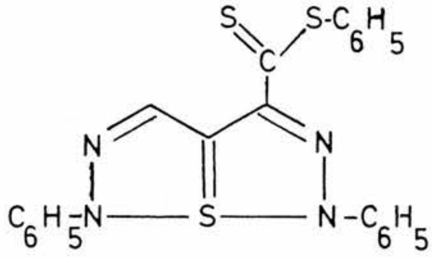
The dithiadiazapentalene (21) was isolated in 58.3% yield. The yield of product (21) was again significantly greater than the yield (38%) from the reaction not involving pyridine.

5. The Reaction of 5-Methyl-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate in the Presence of Pyridine

Three products were obtained from the reaction of 5-methyl-1,2-dithiole-3-thione (22) with benzenediazonium tetrafluoroborate. A few milligrams of impure diphenyl disulphide (23) were recovered.

The other products from the reaction were the dithioester (35) and the methyl ester (27), which were formed in 11.2% and 13.1% yield, respectively. The dithiadiazapentalene (24) was not observed as a reaction product. Dithioester (35) was not formed when the reaction was performed in the absence of pyridine, and ester (27) was only obtained in low yield (3.2%) under these conditions. These facts suggested that pyridine functioned to increase the quantities of higher substitution products at the expense of the yield of compound (24). This would also imply that pyridine was involved in the deprotonation step (Scheme 3) leading to the formation of compounds (35) and (27).

Unreacted thione (22) was not detected.



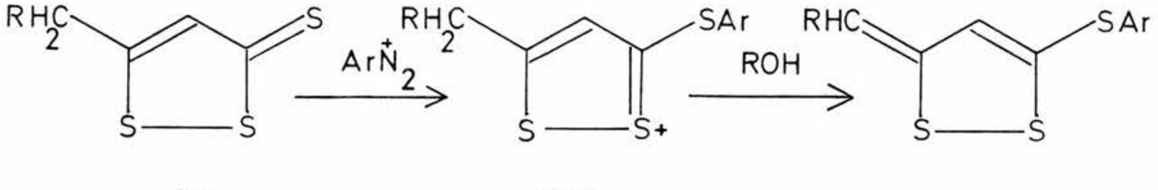
(35)

6. The Reaction of 5-Methyl-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate in the Presence of Pyridine

The thione (22) and p-methoxybenzenediazonium tetrafluoroborate reacted to give four products. Impure p,p′-dimethoxyazobenzene (20) was obtained in low yield (73 mg). The yields of dithiadiazapentalene (29) (4.2%) and dithioester (30) (2.6%) were lower than those found in the reaction without pyridine. However, the yield of the methyl ester (31) was doubled to 11.3% when pyridine was used. The observed product distribution was consistent with compounds (29) and (30) being intermediates, while compound (31) was the ultimate reaction product (Scheme 3). As in the previous reaction, the total yield of triheterapentalene products was increased with respect to the reaction in the absence of pyridine.

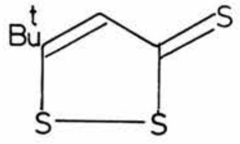
C. THE REACTION OF 5-TERT-BUTYL-AND-5-PHENYL-1,2-DITHIOLE-3-THIONES WITH ARENEDIAZONIUM TETRAFLUOROBORATES

In Section A of this Discussion, a mechanism (Scheme 2) was proposed to account for the formation of dithiadiazapentalenes. Two key steps in this mechanism were S-arylation of the 3-thiocarbonyl group of compounds (8), resulting in the formation of dithiolylium cations (11), and the subsequent solvent-assisted deprotonation of these cations to give the neutral 5-methylene intermediates (12).



(8) (11) (12)

If this mechanism is correct, 1,2-dithiole-3-thiones which possess 5-substituents bearing no hydrogen atoms on the carbon atom attached directly to the dithiole ring cannot form dithiadiazapentalenes. These thiones should, however, form 1,2-dithiolylium salts when treated with arenediazonium tetrafluoroborates. The successful synthesis of dithiolylium salt (37) from thione (36) and benzenediazonium tetrafluoroborate, and dithiolylium salt (39) from thione (38) and p-nitrobenzenediazonium tetrafluoroborate, supported the correctness of this argument and the proposed mechanism.



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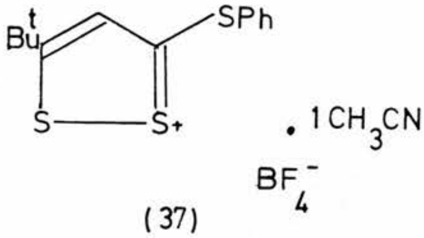
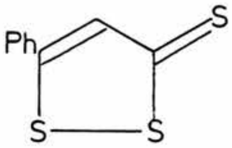
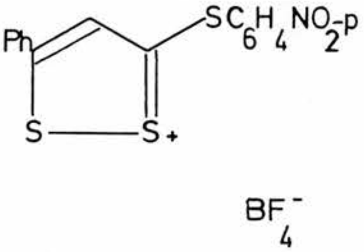


(37)



(38)



(39)

Attempts to prepare other dithiolylium salts using thione (38) were less successful. Benzenediazonium tetrafluoroborate reacted, but gave an ill-defined product which was not characterised. p-Methoxybenzenediazonium tetrafluoroborate failed to react with compound (38). This order of reactivity correlated well with the electron-releasing ability of the p-substituents of the arenediazonium cations. Thus the strongly electron-withdrawing p-nitro group destabilised the cation, thereby increasing its susceptibility to nucleophilic attack and dediazoniation. The strongly electron-releasing p-methoxy group exerted the opposite effect and reduced the reactivity of the cation. When the p-substituent was a hydrogen atom, intermediate behaviour was expected and observed.

The reactivity of thiones (36) and (38) towards benzenediazonium tetrafluoroborate established that thione (36) was the more nucleophilic in character. This is probably due to the greater electron-releasing effect of the 5-*tert*-butyl substituent relative to that of the 5-phenyl substituent.

Conclusion

5-Alkyl(ene)-1,2-dithiole-3-thiones can react with excess arenediazonium tetrafluoroborate to give dithiadiazapentalenes as the primary reaction products. However, the nature and yields of the ultimate reaction products are dependent on the structure of both the thione and the arenediazonium cation. A reaction mechanism has been proposed which accounts satisfactorily for the general features of these reactions. An *S*-arylation step is clearly implicated by the mechanism. The results of this study lend strong support to the proposed involvement of an analogous *S*-arylation step in reaction of trithiapentalenes and arenediazonium salts[113].

D. METAL COMPLEXES OF 1,6,6aλ^4-TRIHETERAPENTALENES

In the introductory section of this thesis, it was shown that 1,6,6aλ^4-trithiapentalenes are capable of forming complexes with metals. Other triheterapentalene systems are expected to behave in a similar manner, but metal complexes of these heterocycles have hitherto not been reported. It was therefore decided to study the complex-forming reactions of some triheterapentalenes. Attention was focussed on the reactions of non-symmetrical triheterapentalenes because, theoretically, in these compounds all the ring heteroatoms, except that at position (6a), are capable of bonding to metal atoms. Thus, the observation of several types of metal-ligand interaction was expected.

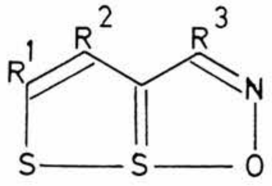
The recent work by Gingerich and Angelici[120,121] was relevant to the present study. These workers have shown that stable tungsten pentacarbonyl derivatives of reactive thiocarbonyl compounds, e.g. thioacetone, are readily prepared. Reid and Pogorzelec[110] have exploited similar complexation reactions in their isolation of the valence isomers of 1,6,6aλ^4-trithiapentalenes. As other triheterapentalene systems are also capable of undergoing valence isomerisation, attempts were made to isolate the possible isomeric structures by preparing the chromium, molybdenum and tungsten pentacarbonyl derivatives of these heterocycles.

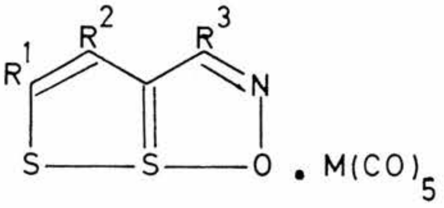
The Group VI A metal carbonyls are known[122] to react with donor ligands by step-wise displacement of carbon monoxide from the metal carbonyl to give complexes of the type: $L_xM(CO)_{6-x}$ (L=ligand, M=Cr, Mo or W, $1\leqslant x\leqslant 6$). However, Connor[123] has reported that attempts to make complexes of the type $L\,M(CO)_5$ by this method are generally unsuccessful, mixtures being the usual products. A more specific synthesis of these complexes has been proposed[123]. This preparation involves the reaction of tetraethylammonium halopentacarbonylmetallates(0) ($(\overset{+}{N}Et_4[M(CO)_5I]^-$, M=Cr, Mo, W), which have been described by Abel[124], with Lewis acids, e.g. the silver cation, Ag^+. The resulting intermediate, thought to be M(CO), is electron deficient and will rapidly fill its vacant d-orbital by reacting with a donor ligand, thereby forming the 1:1 adduct.

The method of Connor, because of its simplicity and specificity, was used to prepare the metal pentacarbonyl derivatives of nitrogen- and oxygen-containing triheterapentalenes. The findings of this work are presented in the following sections.

1. The Preparation of Pentacarbonylchromium(0), Molybdenum(0) and Tungsten(0) Complexes of 1-Oxa-6,6aλ^4-dithia-2-azapentalenes

The reactions of oxadithiapentalenes (40) - (43), in dichloromethane, with the iodopentacarbonylmetallates(0) of chromium, molybdenum and tungsten gave complexes (45) - (56). These compounds produced intensely coloured solutions. The complexes were readily purified by column chromatography, but were decomposed when recrystallised from hot (T > 30°C) solvents. However, recrystallisation at or below 25°C gave good yields of pure material in most cases. All the complexes were unaffected by exposure to air or moisture.

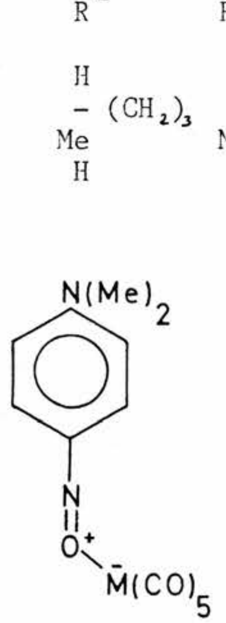




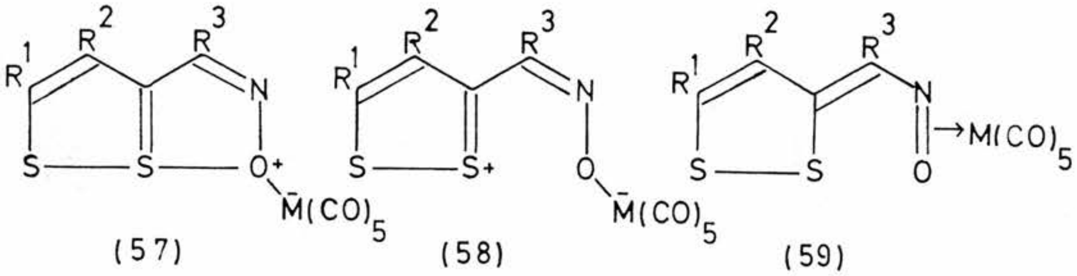
	R^1	R^2	R^3
(40)	Bu^t	H	H
(41)	H	– (CH$_2$)$_3$	–
(42)	H	Me	Me
(43)	H	H	H

	R^1	R^2	R^3	M
(45)	Bu^t	H	H	Cr
(46)	Bu^t	H	H	Mo
(47)	Bu^t	H	H	W
(48)	H	– (CH$_2$)$_3$	–	Cr
(49)	H	– (CH$_2$)$_3$	–	Mo
(50)	H	– (CH$_2$)$_3$	–	W
(51)	H	Me	Me	Cr
(52)	H	Me	Me	Mo
(53)	H	Me	Me	W
(54)	H	H	H	Cr
(55)	H	H	H	Mo
(56)	H	H	H	W

(44)



A number of possibilities exist for the structure of the metal pentacarbonyl-oxadithiaazapentalene adducts. The triheterapentalenes (40) - (43) possess three heteroatoms: O(1), N(2) and S(6), at which complex formation could occur. Sigma-bond formation could take place at any one of these atoms while leaving the bicyclic nucleus intact, e.g. structure (57), or could result in the formation of a monocyclic species, e.g. structure (58). Restricted rotation about the C(3a)-C(3) bond of compound (58) could result in the formation of cis and trans isomers. π -electron donation by the NO group is also possible, but this would require the formation of a monocyclic nucleus (structure 59).



(57) (58) (59)

Analytical data for the complexes helped to eliminate some of these possible structures. Elemental microanalysis established that those compounds which were judged pure by tlc had heterocyclic ligand to metal ratios of 1:1. Hence, the formation of other complexes, i.e. $L_xM(CO)_{6-x}$, where x had a value other than one, could be discounted.

The use of mass spectrometry as a means of confirming the expected stoichiometry of the complexes was investigated. The observation of a molecular ion corresponding to the $LM(CO)_5$ complex would have confirmed the existence of this species. Unfortunately, in every case examined, the molecular ion of the complex could not be detected, even when the energy of the electrons used to ionise the substrates was reduced from 70 eV to 30 eV. It was therefore concluded that complexes were breaking down while being heated at the sample inlet of the mass spectrometer. Although the molecular ions of the complexes were not apparent, there was clear evidence for the presence of the oxadithiaazapentalene and metal pentacarbonyl fragments in the mass spectra of the complexes. The metal pentacarbonyl was readily recognised by its fragmentation pattern, which showed the characteristic[125] stepwise loss of carbon monoxide units. Detection of the triheterapentalene and metal pentacarbonyl fragments does not prove that the stoichiometry of the complexes is 1:1, but it does indicate that the complexes contain an intact oxadithiaazapentalene skeleton and $M(CO)_5$ unit. That thermal breakdown of the complexes resulted in the regeneration of the triheterapentalene nucleus was confirmed by decomposing complex (53) in boiling xylene. 3,4-Dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (42) was recovered in good yield (68%).

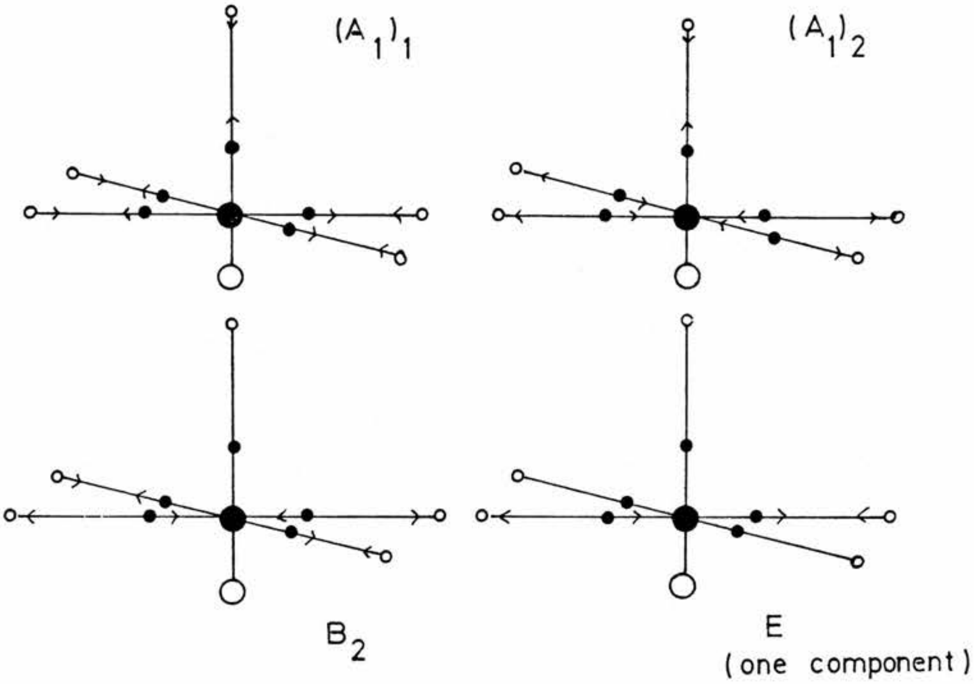
Infra-red spectroscopy provided further insight into the structure of the complexes by establishing the geometry of the $M(CO)_5$ unit. The infra-red spectra of compounds (45)-(56) showed four absorption bands in the region 1900-2100 cm^{-1} (Figure 1). Absorption bands in this region are attributable to various stretching modes of the metal pentacarbonyl group[124]. Some of the characteristic M-C-O stretches are given in Figure 2. The carbonyl (CO) groups in the fragment $M(CO)_5$ are expected to be disposed in a square pyramidal arrangement and as such will belong to the symmetry point group C_{4v}[122]. The results of normal coordinate analysis by Stoltz and co-workers[126] have indicated that this geometry should give rise to only three infra-red active modes. These modes are designated $(A_1)_1$, E and $(A_1)_2$. However, Braterman[133] has observed that when the ligand, L, in the complex $LM(CO)_5$ is polyatomic and non-linear and does not possess a four-fold axis of symmetry, the maximum allowable symmetry becomes C_s and an additional mode, B_2, becomes infra-red active.[126,133] Band positions are predicted to be, in order of decreasing frequency, $(A_1)_1$, B_2, E and $(A_1)_2$.

Exceptionally, the infra-red spectra of compounds (47), (48)

Figure 1: Typical Infra-Red Spectrum of an L $M(CO)_5$ complex, where L = Triheterapentalene and M = Cr, Mo or W

and (51) showed partial resolution of the E band. This phenomenon is rare and is thought[124,133] to arise from the influence of ligand asymmetry on the stretching parameters of the equatorial carbonyl groups.

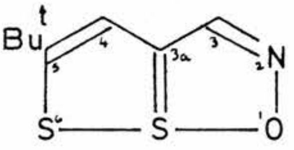
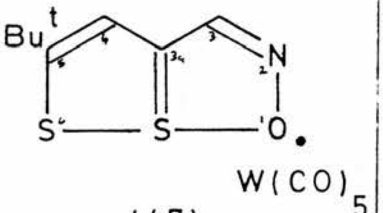
Figure 2 Normal CO Stretching Modes of Square Pyramidal $M(CO)_5$



Having ascertained the stoichiometry of the adduct and the spatial disposition of its carbonyl groups, attention was directed to the nature of the metal-ligand bonding interaction. Useful qualitative data in this respect came from the work of Reid and Pogorzelec[110]. These workers observed that the pentacarbonyltungsten complex of 5-tert-butyl-1,6,6aλ^4-trithiapentalene did not exhibit fluctional behaviour in solution, whereas the corresponding 3,4-dimethyl and 3,4-propano derivatives were able to do so. This observation suggested that the large $M(CO)_5$ unit was unable to complex at sulphur atom S(1) because of the steric bulk of the 2-*tert*-butyl group. It therefore appears reasonable to suggest that a similar effect might be possible in the case of oxadithiaazapentalene (40). As compound (40) formed stable metal complexes, this would imply that reaction occurred through atoms N(2) or O(1).

Data from nmr spectral studies provided support for this suggestion. A ^{13}C nmr study of complex (47) and the corresponding oxadithiaazapentalene (40) showed that only the chemical shift of ring carbon atom C(3) was affected by complex formation. This carbon atom experienced a paramagnetic shift of 6.3 ppm (Table 1). Carbon atom C(3) was therefore considered to be adjacent to the site where the ligand-metal interaction was occurring. The ^{13}C nmr spectrum of complex (47) also showed two low-field signals of relative intensity ca. 3:1 at 196.69 ppm and 203.8 ppm. These signals were tentatively identified as the equatorial and axial carbonyl groups on the basis of known chemical shift data for metal carbonyl complexes[134].

Table 1. ^{13}C nmr Data for Compound (40) and Complex (47)

Compound	Chemical Shift ppm	Relative Intensity	Assignment
 (40)	31.9 40.2 124.1 143.9 165.7 197.6	120 13 34 35 7 5	$\underline{(Me)}_3$C (Me)$_3\underline{C}$ C(4) C(3) C(3a) C(5)
 (47)	31.9 40.2 125.0 150.2 165.9 198.1 196.7 203.8	120 17 60 49 12 11 11 4	$\underline{(Me)}_3$C (Me)$_3\underline{C}$ C(4) C(3) C(3a) C(5) CO equatorial CO axial

^{1}H nmr spectral studies of complexes (45) - (56) endorsed the findings obtained by ^{13}C nmr. Proton spectroscopy showed that complex formation caused small but distinct changes in the chemical shifts of C(3) substituents. The magnitude of these shifts did not depend significantly on the metal used. Findings are summarised in Table 2. These data show the average chemical shift difference (Δ) for substituents of the three metal complexes relative to that of the substituent in the uncomplexed triheterapentalene.

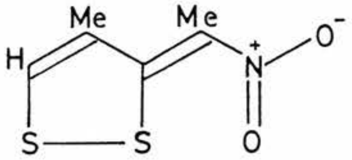
Table 2 Average Chemical Shift Differences (Δ) Between Substituents of Complexes (45) - (56) and Compounds (40) - (43)

	R^1	R^2		R^3
(40)	Bu^t	H		H
	- 0.01	- 0.07		+ 0.15
(41)	H	CH_2	CH_2	CH_2
	- 0.07	- 0.04	+ 0.07	+ 0.07
(42)	H	Me		Me
	+ 0.05	0.0		+ 0.2
(43)	H	H		H
	- 0.16	- 0.1		+ 0.13

Note: + = paramagnetic shift Δ values in ppm

The chemical shifts of all C(3)-substituents of complexes (45) - (56) were found to be downfield relative to those of the starting triheterapentalene. As complex formation causes both the protons attached to ring atom C(3) and those protons of methyl and methylene groups attached to this carbon to undergo significant paramagnetic shifts, it appears that the $M(CO)_5$ unit has a strong deshielding effect as well as inductive effect.

The observed ^1H nmr chemical shifts for the R^3 substituents of compounds (45) - (56) were consistent with complex formation occurring by reaction at ring atoms N(2) or O(1). However, evidence against the involvement of a direct metal - N(2) bond in the complexes came from the work of Reid[86], who has shown that the 5-H ring proton of 3-nitromethylene-1,2-dithiole (60) resonates at ca. 1 ppm upfield from the corresponding 5-H proton in oxadithiaazapentalenes. By analogy, if complex formation did occur through ring atom N(2) of compounds (40) - (43), compounds (45) - (56) would be structurally similar to compound (60) (except that the charged oxygen atom, O^-, of (60) would be replaced by the metal carbonyl fragment, $M(CO)_5$). The resonance position of the 5-H proton of complexes (48) - (56) would then be expected to occur significantly upfield from its position in the corresponding uncomplexed oxadithiaazapentalenes, compounds (41) - (43). As the data in Table 2 show that complex formation does not cause a substantial diamagnetic shift in the resonance position of the 5-H protons, this suggests that the metal pentacarbonyl fragments are not directly bonded to N(2) ring sites.

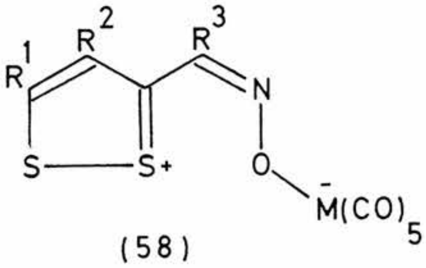


(60)

The most probable structures for complexes (45) - (56) are therefore those involving metal-oxygen bonding, e.g. structures (57), (58) and (59). As mentioned previously, if the complexes possess a monocyclic structure (58), cis and trans isomers may exist. At 31°C, the spectra of all complexes were consistent with the presence of a single species. A variable temperature study of complex (56) confirmed that no isomerisation was occurring. At 80°C, the spectrum of this complex was identical to that observed at

31°C. There was no evidence of line broadening which would have been indicative of the removal of partially restricted bond rotation. Similarly, the spectrum of complex (56) at -50°C was unchanged from that at 31°C, hence no fluctional behaviour was observed. It was therefore concluded that the geometry of the complex was fixed and probably similar to that of the starting triheterapentalene.

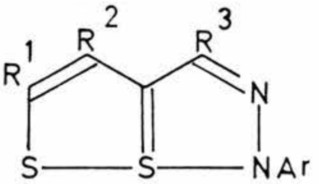
Finally, in an attempt to differentiate between structures (57), (58) and (59), the nitroso complex (44) was prepared. In this complex, the tungsten-oxygen bond is of purely sigma character. The infra-red absorption frequences for the carbonyl group of compound (44) were found to be very similar in intensity and shape to those of complexes (45) - (56). This implied that the complexes did not have the π -bonded structure (59). The bicyclic structure (57) could also be discounted because the $(A_1)_2$ band of oxonium-tungsten complexes usually falls[126] below 1900 cm^{-1}. It was therefore concluded that the most probable structure for these complexes is (58).

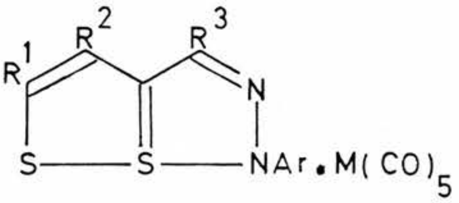


(58)

2. The Preparation of Pentacarbonylchromium(0), Molybdenum(0) and Tungsten(0) Complexes of 6,6aλ^4-Dithia-1,2-diazapentalenes

6,6aλ^4-Dithia-1,2-diazapentalenes (61) - (63) reacted with Group VI A iodopentacarbonylmetallates(0) to give complexes (65) - (73).





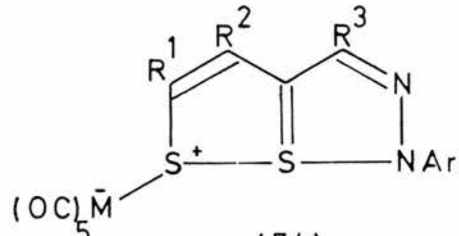
Ar = C_6H_5

	R^1	R^2	R^3
(61)	H	- $(CH_2)_3$	-
(62)	H	Me	Me
(63)	H	H	H
(64)	Bu^t	H	H

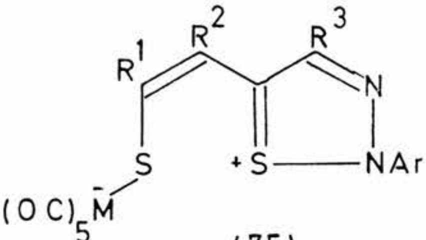
	R^1	R^2	R^3	M
(65)	H	- $(CH_2)_3$ -		Cr
(66)	H	- $(CH_2)_3$ -		Mo
(67)	H	- $(CH_2)_3$ -		W
(68)	H	Me	Me	Cr
(69)	H	Me	Me	Mo
(70)	H	Me	Me	W
(71)	H	H	H	Cr
(72)	H	H	H	Mo
(73)	H	H	H	W

Significantly, dithiadiazapentalene (64) did not form complexes with any of the metallate salts. This was good evidence that complex formation occurred only by reaction at sulphur atom S(6). The alternative bonding possibilities of complexation at nitrogen atoms N(1) or N(2) or π-bond formation through the azo group[136] were therefore discounted.

Elemental microanalysis results for the complexes (65) - (73) showed them to possess the expected (1:1) stoichiometry. Mass spectrometry indicated that the complexes did not produce observable molecular ions, but the parent ions of the dithiadiazapentalene nucleus and $M(CO)_5$ fragment were always observed. This helped to confirm the nature of the constituents forming the complexes. Infrared data were consistent with the pentacarbonyl group having C_{4v} symmetry and square pyramidal geometry. The uv spectral patterns produced by the complexes were all similar, which implied that the same type of metal-ligand bonding occurred in each case. Disappointingly, ^1H nmr spectral data proved to be of little use in determining the structure of the complexes. In all cases, the chemical shift of the proton R^1 was found not to be significantly affected by complex formation. The chemical shifts of the other substituents were also unaffected by the complexation reaction. A ^1H nmr study of complex (71) showed that the spectrum of this compound was unchanged over the temperature range -50° - 80°C. This suggested that the occurrence of cis and trans isomers or fluxional behaviour was unlikely. On the basis of the available evidence, the two possible structures for this class of complexes are therefore (74) and (75). It is not possible to distinguish between these.



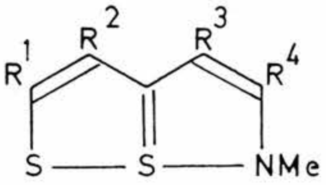
(74)

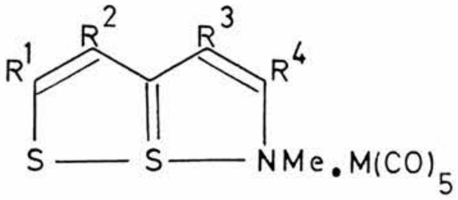


(75)

3. The Preparation of Pentacarbonylchromium(0), Molybdenum(0) and Tungsten(0) Complexes of 6,6aλ^4-Dithia-1-azapentalenes

The iodopentacarbonylmetallate(0) salts of chromium, molybdenum and tungsten reacted with dithiaazapentalenes (76) - (78) to give the complexes (79) - (86).





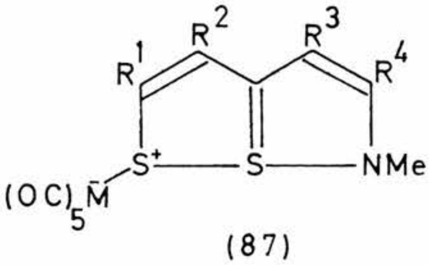
	R^1	R^2	R^3	R^4
(76)	H	– $(CH_2)_3$	–	H
(77)	H	Me	Me	H
(78)	Me	H	H	Me

	R^1	R^2	R^3	R^4	M
(79)	H	– $(CH_2)_3$ –		H	Cr
(80)	H	– $(CH_2)_3$ –		H	Mo
(81)	H	– $(CH_2)_3$ –		H	W
(82)	H	Me	Me	H	Cr
(83)	H	Me	Me	H	Mo
(84)	H	Me	Me	H	W
(85)	Me	H	H	Me	Cr
(86)	Me	H	H	Me	W

Results from elemental microanalyses demonstrated that the complexes were of the expected metal to ligand ratio (1:1). Complexes (79) - (86), like those described previously, did not produce a molecular ion when examined by mass spectrometry. However, the molecular ions of the triheterapentalene and $M(CO)_5$ fragment were clearly discernable. The infra-red spectra of the complexes were consistent with the metal carbonyl geometry being square pyramidal and of C_{4v} symmetry. Complexes (79) - (86) could arise through reaction of either sulphur atom S(6) or nitrogen atom

N(1). These bonding possibilities would give rise to complexes (87) and (88), respectively. These complexes are formulated as bicyclic species, however, they may exist in monocyclic form. If the bicyclic nucleus were destroyed, restricted rotation about the C(3)-C(3a) or C(4)-C(3a) bond would give rise to *cis* and *trans* isomers, e.g. structure (89). Variable temperature ^{1}H nmr studies of complex (84) showed that over the range -50°-80°C, the spectrum of the complex did not change. The possible existence of *cis* and *trans* isomers was therefore unlikely.

^{1}H nmr studies of compounds (79) - (86) showed that complex formation resulted in the *NMe* protons being shifted downfield by ca. 0.2 ppm, as were the 2-H protons of complexes derived from compounds (76) and (77). In contrast, the R^1 proton substituents of compounds (76) and (77) suffered a diamagnetic shift of ca. 0.25 ppm. These data suggested that coordination to the metal was occurring through the nitrogen atom N(1). The most likely structure for these complexes is therefore (88). In this structure, the increased positive charge on atom N(1) would cause the *NMe* protons to resonate at lower field, while the protons in the dithiole ring are less deshielded than in the triheterapentalene structure and will resonate at smaller δ values.



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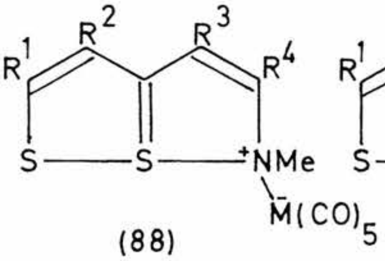

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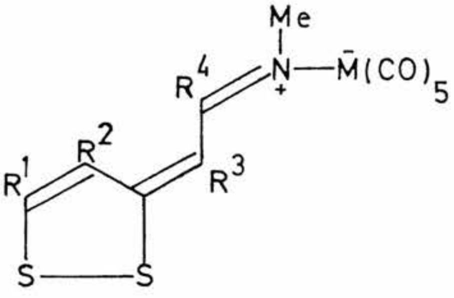
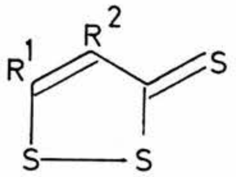
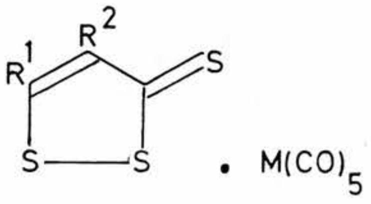


(89)

4. The Preparation of Pentacarbonylchromium(0), Molybdenum(0) and Tungsten(0) Complexes of Substituted 1,2-Dithiole-3-thiones

The reaction of 4,5-dimethyl-1,2-dithiole-3-thione (9) and 5-phenyl-1,2-dithiole-3-thione (38) with iodopentacarbonylmetallates(0) of chromium, molybdenum and tungsten gave high yields of complexes (90) - (92).





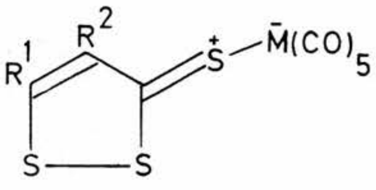
	R^1	R^2
(9)	Me	Me
(38)	Ph	H

	R^1	R^2	M
(90)	Me	Me	W
(91)	Me	Me	Mo
(92)	Ph	H	Cr

Elemental analysis indicated the pure materials to be of the expected (1:1) stoichiometry. Examination of the complexes by mass spectrometry showed that the molecular ions were not evident. However, the molecular ions of the thione and $M(CO)_5$ unit were readily detected. The infra-red spectra of the complexes established that the pentacarbonyl geometry was square pyramidal (C_{4v}), as in previous examples.

In view of these data and the structure of the thiones, the structural possibilities for these complexes are limited. Furthermore, results from previous work described in Section C of this Discussion suggest that complex formation should occur by coordination at the sulphur atom of the thiocarbonyl group. This would give rise to structure (93). Steric effects appeared to rule out the possibility of a π-bonded structure (94). Additionally, infra-red data were not consistent with this type of bonding[135]. ^1H nmr spectral data for the complexes (90), (91) and (92) showed that the chemical shifts of substituents R^1 were unperturbed by complex formation. In contrast, complex formation caused a downfield movement in the resonance positions of the R^2 substituents. This chemical shift difference was ca. 0.1 ppm for the 4-methyl substituents of complexes (90) and (91). The 4-H proton of complex (92) showed a greater downfield shift of ca. 0.24 ppm. The corresponding protons of complexes of trithiapentalenes which are the higher vinylogues of 1,2-dithiole-3-thiones, and Group VI A metal pentacarbonyls[110] show similar chemical shift values.

Angelici[120,121] has noted that certain thiocarbonyl compounds, e.g. thioacetone, form complexes with Group VI A metal pentacarbonyls in which angular bonding exists in the W-S-C unit. The possibility therefore exists that two isomers (95) and (96) may occur. Where R^2=Me, formation of isomer (95) would be preferred on steric grounds, but when R^2=H, isomer (96) may also exist. These isomers, if formed, should be observable by nmr spectroscopy. However, no evidence for the existence of more than one isomer was obtained by this method. This suggested that either only one isomer was formed or the two isomeric forms interconvert rapidly.



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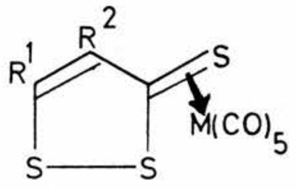

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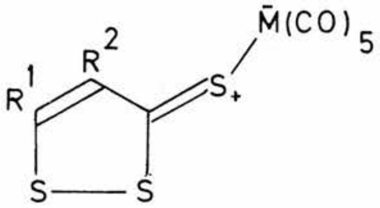

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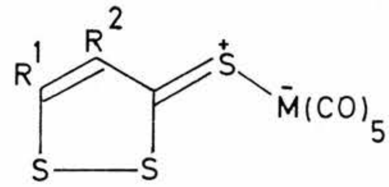
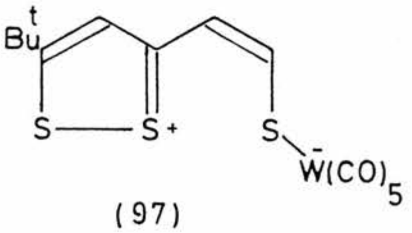


(96)

5. The Attempted Preparation of Pentacarbonyl(5-tert-butyl-1-oxa-6,6aλ^4-dithia-pentalene)tungsten(0)

Recently, Reid and Pogorzelec[110] have reported that the reaction of 5-tert-butyl-1,6,6aλ^4-trithiapentalene and tetraethylammonium iodopentacarbonyltungstate(0) occurs to give the thioaldehyde complex (97). It was therefore of interest to determine whether the analogous oxadithiapentalene (98) would form a similar tungsten complex. Two structures are theoretically possible for this complex. If the donor atom is S(6), then the oxathiolylium cation structure (99) would result. Cations of this type are unusual and have only recently been reported in the literature[106]. The formation of this type of structure appears unlikely as the steric bulk of the tert-butyl substituent is expected to impair the reactivity of the sulphur atom S(6). The failure of 5-*tert*-butyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (64) to form a tungsten complex (Section D2) is cited as an example of the reduced reactivity of atom S(6) for this reason.

If complex formation occurred through oxygen atom O(1), the product would be a dithiolylium cation (100). This cation is expected to be thermodynamically more stable than the oxathiolylium cation (99) because the oxygen atom of the latter molecule is less well able to tolerate positive charge. Another factor which must be considered is the basicity of the ligand donor atom. In the case of cations (99) and (100), the oxygen atom of compound (100) will be a poorer Lewis base than the sulphur atom of compound (99). The oxygen-tungsten bond of compound (100) is therefore expected to be rather weak. In view of these various factors, the adduct of oxadithiapentalene (98) was not expected to be very stable. This was borne out by the experimental results. Compound (98), in dichloromethane, reacted with tetraethylammonium iodopentacarbonyl-



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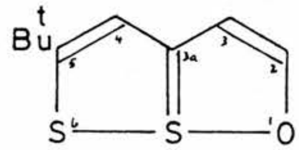

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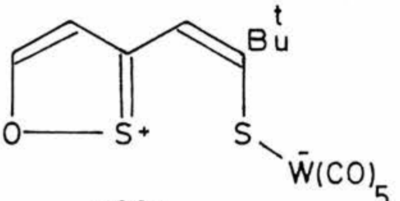

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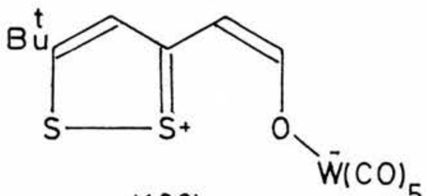

(100)

tungstate(0) to form a small amount of an orange-coloured complex. The complex appeared to be stable in solution, but rapidly decomposed in air. Stoltz[126] has noted that the complex pentacarbonyl-(acetone)tungsten(0) behaves in a similar manner in air.

Conclusion

Triheterapentalenes and 1,2-dithiole-3-thiones were found to form metal complexes with the metal pentacarbonyls of chromium, molybdenum and tungsten. The nature of the metal-ligand interaction was probed using mainly spectroscopic methods. Results suggested that, in the case of triheterapentalenes, reaction occurred at the ring heteroatoms. The substitution pattern of the triheterapentalene and the relative basicity of the ring heteroatoms were found to be important factors in determining the structure of the complex. Possible structures for the complexes have been proposed, however, X-ray crystallographic studies of the complexes will be required to settle the true nature of the bonding in these compounds.

EXPERIMENTAL

Introductory Notes

Melting points were determined using a Kofler hot-stage apparatus and are corrected. Quoted yield values refer to recrystallised tlc pure material, unless otherwise stated. Ultraviolet and visible absorption spectral data were obtained using a Unicam SP800 spectrophotometer. Light absorption data are for solutions in cyclohexane, unless otherwise stated. Where descriptions of absorption peaks are given, the notation br=broad, inf=inflection and sh=shoulder applies. Infrared spectra were recorded using a Perkin-Elmer 621 spectrometer. Solution spectral data were obtained using sodium chloride cells of path-length 1mm. All samples were examined as 0.002 M solutions in carbon tetrachloride. Light transmittance values, as measured from peak maxima to the solution base-line, are defined as follows: 0-20% = very strong, 21-40% = strong, 41-60% = medium, 61-80% = weak, 81-100% = very weak. Solid state spectra refer to dispersions of test material in KBr discs. Mass spectra and accurate mass determinations were obtained with an A.E.I. MS 902 spectrometer. ^1H Nmr spectra were recorded at ca. 31.4°C (except in variable temperature studies) using a Varian HA 100 spectrometer operating at 100 MHz. Solutions in chloroform - D_3 were 0.4 M or saturated, unless otherwise stated. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane as internal reference, except in some variable temperature studies where hexamethyldisiloxane was used. J values were measured on the 100 Hz scale. Chemical shift values refer to singlet absorptions, unless stated otherwise, in which case the following notation is used: d=doublet, t=triplet, q=quartet, quint=quintet, dd=double doublet, dt=double triplet, m=multiplet and b=broad.

The microanalytical determinations of carbon, hydrogen and nitrogen were carried out by Mr. J. Bews and Mrs S. Smith, Department of Chemistry, University of St. Andrews.

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

Column chromatography was carried out with Merck Activity II - III (100 - 200 mesh) alumina. Chromatographic silica was Sorbsil Silica Gel M 60. Solvent mixtures are described in ratios by volume.

Thin layer chromatography (tlc) was performed with alumina (Macherey Nagel Aluminium Oxide - G) and silica (Macherey Nagel Kieselgel - G) coated plates. The coating was ca. 0.25 mm thick.

Solutions were dried over anhydrous sodium sulphate and evaporated at reduced pressure using a rotary film evaporator. Solid materials were dried in vacuo over phosphorus pentoxide.

Materials. "Petrol" refers to the petroleum ether fraction of boiling range 40-60°C and "ether" refers to diethyl ether. Acetic anhydride, acetone, cyclohexane, ethanol, methanol, n-hexane and petrol were all redistilled commercial grade solvents. Benzene, ether and toluene were refluxed over sodium wire for one hour then distilled to give the dried solvents. These dry solvents were stored over sodium wire. Before being dried with sodium, the ether was pre-dried by standing over calcium chloride for ca. 3 days.

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

Methylene chloride, chloroform and carbon tetrachloride were refluxed over phosphorus pentoxide for one hour and then distilled. The distillate was redistilled before use.

Acetonitrile was refluxed over sodium hydride (50 per cent dispersion in oil, 2g per litre) for 30 minutes, then distilled. The distillate was refluxed over phosphorus pentoxide for one hour, distilled, and distilled once more.

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

Chromium, tungsten, and molybdenum hexacarbonyls, tetraethylammonium iodide, silver tetrafluoroborate and diglyme were all commercial reagents.

A. THE REACTION OF 5-SUBSTITUTED-1,2-DITHIOLE-3-THIONES WITH ARENEDIAZONIUM TETRAFLUOROBORATES

Preparation of Arenediazonium Tetrafluoroborates

p-Methoxybenzenediazonium Tetrafluoroborate

The tetrafluoroborate was prepared by modification of the method of Roe[127].

p-Aminomethoxybenzene (227 mmol, 27.97g) was dissolved with warming and stirring in fluoroboric acid solution (20%; 180 ml). The resulting solution was filtered and cooled to 5°C. To the fluoroborate solution was then added a filtered solution of sodium nitrite (227 mmol, 15.86 g) in water (46 ml) at such a rate that the temperature of the fluoroborate solution remained below 10°C. When the addition was complete, the solution was cooled to 0°C and stirring continued for a further 30 minutes. The product was then filtered off and washed successively with ice-cold fluoroboric acid solution (6%; 34 ml), methanol (2 x 20 ml) and ether (5 x 40 ml), then dried in vacuo overnight. The product (38.03 g, 75%) crystallised as transparent needles, m.p. 134-138°C (decomp.) (lit.[127] 139°C). Storage in darkness and under refrigeration was necessary.

Benzenediazonium Tetrafluoroborate

The tetrafluoroborate was prepared by modification of the method of Starkey[128]. Filtered aniline AR (250 mmol, 23 ml) was cooled to 5°C in a 250 ml round-bottomed flask. Fluoroboric acid (40%; 138 ml) was then added over five minutes, while the flask was gently agitated. When the solution temperature had returned to 5°C, a filtered solution of sodium nitrite (250 mmol, 17.25 g) in water (40 ml) was added, with stirring, over 15 minutes. After a further 15 minutes, the curdy white precipitate was filtered off and washed successively with cold fluoroboric acid solution (6%; 35 ml), ethanol (2 x 50 ml), and ether (3 x 50 ml), then dried in vacuo. The product (37.86 g, 77%) was obtained as transparent needles, m.p. 92-94°C (lit.[128] 121-122°), and was stored under refrigeration.

p-Nitrobenzenediazonium Tetrafluoroborate

This diazonium salt was prepared by the method of Roe[127].

Substituted 1,2-Dithiole-3-thiones

4,5-Dimethyl-1,2-dithiole-3-thione was prepared by the method of Vialle[129]. 5-Phenyl-1,2-dithiole-3-thione was prepared by the method of Klingsberg[130,131]. 5-Methyl-1,2-dithiole-3-thione, 5-*tert*-butyl-1,2-dithiole-3-thione and 4,5,6,7-tetrahydrobenzo[d]-1,2-dithiole-3-thione were generously donated by other workers in this laboratory.

The Reactions of 5-Substituted 1,2-Dithiole-3-thiones with Arenediazonium Tetrafluoroborates

General Method:

The thione (10 mmol) was dissolved, with stirring, in methanol (160 ml) at 50°C. To this solution was added the tetrafluoroborate in portions (4 x 10 mmol) over a period of two minutes. Residual salt was washed in with pre-heated methanol (40 ml). The reaction mixture was stirred at 50° for a further 30 minutes and then poured cautiously into sodium carbonate solution (0.1 M, 500 ml). Organic material was extracted into benzene (see individual experiments for details). The combined benzene extracts were washed with water (x 2), dried, and the solvent evaporated. Subsequent purification was by chromatography on a column of alumina (see individual experiments for details).

1. The Reaction of 4,5-Dimethyl-1,2-dithiole-3-thione with Benzenediazonium-Tetrafluoroborate

The thione (9) (10 mmol, 1.623 g) and tetrafluoroborate (40 mmol, 7.677 g) were used. Organic products were extracted into benzene (2 x 700 ml + 2 x 400 ml). Chromatography (60 x 2.7 cm, column I) of the residue with petrol-benzene (2:1, 1050 ml) afforded coloured eluates which were discarded. Continued elution with the same solvent mixture (100 ml), followed by benzene (300 ml), gave red eluates. Rechromatography of this fraction on a column of alumina (70 x 2.4 cm, column II) using petrol-benzene (3:1, 4600 ml) gave a fraction which was discarded. Further elution with the same solvent mixture (4000 ml) gave red eluates which afforded 4-methyl-1-phenyl-5-phenylthio-6,6aλ^4-dithia-1,2-diazapentalene (10) (0.246 g, 7.2%) as red microneedles from hexane, m.p. 120-123°.

Found : C 59.5; H 4.0; N 8.1

$C_{17}H_{14}N_2S_3$ requires : C 59.6; H 4.1; N 8.2.

Accurate mass determination : 342.0334

$C_{17}H_{14}N_2S_3$ requires : 342.0319

^{1}H nmr ($CDCl_3$) : δ 2.61 (3H, s, 4-Me), 7.16-7.72 (10H, m, 2<u>o</u> + 2 <u>m</u> + <u>p</u>-protons of 1- and 5-Ar), 8.16 (1H, s, 3-H) uv spectrum : λ max (nm) 508 (log ϵ 4.32), 343 (3.41), 294 (4.07), 235 (4.58), 211 (4.55).

Further elution of column II with benzene-petrol (1:1, 1000 ml and 3:1, 600 ml) gave eluates which were discarded. Benzene (900 ml) gave yellow eluates which were rechromatographed on a column of silica (33 x 2.4 cm). Petrol-benzene (2:1, 1600 ml) gave eluates which were discarded. Further elution (2:1, 1600 ml and 1:1, 1300 ml) gave 4,5-dimethyl-1,2-dithiole-3-thione (9) (0.881 g, 54%) as yellow plates from hexane, m.p. 94-95° (lit.[129] 95-96°); mixed m.p. 94-96°. M^+ at m/e 162.

^1H nmr ($CDCl_3$) : δ 2.16 (3H, q, 4-Me) $J_{4,5}$ 0.5, 2.50 (3H, q, 5-Me)

2. The Reaction of 4,5 Dimethyl-1,2-dithiole-3-thione with p-Nitrobenzendiazonium Tetrafluoroborate

The thione (9) (10 mmol, 1.623 g) and tetrafluoroborate (40 mmol, 9.478 g) were used. A variation of the usual work-up procedure was necessary because the dithiadiazapentalene had low solubility in aromatic solvents.

After the reaction mixture was poured into sodium carbonate solution, the mixture was diluted with benzene (500 ml) and filtered through a glass-wool plug. The inorganic layer was then separated and discarded. The organic extracts were transferred to a 2-litre conical flask and diluted with more benzene (400 ml). To this solution was added the insoluble material which had been filtered off, and the glass-wool plug. The insoluble organic material was induced to dissolve by heating the solution to near boiling, decanting off the clear supernatant, replenishing with more benzene (900 ml), and reheating. By repeating this process six times, all the product was dissolved in benzene. The extracts were allowed to cool over night, and were then divided into three equal portions. Each portion was diluted with more benzene (2000 ml), washed with water (2 x 1000 ml), and dried. The solutions were combined and evaporated to give a viscous red oil which had the characteristic odour of nitrobenzene. The oil was divided into two parts. Each part was dissolved in hot toluene (800 ml) then cooled and diluted with an equal volume of benzene. When the solution had cooled to 40°, it was passed through a column of warm (40°) alumina (15 x 6 cm). Elution was completed with hot (50°) benzene (7000 ml). The eluates from each column were combined and evaporated. The residue was 4-methyl-1-(p-nitrophenyl)-5-(p'-nitrophenylthio)-6,6aλ^4-dithia-1,2-diazapentalene (15) (3.57 g, 83%), as red needles from toluene, m.p. 259-264°.

Found : C 47.3; H 2.6; N 13.0

$C_{17}H_{12}N_4O_4S_3$ requires : C 47.2; H 2.8; N 13.0

Accurate mass determination : 432.0012

$C_{17}H_{12}N_4O_4S_3$ requires : 432.0020

^{1}H nmr (DMSO-D_6, 0.2M solution, 143°) : δ 2.63 (3H, s, 4-Me), 7.60 and 7.68 (2H, 2 o-protons of 5-Ar), 7.79 and 7.88 (2H, 2 o-protons of 1-Ar), 8.08 and 8.16 (2H, 2 m-protons of 5-Ar), 8.10 and 8.19 (2H, 2 m-protons of 1-Ar), 8.61 (1H, s, 3-H)

uv spectrum : compound not sufficiently soluble

3. Reaction of 4,5-Dimethyl-1,2-dithiole-3-thione-with p-Methoxybenzenediazonium Tetrafluoroborate

The thione (9) (10 mmol, 1.623 g) and tetrafluoroborate (40 mmol, 8.878 g) were used. Organic products were extracted into benzene (2 x 700 ml). Chromatography (68 x 2.7 cm, column I) of the impure product with petrol-benzene (2:1, 1000 ml) gave eluates which were discarded. Petrol-benzene (1:1, 900 ml) afforded a yellow oil (1.0 g) which was found to contain the starting thione (M^+ at m/e 162) and methoxybenzene (16) (M^+ at m/e 108). Further elution (500 ml), followed by benzene-petrol (2:1, 450 ml) and benzene (600 ml) produced impure eluates. More benzene (400 ml) and benzene-ether (99:1, 250 ml) gave 4-methyl-1-(p-methoxyphenyl)-5-(p′-methoxyphenylthio)-6,6a λ^4-dithia-1,2-diazapentalene (17) (1.276 g, 32%) as red microplatelets from acetonitrile, m.p. 119-121°C.

Found : C 56.6; H 4.3; N 6.9

$C_{19}H_{18}N_2O_2S_3$ requires : C 56.7; H 4.5; N 7.0

Accurate mass determination : 402.0516

$C_{19}H_{18}N_2O_2S_3$ requires : 402.0530

^{1}H nmr ($CDCl_3$) : δ 2.58 (3H, s, 4-Me), 3.87 (3H, s, MeO of 1-Ar or 5-Ar), 3.90 (3H, s, MeO of 5-Ar or 1-Ar), 6.83 and 6.92 (2H, 2 m-protons of 5-Ar), 6.88 and 6.97 (2H, 2 m-protons of 1-Ar), 7.40 and 7.49 (2H, 2 o-protons of 5-Ar), 7.52 and 7.61 (2H, 2 o-protons of 1-Ar), 8.11 (1H, s, 3-H)

uv spectrum : λ max (nm), 510 (log ϵ 4.36), 300 (4.11), 236 (4.67), 204 (4.57)

4. Reaction of 4,5,6,7-Tetrahydrobenzo[d]-1,2-dithiole-3-thione with *p*-Methoxybenzenediazonium Tetrafluoroborate

The thione (19) (10 mmol, 1.887 g) and tetrafluoroborate (40 mmol, 8.882 g) were used. Organic products were extracted into benzene (2 x 1000 ml + 2 x 700 ml). Chromatography (80 x 2.7 cm, column I) of the residue with petrol-benzene (2:1, 1600 ml), gave pale yellow eluates which were discarded. Continued elution (1500 ml) afforded a pale-yellow fraction. Rechromatography (17.5 x 1.6 cm, column II) of this fraction using petrol-benzene (2.1, 50 ml) gave eluates which were discarded. Further elution (250 ml) gave 4,5,6,7-tetrahydrobenzo[d]-1,2-dithiole-3-thione (19) (0.022 g, 1.2%) as yellow needles from cyclohexane-hexane mixture (1:1), m.p. 100-102° (lit.[119] 102°). M^+ at m/e 183. The product was also identified by comparative tlc.

Continued elution of column I gave eluates (2500 ml) which were discarded. Further elution (4200 ml) gave a fraction which was rechromatographed (50 x 2.4 cm, column III) using petrol-benzene (2:1, 2100 ml). Initial eluates were discarded. Further elution (600 ml), followed by petrol-benzene (1:1, 400 ml), gave a coloured fraction, which on evaporation of the solvents afforded *p*,*p*′-dimethoxyazobenzene (20) (0.054 g, 2.2%) as orange platelets and needles from hexane, m.p. 162.5-164.5° (lit.[132] 165°).

Found : C 69.4; H 5.7; N 11.5

$C_{14}H_{14}N_2O_2$ requires : C 69.4; H 5.8; N 11.6

Accurate mass determination : 242.1066

$C_{14}H_{14}N_2O_2$ requires : 242.1056

^{1}H nmr ($CDCl_3$) : δ 2.87 (6H, s, *p*- and *p*'-MeO), 6.92 and 7.07 (4H, 4 *m*-protons of aryl rings), 7.80 and 7.95 (4H, 4 *o*-protons of aryl rings)

Further development of column I with petrol-benzene (2:1, 1300 ml) and benzene (300 ml) gave eluates which were discarded. Elution with benzene (1300 ml) afforded a red fraction which was rechromatographed on a column of silica (55 x 2.8 cm, column IV). Petrol-benzene (1:1, 2100 ml) eluates were discarded. Continued elution with the same solvent system (600 ml), followed by benzene (2400 ml), afforded 1-(p-methoxyphenyl)-5-(p'-methoxyphenylthio)-3,4-propano-6,6a λ^4-dithia-1,2-diazapentalene (21) (1.638 g, 38%) as red platelets from acetonitrile, m.p. 144.5-147°.

Found : C 59.0; H 4.7; N 6.7

$C_{21}H_{20}N_2O_2S_3$ requires : C 58.8; H 4.7; N 6.5

Accurate mass determination : 428.0669

$C_{21}H_{20}N_2O_2S_3$ requires : 428.0687

^{1}H nmr ($CDCl_3$) : δ 2.11 (2H, quint, 4'-H_2), 3.02 (4H, t, 3'- and 5'-H_2), 3.75 (3H, s, MeO of 1-Ar or 5-Ar), 3.81 (3H, s, MeO of 5-Ar or 1-Ar), 6.83 and 6.92 (2H, 2 *m*-protons of 5-Ar), 6.89 and 6.98 (2H, 2 *m*-protons of 1-Ar), 7.41 and 7.50 (2H, 2 *o*-protons of 5-Ar), 7.50 and 7.59 (2H, 2 *o*-protons of 1-Ar)

uv spectrum : λ max (nm), 527 (log ϵ 4.38), 350 (3.53), 303 (4.10), 247 sh (4.64), 236 (4.67), 204 (4.57).

5. Reaction of 5-Methyl-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate

The thione (10 mmol, 1.486 g) and tetrafluoroborate (40 mmol, 7.674 g) were used. Organic products were extracted into hot (70°) benzene (2 x 500 ml). Chromatography (70 x 2.7 cm, column I) of the residue with petrol-benzene (1:1, 250 ml) afforded eluates which were discarded. Further elution (400 ml) gave a buff-coloured compound. This compound was crystallised by dissolving it in a small volume of petrol (5 ml) at 20°, then cooling the solution to -10° and collecting the white needles of diphenyl disulphide (23) (90 mg, 1%), m.p. 57-59° (lit.[132] 60°).

Accurate mass determination : 218.0223

$C_{12}H_{10}S_2$ requires : 218.0224

The next eluates (400 ml) from column I were discarded. Continued elution (1100 ml) gave a red fraction. Rechromatography on a column of silica (53 x 2.4 cm, column II) with petrol-benzene (2:1, 600 ml) gave eluates which were discarded. Further elution gave a red fraction (600 ml) (fraction A). Benzene (400 ml) also gave red eluates (fraction B).

Rechromatography of fraction A on a column of silica (67 x 2.0 cm, column III) with petrol-benzene (2:1, 1050 ml) afforded no useful material. Further elution (150 ml) gave eluates (fraction C) which were set aside. The residue from the next fraction (500 ml) was crystallised from cyclohexane. The mother liquors were combined with fractions B and C, evaporated and the residue crystallised from cyclohexane. This procedure gave 1-phenyl-5-phenylthio-6,6aλ^4-dithia-1,2-diazapentalene (24) (165 mg, 5%) as red microneedles, m.p. 111-112°.

Found : C 58.5; H 3.4; N 8.5

$C_{16}H_{12}N_2S_3$ requires : C 58.85 H 3.7; N 8.5

Accurate mass determination : 328.0155

$C_{16}H_{12}N_2S_3$ requires : 328.0162

^{1}H nmr ($CDCl_3$) : δ 7.14 (1H, s, 4-H), 7.21-7.77 (10H, m, protons of 1- and 5-Ar), 8.07 (1H, s, 3-H)

uv spectrum : λ max (nm), 497 (log ε 4.32), 351 br (3.60), 284 (4.04), 237 (4.54), 213 (4.36).

Continued elution (600 ml) of column II gave eluates which were discarded. Elution with ether (500 ml) afforded yellow material (fraction D).

Further elution of column I gave yellow eluates which were combined with fraction D of column II. Rechromatography on a column of silica (60 x 2.0 cm) with petrol-benzene (1:1, 1400 ml and 3:1, 400 ml) afforded no useful material. Benzene-ether (99:1, 600 ml) gave yellow eluates. Rechromatography of these on a column of silica (32 x 2.4 cm) with benzene (500 ml), followed by benzene-ether (49:1, 600 ml) gave 5-methyl-1,2-dithiole-3-thione (22) (234 mg, 16%) as a viscous yellow-brown liquid at room temperature. M^+ at m/e 148.

^{1}H nmr ($CDCl_3$) : δ 2.57 (3H, s, 5-Me), 7.07 (1H, s, 4-H). The thione was identified by comparative tlc.

Further development of column I using petrol-benzene (1:1, 250 ml and 2.5:1, 1000 ml) and benzene (350 ml) gave eluates which were discarded. Benzene (350 ml) and benzene-ether (24:1, 450 ml) gave eluates (fraction E) which were set aside. More benzene-ether (24:1, 100 ml and 4:1, 150 ml) afforded, after solvent evaporation, a residue which was rechromatographed on a column of silica (25 x 1.4 cm, column III). Elution of this column with benzene (150 ml) gave purple eluates which were combined with fraction E and rechromatographed on a column of silica (47 x 1.8 cm). Elution of this column with benzene-ether (4:1, 350 ml; 3:1, 400 ml; and 2:1, 450 1) gave no useful material. Subsequent elution (100 ml) gave a slightly impure compound, tentatively identified as phenyl 1,6-diphenyl-4-phenylazo-6aλ^4-thia-1,2,5,6-tetraazapentalene-3-dithiocarboxylate (28) (6 mg, 0.1%) as purple microrods from acetonitrile. M^+ at m/e 536.

Final elution of column III with benzene-ether (1:1, 500 ml) gave an orange eluate (fraction F).

Final elution of column I with benzene-ether (4:1, 350 ml and 1:1, 300 ml) gave eluates which were combined with fraction F. Rechromatography on a column of silica (39 x 2.7 cm) with benzene (1800 ml) gave eluates which were discarded. Further elution with benzene (900 ml) and benzene-ether (49:1, 400 ml) gave 3-carbomethoxy-1,6-diphenyl-6aλ^4-thia-1,2,5,6-tetraazapentalene (27) (109 mg, 3.2%) as orange spars from acetonitrile, m.p. 179-182°.

Found : C 60.2; H 3.9; N 16.4

$C_{17}H_{14}N_4O_2S$ requires : C 60.3; H 4.2; N 16.6

Accurate mass determination : 338.0854

$C_{17}H_{14}N_4O_2S$ requires : 338.0837

^{1}H nmr ($CDCl_3$) : δ 4.04 (3H, s, MeO-), 7.16-7.52 (6H, m, 2m + p-protons of 1- and 6-Ar), 7.69-7.85 (4H, m, 2 o-protons of 1- and 6-Ar), 9.35 (1H, s, 4-H)

uv spectrum : λ max (nm), 466 (log ϵ 4.25), 346 sh (3.97), 325 (4.12), 242 (4.23), 204 (4.32)

ir spectrum : ν max (C=O) 1705 cm^{-1}

6. The Reaction of 5-Methyl-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate

The thione (22) (10 mmol, 1.48 g) and tetrafluoroborate (40 mmol, 8.878 g) were used. Organic products were extracted into benzene (2 x 1000 ml). Chromatography (78 x 2.7 cm, column I) of the residue with petrol-benzene (2:1, 1000 ml and 1:1, 700 ml) and benzene (400 ml) gave yellow eluates which were discarded. More benzene (600 ml) and benzene-ether (98:2, 250 ml) afforded red eluates which were rechromatographed on a column of silica (58 x 2.7 cm, column II). Elution with benzene-petrol (2:1, 1600 ml) gave no useful product. Further elution with benzene (1000 ml) and benzene-ether (99:1, 250 ml) gave a red-coloured fraction. The residue from this fraction was crystallised from acetonitrile. The mother liquors were rechromatographed on a column of silica (33 x 2.7 cm, column III). Elution with benzene-petrol (3:1, 300 ml) gave no useful product. The next fraction (benzene, 200 ml) was stripped of solvent and the residue crystallised from acetonitrile. This procedure gave 1-(p-methoxyphenyl)-5-(p'-methoxyphenylthio)-6,6a λ^4-dithia-1,2-diazapentalene (29) (0.318 g, 8.2%) as red microneedles, m.p. 102-103.5°.

Found : C 55.9; H 4.3; N 7.5

$C_{18}H_{16}N_2O_2S_3$ requires : C 55.6; H 4.2; N 7.2

Accurate mass determination : 388.0376

$C_{18}H_{16}N_2O_2S_3$ requires : 388.0374

^{1}H nmr ($CDCl_3$) : δ 3.79 (3H, s, MeO of 1- or 5-Ar), 3.84 (3H, s, MeO of 5- or 1-Ar), 6.87 and 6.96 (2H, 2 m-protons of 5-Ar), 7.02 (1H, s, 4-H), 6.93 and 7.02 (2H, 2 m-protons of 1-Ar), 7.47 and 7.56 (2H, 2 o-protons of 5-Ar), 7.53 and 7.62 (2H, 2 o-protons of 1-Ar), 8.03 (1H, s, 3-H)

uv spectrum : λ max (nm), 509 (log ϵ 4.32), 349 (3.62), 287 (4.05), 240 (4.65), 204 (4.57)

Continued elution of column I with benzene-ether (8:1, 300 ml) gave no useful products. Further elution with the same solvents (1:1, 300 ml) afforded a red fraction. The residue from this fraction was crystallised from benzene/cyclohexane (1:1). The solid (A) obtained was set aside while the mother liquors were rechromatographed on a column of silica (68 x 2.2 cm, column IV). Benzene-petrol (4:1, 1300 ml) gave eluates which were discarded. The next fraction (benzene, 900 ml) was evaporated and the residue crystallised from acetonitrile. The product collected was combined with solid (A) and the whole rechromatographed on a column of silica (58 x 3.5 cm, column V). Elution with benzene (1200 ml) and benzene-ether (99:1, 300 ml) gave no useful product. The next fraction, eluted using the same solvent mixture, gave p-methoxyphenyl 1,6-di(p-methoxyphenyl)-6a λ^4-thia-1,2,5,6-tetraazapentalene-3-dithiocarboxylate (30) (0.137 g, 2.6%) as red microneedles from acetonitrile, m.p. 197-199°.

Found : C 57.4; H 4.4; N 10.8

$C_{25}H_{22}N_4O_3S_3$ requires : C 57.5; H 4.2; N 10.7

Accurate mass determination : 522.0854

$C_{25}H_{22}N_4O_3S_3$ requires : 522.0841

^{1}H nmr ($CDCl_3$) : δ 3.82 (6H, s, MeO of 1- and 6-Ar), 3.86 (3H, s, MeO.CS.), 6.66 - 7.10 (7H, m, 4-H and 6 m-protons of 1-, 3- and 6-Ar), 7.38 and 7.46 (2H, 2 o-protons of 3-Ar), 7.63 and 7.72 (2H, 2 o-protons of 1- or 6-Ar), 7.81 and 7.90 (2H, 2 o-protons of 6- or 1-Ar)

uv spectrum : λ max (nm), 499 sh (log ϵ 4.39), 462 (4.46), 351 (4.15), 236 (4.48), 204 (4.44)

Further elution of column I using benzene-ether (1:1, 100 ml) gave eluates which were discarded. Benzene-ether (1:1, 100 ml), ether (1000 ml) and ether-methanol (399:1, 600 ml) gave red material which was rechromatographed on a column of alumina (25 x 2.7 cm, column VI). Elution with benzene-ether (97:3) gave four fractions of equal volume. The first of these contained a fast-running impurity. This fraction was rechromatographed on a column of alumina (30 x 2.7 cm, column VII). Elution with benzene (250 ml) and benzene-ether (98:2, 250 ml; 96:4, 200 ml; and 90:10, 200 ml) gave no useful product. Continued elution with benzene-ether (90:10, 200 ml) gave red-coloured eluates. These were combined with fractions 2-4 of column VI and the whole rechromatographed on a column of silica (58 x 2.3 cm, column VIII). Benzene-ether (98:2, 2000 ml) gave eluates which were discarded. Elution with the same solvents (96:4, 2250 ml) gave 3-carbomethoxy-1,6-di(p-methoxyphenyl)-6aλ^4-thia-1,2,5,6-tetraazapentalene (31) (0.211 g, 5.3%) as red microneedles from acetonitrile, m.p. 191-193°.

Found : C 57.3; H 4.8; N 13.8

$C_{19}H_{18}N_4SO_4$ requires : C 57.3; H 4.6; N 14.1

Accurate mass determination : 398.1038

$C_{19}H_{18}N_4SO_4$ requires : 398.1048

^{1}H nmr ($CDCl_3$) : δ 3.84 (6H, s, MeO of 1- and 6-Ar), 4.06 (3H, s, MeO.CO.-), 6.93 and 7.02 (2H, 2 m-protons of 1- or 6-Ar), 6.95 and 7.04 (2H, 2 m-protons of 6- or 1-Ar), 7.65 and 7.74 (2H, 2 o-protons of 1- or 6-Ar), 7.72 and 7.81 (2H, 2 o-protons of 6- or 1-Ar), 9.34 (1H, s, 4-H)

uv spectrum : λ max (nm), 486 (log ϵ 4.30), 341 (4.26), 237 (4.29), 203 (4.44)

ir spectrum : ν max (C=O) 1639 cm^{-1}

B. THE REACTIONS OF SUBSTITUTED 1,2-DITHIOLE-3-THIONES WITH ARENEDIAZONIUM TETRAFLUOROBORATES IN THE PRESENCE OF PYRIDINE

General Method:

The thione (10 mmol) was dissolved, with stirring, in methanol (190 ml) at 50°C to which pyridine (10 ml) had been added. To this solution was added the tetrafluoroborate in portions (3 x 20 mmol) over a period of 10 minutes. Residual salt was washed in with preheated methanol (30 ml). The reaction mixture was kept at 50°C for a further 30 minutes and then poured into sodium carbonate solution (0.1M, 500 ml). Organic material was extracted with benzene (see individual experiments for details). The combined benzene extracts were washed thoroughly with water (x4), dried, and the solvent evaporated. Subsequent purification was by chromatography on a column of alumina: conditions are described in each experiment.

1. Reaction of 4,5-Dimethyl-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate in the Presence of Pyridine

The thione (9) (10 mmol, 1.623 g) and tetrafluoroborate (60 mmol, 11.515 g) were used. Organic products were extracted into benzene (2 x 600 ml). Exceptionally, efficient removal of pyridine by water washing required a total of six extractions. Chromatography (65 x 2.7 cm, column I) of the residue with petrol-benzene (2:1, 250 ml) gave colourless eluates which were discarded. Further elution with petrol-benzene (1.5:1, 500 ml) afforded a yellow fraction which was rechromatographed on a column of alumina (32 x 2.2 cm, column II). Petrol-benzene (3:1, 150 ml) gave eluates which were discarded. The next fraction (120 ml) afforded diphenyl disulphide (23) (0.1 g). M^+ at m/e 218. The material was not purified further.

Continued elution of column I with petrol-benzene (2:1, 200 ml) gave no useful material. Further elution using the same solvent system (800 ml), followed by benzene (200 ml), afforded red eluates. Rechromatography of this fraction on a column of silica (60 x 3.5 cm, column III), using petrol-benzene (2.3:1, 6000 ml) gave eluates which were discarded. The next fraction (1000 ml) afforded 4-methyl-1-phenyl-5-phenylthio-6,6aλ^4-dithia-1,2-diazapentalene (10) (1.289 g, 37.6%) as red needles from acetonitrile, m.p. 120.5-122°; mixed m.p. 120.5-122°. M^+ at m/e 342.

> ^{1}H nmr ($CDCl_3$) : δ 2.60 (3H, s, 4-Me), 7.08-7.72 (10H, m, 2 <u>o</u> + 2 <u>m</u> + <u>p</u>-protons of 1-and 5-Ar), 8.14 (1H, s, 3-H)

2. The Reaction of 4,5,6,7-Tetrahydrobenzo[d]-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate in the Presence of Pyridine

The thione (19) (10 mmol, 1.883 g) and tetrafluoroborate (60 mmol, 11.516 g) were used. Organic products were extracted into benzene (3 x 500 ml). Chromatography (65 x 2.7 cm, column I) of the residue using benzene-petrol (4:1, 200 ml) gave eluates which were discarded. Further elution with benzene (100 ml) gave crude diphenyl disulphide (23) (90 mg). M^+ at m/e 218. The next fraction (benzene, 25 ml) was discarded. Continued use of the same solvent (150 ml) then gave red eluates (fraction A). Finally, elution with benzene (700 ml), ether (900 ml) and ether-methanol (99:1, 500 ml) afforded eluates which were rechromatographed (55 x 2.2 cm, column II). Petrol-benzene eluates (2:1, 750 ml) were discarded. Further elution (2:1, 450 ml and 1:1, 50 ml) gave material which was combined with fraction A and rechromatographed (63 x 2.7 cm, column III). Initial orange eluates from petrol-benzene (3:1, 350 ml) were discarded. The next eluates (150 ml) were retained (fraction B). Elution with petrol-benzene (1.5:1, 1000 ml and 1:1, 200 ml) gave material which was crystallised from cyclohexane. The mother liquors were combined with fraction B and a fraction consisting of petrol-benzene (1:1, 300 ml) and benzene (400 ml) collected from column III, then evaporated and recrystallised to give 1-phenyl-5-phenylthio-3,4-propano-6,6a λ^4-dithia-1,2-diazapentalene (34) (1.909 g, 51.8%) as red platelets from cyclohexane, m.p. 131.5-136.5°.

Found : C 62.2; H 4.4; N 7.8

$C_{19}H_{16}N_2S_3$ requires : C 62.2; H 4.4; N 7.6

Accurate mass determination : 368.0478

$C_{19}H_{16}N_2S_3$ requires : 368.0476

^{1}H nmr ($CDCl_3$) : δ 2.10 (2H, quint, 4-H'_2), 3.02 (4H, bt, 3$'$- and 5$'$-H_2), 7.01-7.67 (10H, m, 2 o + 2 m + p-protons of 1 and 5-Ar)

uv spectrum : λ max (nm), 521 (log ϵ 4.15), 348 (3.26), 295 (3.86), 239 (4.03), 208 (4.21)

3. The Reaction of 4,5-Dimethyl-1,2-dithiole-3-thione with *p*-Methoxybenzenediazonium Tetrafluoroborate in the Presence of Pyridine

The thione (9) (10 mmol, 1.623 g) and tetrafluoroborate (60 mmol, 13.317 g) were used. Organic products were extracted into benzene (2 x 750 ml). Chromatography (68 x 2.7 cm, column I) of the residue with petrol-benzene (2:1, 500 ml and 1:1, 2000 ml) followed by benzene-petrol (2:1, 500 ml), afforded no useful products. Continued elution with the same solvent system (400 ml), benzene (1000 ml) and benzene-ether (99:1, 100 ml) gave 4-methyl-1-(*p*-methoxyphenyl)-5-(*p'*-methoxyphenylthio)-6,6aλ^4-dithia-1,2-diazapentalene (17) (0.728 g, 18.0%) as red microplatelets from acetonitrile, m.p. 119-121°; mixed m.p. 118.5-121°. M^+ at m/e 402.

^{1}H nmr ($CDCl_3$) : δ 2.58 (3H, s, 4-Me), 3.76 (3H, s, MeO of 1- or 5-Ar), 3.79 (3H, s, MeO of 5- or 1-Ar), 6.82 and 6.91 (2H, 2 *m*-protons of 5-Ar), 6.86 and 6.95 (2H, 2 *m*-protons of 1-Ar), 7.38 and 7.47 (2H, 2 *o*-protons of 5-Ar), 7.54 and 7.63 (2H, 2 *o*-protons of 1-Ar), 8.10 (1H, s, 3-H).

4. The Reaction of 4,5,6,7-Tetrahydrobenzo[d]-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate

The thione (19) (10 mmol, 1.883 g) and tetrafluoroborate (60 mmol, 13.317 g) were used. Organic products were extracted into benzene (2 x 700 ml). Chromatography (60 x 2.7 cm, column I) of the residue using petrol-benzene (3:1, 500 ml; 2:1, 900 ml and 1:1, 100 ml) gave no useful products. The next fraction (1:1, 750 ml) was rechromatographed (30 x 2.2 cm, column II). Initial petrol-benzene eluates (2:1, 500 ml) were discarded. The next fraction (1:1, 800 ml) gave p,p′-dimethoxyazobenzene (20) (55 mg, 2.3%) as orange needles from hexane. M^+ at m/e 242.

Continued elution of column I with petrol-benzene (1:1, 1750 ml; 1:2, 450 ml) and benzene (800 ml) afforded red eluates which, after solvent evaporation, gave a residue which was crystallised from acetonitrile. The mother liquors were chromatographed (33 x 2.2 cm, column IV). Petrol-benzene (2:1, 500 ml; 1:1, 200 ml; and 1:2, 450 ml) gave no useful material. Further elution with benzene-petrol (3:1, 150 ml) and benzene (300 ml) gave the product. The material from this fraction was combined with that obtained by crystallisation and rechromatographed on a column of silica (40 x 2.2 cm, column III). Elution with petrol-benzene (2:1, 500 ml; 1:1, 100 ml; and 1:2, 450 ml) and benzene (2000 ml) gave eluates which were discarded. Benzene (2000 ml) and benzene-ether (99:1, 500 ml; 48:1, 500 ml; 9:1, 500 ml; and 1:1, 500 ml) afforded eluates which gave 1-(p-methoxyphenyl)-5-(p′-methoxyphenylthio)-3,4-propano-6,6aλ^4-dithia-1,2-diazapentalene (21) (2.499 g, 58.3%) as red platelets from acetonitrile, m.p. 145-147°; mixed m.p. 144.5-147°C. M^+ at m/e 428.

^{1}H nmr ($CDCl_3$) : δ 2.10 (2H, quint, 4′-H_2), 3.02 (4H, t, 3′ and 5′-H_2), 3.75 (3H, s, MeO of 1- or 5-Ar), 3.79 (3H, s, MeO of 5- or 1-Ar), 6.81 and 6.90 (2H, 2 m-protons of 5-Ar), 6.87 and 6.96 (2H, 2 m-protons of 1-Ar), 7.39 and 7.48 (2H, 2 o-protons of 5-Ar), 7.48 and 7.57 (2H, 2 o-protons of 1-Ar)

5. The Reaction of 5-Methyl-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate in the presence of Pyridine

The thione (22) (10 mmol, 1.483 g) and tetrafluoroborate (60 mmol, 11.615 g) were used. Organic products were extracted into benzene (2 x 700 ml). The organic extracts were washed with water (x 6). Chromatography (51 x 2.7 cm, column I) of the residue using petrol-benzene (1:1, 500 ml) gave no useful product. The next fraction (1:1, 300 ml) contained mainly diphenyl disulphide (23). M^+ at m/e 218. Further elution (1:1, 650 ml; and 1:3, 400 ml) gave a red-coloured fraction which was rechromatographed (44 x 2.2 cm, column II). Petrol-benzene (4:1, 350 ml; 3:1, 400 ml; and 2:1, 500 ml) afforded no useful material. Continued development with the same solvent system (1:1, 500 ml; 1:2, 500 ml) gave orange-red eluates. Rechromatography of this fraction on a column of silica (30 x 2.2 cm, column III), using petrol-benzene (1:1) gave phenyl 1,6-diphenyl-6a λ^4-thia-1,2,5,6-tetraazapentalene-3-dithiocarboxylate (35) (0.483 g, 11.2%) as red needles from cyclohexane-acetone (1:1), m.p. 204.5-209°.

Found : C 60.8; H 3.5; N 12.8

$C_{22}H_{16}N_4S_3$ requires : C 61.1; H 3.7; N 13.0

Accurate mass determination : 432.0524

$C_{22}H_{16}N_4S_3$ requires : 432.0537

^1H nmr ($CDCl_3$) : δ 7.22-7.58 (11H, m, 4-H, and 2 o + 2 m + p-protons of 1- and 6-Ar), 7.75-8.01 (4H, m, 2 o-protons of 1- and 6-Ar) uv spectrum : λ max (nm), 482 sh (log ϵ 4.33), 442 (4.43), 347 (4.10), 242 (4.34), 212 (4.46), 203 (4.50)

Continued elution of column I with benzene (300 ml) gave eluates which were discarded. Benzene-ether (33.3:1, 300 ml; 4:1, 500 ml; and 1:4, 400 ml) and ether (50 ml) afforded a dark red fraction from which the solvents were removed. Trituration of the residue with acetonitrile gave an almost pure solid (A). The supernatant liquid was chromatographed on a column of alumina (37 x 2.2 cm, column IV). After elution using benzene (250 ml), benzene-ether (99:1, 300 ml) and ether (400 ml) gave a red fraction which was rechromatographed under identical conditions. This procedure afforded an impure red solid which was rechromatographed on a column of silica (43 x 2.2 cm, column V). Elution with benzene-petrol (4:1, 1250 ml) and benzene (900 ml) afforded no useful material. Benzene-ether (48:1, 300 ml; and 2.3:1, 300 ml) gave a fraction from which the solvents were removed and the residue triturated with acetonitrile. The solid material collected was combined with (A) and recrystallised to give 3-carbomethoxy-1,6-diphenyl-6aλ^4-thia-1,2,5,6-tetraazapentalene (27) (0.442 g, 13.1%) as red needles from acetonitrile, m.p. 179-181°; mixed m.p. 179-182°.

Mass spectrum : M^+ at m/e 338.

^{1}H nmr ($CDCl_3$) : δ 4.02 (3H, s, MeO-), 7.16-7.51 (6H, m, 2 m + p-protons of 1- and 6-Ar), 7.69-7.82 (4H, m, 2o-protons of 1-and 6-Ar), 9.34 (1H, s, 4-H)

ir spectrum : ν max C=O 1705 cm^{-1}

6. The Reaction of 5-Methyl-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate in the Presence of Pyridine

The thione (22) (10 mmol, 1.484 g) and tetrafluoroborate (60 mmol, 13.317 g) were used. Organic products were extracted into benzene (2 x 500 ml). Chromatography (70 x 2.7 cm, column I) of the residue with petrol-benzene (2:1, 1050 ml and 1:1, 850 ml) gave no useful products. The same solvent system (650 ml), then benzene-petrol (3:1, 350 ml,) afforded yellow eluates which gave almost pure p,p′-dimethoxyazobenzene (20) (73 mg) as yellow needles from hexane. M^+ at m/e 242.

Further elution of column I using benzene (180 ml) gave eluates which were discarded, but the following fraction (180 ml) was rechromatographed on a column of silica (37 x 2.2 cm column II). Petrol benzene (2:1, 460 ml and 1:1, 500 ml) and benzene (240 ml) gave eluates which were discarded. Benzene (260 ml), benzene-ether (99:1, 250 ml and 48:1, 40 ml) then gave 1-(p-methoxyphenyl)-5-(p′-methoxyphenylthio)-6,6a λ^4-dithia-1,2-diazapentalene (29) (0.164 g, 4.2%) as red microneedles from acetonitrile, m.p. 101.5-103.5°; mixed m.p. 102-103°. M^+ at m/e 388.

> ^{1}H nmr ($CDCl_3$) : δ 3.81 (3H, s, MeO of 1- or 5-Ar), 3.86 (3H, s, MeO of 5- or 1-Ar), 6.88 and 6.97 (2H, 2 m-protons of 5-Ar), 6.94 and 7.03 (2H, 2 m-protons of 1-Ar), 7.02 (1H, s, 4-H), 7.48 and 7.57 (2H, 2 o-protons of 5-Ar), 7.55 and 7.64 (2H, 2 o-protons of 1-Ar), 8.03 (1H, s, 3-H)

The next benzene eluates (750 ml) from column I were discarded.

Benzene-ether (99:1, 500 ml and 97:3, 500 ml) gave red-orange eluates which were rechromatographed on a column of alumina (18 x 5.5 cm, column III). Elution with benzene-petrol (4:1, 100 ml), benzene-ether (48:1, 250 ml; 19:1, 250 ml and 9:1, 200 ml) gave no useful products. Further elution gave a red fraction which was evaporated and crystallised from benzene-cyclohexane (2:1). Recrystallisation of the product gave p-methoxyphenyl 1,6-di(p-methoxyphenyl)-6aλ^4-thia-1,2,5,6-tetraazapentalene-3-dithiocarboxylate (30) (0.1324 g, 2.6%) as red microneedles from acetonitrile, m.p. 196-199°; mixed m.p. 196-199°. M^+ at m/e 522.

> ^{1}H nmr ($CDCl_3$) : δ 3.81 (6H, s, MeO of 1- and 6-Ar), 3.84 (3H, s, MeO.CS.), 6.66-7.08 (7H, m, 4H and 6 m-protons of 1-, 3- and 6-Ar), 7.36 and 7.45 (2H, 2 o-protons of 3-Ar), 7.64 and 7.73 (2H, 2 o-protons of 1- or 6-Ar), 7.82 and 7.91 (2H, 2 o-protons of 6- or1-Ar)

Continued elution of column I with benzene-ether (9:1, 370 ml and 4:1, 520 ml) gave red eluates. Rechromatography on a column of silica (50 x 2.2 cm, column IV) using benzene (1500 ml), benzene-ether (199:1, 500 ml and 99:1, 500 ml) afforded no useful material. Further elution with benzene-ether (99:1, 250 ml; 19:1, 250 ml; 9:1, 250 ml; and 4:1, 130 ml) gave, after solvent evaporation, a residue which was crystallised from benzene-cyclohexane (2:1). This gave product A which was set aside. Further elution of column I using benzene-ether (1:1, 960 ml) gave red eluates which, after solvent evaporation and crystallisation of the residue from benzene, gave product B. The mother liquors were chromatographed (48 x 2.2 cm, column V). Elution with benzene-ether (99:1, 350 ml and 48:1, 1050 ml) gave no useful product. Further elution with benzene-ether (9:1, 300 ml) and ether (250 ml) afforded eluates which were rechromatographed on a column of silica (58 x 2.2 cm, column VI). Initial elution with benzene (200 ml) and benzene-ether (49:1, 800 ml and 24:1, 150 ml) gave eluates which were discarded. Further elution with benzene-ether (24:1, 250 ml; 8:1, 440 ml; 7:1, 350 ml) and ether (160 ml) gave a red fraction. The residue from this fraction was crystallised from acetonitrile and the recovered solid combined with products A and B. This mixture was chromatographed on a column of silica (32 x 2.7 cm, column VII). After discarding the initial benzene-ether eluates (99:1, 500 ml and 48:1, 360 ml), the product was eluted using the same solvent system (48:1, 140 ml; 7:1, 260 ml; and 2.5:1, 250 ml) and ether (150 ml). Solvent evaporation, followed by crystallisation, gave some pure product. More of the same material resulted from chromatography of the mother liquors on a column of silica (36 x 2.2 cm, column VIII). Elution with benzene-ether (99:1, 200 ml; 48:1, 500 ml; and 25:1, 250 ml) gave no useful products. Further elution with benzene-ether (7:1, 360 ml) gave red eluates which yielded 3-carbomethoxy-1,6-di(p-methoxyphenyl)-6aλ^4-thia-1,2,5,6-tetraazapentalene (31) (0.452 g, 11.3%) as red microneedles from acetonitrile, m.p. 189.5-192°; mixed m.p. 189.5-192°. M^+ at m/e 398.

^{1}H nmr : δ 3.85 (6H, s, MeO of 1- and 6-Ar), 4.06 (3H, s, MeO.CO.-), 6.92 and 7.01 (2H, 2 m-protons of 1- or 6-Ar), 6.94 and 7.03 (2H, 2 m-protons of 6- or 1-Ar), 7.64 and 7.73 (2H, 2 o-protons of 1- or 6-Ar), 7.71 and 7.80 (2H, 2o-protons of 6- or 1-Ar), 9.31 (1H, s, 4-H)

ir spectrum : ν max (C=O) 1690 cm^{-1}

C. THE REACTION OF 5-TERT-BUTYL- AND 5-PHENYL-1,2-DITHIOLE-3-THIONES WITH ARENEDIAZONIUM TETRAFLUOROBORATES

General Method:

The thione (5 mmol) was dissolved with stirring in acetonitrile (50 ml) at 50°C and to this solution was added the arenediazonium tetrafluoroborate (5 mmol). The reaction mixture was stirred for 30 minutes at 50°C, then refluxed for 15 minutes. When cool, the mixture was poured into ether (100 ml), then further ether (400 ml) was added. The precipitated salt was collected by filtration, then redissolved in hot acetonitrile, filtered and precipitated as before. The product was dried in vacuo for 12 hours.

1. The Reaction of 5-tert-Butyl-1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate

The thione (36) (5 mmol, 0.952 g) and tetrafluoroborate (5 mmol, 0.959 g) were reacted. The product, 5-*tert*-butyl-3-phenylthio-1,2-dithiolylium tetrafluoroborate (37) (1.207 g, 68%) was obtained as yellow needles, m.p. 104-107.5°. The product was a 1:1 adduct with acetonitrile.

Found : C 45.4; H 4.4; N 3.4

$C_{15}H_{18}BF_4NS_3$ requires : C 45.6; H 4.6; N 3.5

^{1}H nmr (CF_3CO_2H, 0.4 M) : δ 2.40 (9H, s, 5-Bu^t), 2.74 (3H, s, *Me*CN), 7.33 (1H, s, 4-H), 7.42-7.64 (2H, m, 2 *m*-protons of 3-Ar), 7.74-7.94 (3H, m, 2 *o*- and *p*-protons of 3-Ar) uv spectrum : λ max (nm), 339 br (log ∈ 3.96), 232 (4.27), 208 (4.24)

ir spectrum : no C≡N absorption evident

2. The Attempted Reaction of 5-tert-Butyl-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate

The thione (36) (5 mmol, 0.952 g) and tetrafluoroborate (5 mmol, 1.109 g) were reacted. The expected salt was not formed, but the greater part of the starting tetrafluoroborate was recovered (0.968 g, 89%).

3. The Reaction of 5-Phenyl-1,2-dithiole-3-thione with p-Nitrobenzenediazonium Tetrafluoroborate

The thione (38) (5 mmol, 1.052 g) and tetrafluoroborate 5 mmol, 1.184 g) were used. The product, 3-(p-nitrophenylthio)-5-phenyl-1,2-dithiolylium tetrafluoroborate (39) (1.619 g, 77%) was obtained as golden platelets, m.p. 155-159°.

Found : C 48.2; H 2.4; N 3.2

$C_{15}H_{10}BF_4NO_2S_3$ requires : C 43.0; H 2.4; N 3.4

^{1}H nmr (CF_3CO_2H, 0.4 M) : δ 7.56-8.04 (5H, m, protons of 5-Ar), 8.11 and 8.19 (2 o-protons of 3-Ar), 8.46 (1H, s, 4-H), 8.54 and 8.62 (2 m-protons of 3-Ar)

uv spectrum : λ max (nm), 357 (log ∈ 4.20), 249 sh (4.19), 203 (4.40)

4. The Attempted Reaction of 5-Phenyl 1,2-dithiole-3-thione with Benzenediazonium Tetrafluoroborate

The thione (5 mmol, 1.052 g) and tetrafluoroborate (5 mmol, 0.959 g) were used. The attempted precipitation of the product was unsuccessful, giving instead a yellow-orange coloured solution which turned green on standing for 48 hours. The reaction was not investigated further.

5. The Attempted Reaction of 5-Phenyl-1,2-dithiole-3-thione with p-Methoxybenzenediazonium Tetrafluoroborate

The thione (38) (5 mmol, 1.052 g) and tetrafluoroborate (5 mmol, 1.109 g) were used. The expected salt was not formed, but the starting tetrafluoroborate was recovered almost quantitatively (1.076 g, 97%).

D. METAL COMPLEXES OF 1,6,6aλ^4-TRIHETERAPENTALENES

The Preparation of Tetraethylammonium Iodopentacarbonylmetallates(0)

The tetraethylammonium iodopentacarbonyl derivates of chromium, molybdenum and tungsten were prepared by the method of Abel, Butler and Reid[124]. For the preparation of the molybdenum and tungsten compounds, the reactions were performed on three times the recommended scale. Attempts to do likewise with the chromium compound were not successful.

The Preparation of Complexes of the Type $LM(CO)_5$, Where M=Cr, Mo or W and L=Triheterapentalene

General Method:

Metal complexes were prepared by a modification of the method of Connor, Jones and McEwan[123].

The triheterapentalene (2 mmol) and the iodopentacarbonylmetallate(0) (2.6 mmol) were stirred together in dichloromethane (80 ml) at 22°C under an atmosphere of nitrogen. Silver tetrafluoroborate (2.6 mmol) was then added. Stirring was continued for the appropriate time (see individual reactions for details). The mixture was then filtered through Celite and the solvent evaporated at temperatures not exceeding 25°C. Treatment of the residue with alternately hexane and ethanol (2 x 25 ml) followed by evaporation of the solvent removed any metal hexacarbonyl present. The resulting product was chromatographed on a column of silica. Eluates containing the metal complexes were evaporated using a cool water bath ($T < 30°C$). The residue was dissolved in dichloromethane, acetone or diethyl ether (25 ml), filtered, and then diluted with an equivalent volume of filtered hexane. The complex was crystallised by allowing the solvents to evaporate while the flask was cooled at 0°C. The product was collected by filtration, washed with a little cold hexane, then dried in vacuo and in darkness. Second crops of material were collected after the mother liquors had been chromatographed on a short column of silica.

1. The Preparation of Pentacarbonylchromium(0), Molybdenum(0), and Tungsten(0) Complexes of 1-Oxa-6,6aλ^4-dithia-2-azapentalenes

a. 5-*tert*-Butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (40) (2 mmol, 0.403 g), tetraethylammonium iodopentacarbonylchromate(0) (2.4 mmol, 1.078 g) and silver tetrafluoroborate (2.4 mmol, 0.466 g) were reacted for 15 minutes. Chromatography was on a column of silica (42 x 2.7 cm). Benzene gave eluates (120 ml) which were discarded. Further elution with benzene (600 ml) gave pentacarbonyl(5-*tert*-butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene) chromium(0) (45) (0.725 g, 92.1%) as dark purple rods from hexane-ether, m.p. 136-141°C (decomp.).

Found : C 39.7; H 3.1; N 3.6

$C_{13}H_{11}NO_6S_2Cr$ requires : C 39.7; H 2.8; N 3.6

Mass spectrum : M^+ of complex at m/e 393 absent, but M^+ of triheterapentalene at m/e 201 evident

^1H nmr ($CDCl_3$) : δ 1.48 (9H, s, $(\underline{Me})_3C$- protons), 7.88 (1H, s, 4-H), 9.17 (1H, s, 3-H) ir spectrum : ν max CO (cm^{-1}) 2067 (m), 1999 (w), 1950 (s), 1923 (s)

uv spectrum : λ max (nm), 594 (log ϵ 4.11), 389 (3.81), 235 (4.60), 208 sh (4.49)

b. 5-tert-Butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (40) (2 mmol, 0.402 g), tetraethylammonium iodopentacarbonylmolybdate(0) (2.4 mmol, 1.184 g) and silver tetrafluoroborate (2.4 mmol, 0.467 g) were reacted for 15 minutes. Chromatography was on a column of silica (38 x 2.7 cm). Initial benzene eluates (250 ml) were discarded. The next fraction (600 ml) afforded pentacarbonyl (5-tert-butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene)molybdenum(0) (46) (0.341 g, 39.0%) as red rods from hexane-ether, m.p. 114-118°C (decomp.).

Found : C 35.7; H 2.5; N 3.2

$C_{13}H_{11}NO_6S_2Mo$ requires : C 35.7; H 2.6; N 3.4

Mass spectrum : M$^+$ of complex at m/e 437 absent, but M$^+$ of triheterapentalene at m/e 201 evident

^{1}H nmr (CDCl$_3$) : δ 1.52 (9H, s, (Me)$_3$C- protons), 7.97 (1H, s, 4-H), 9.16 (1H, s, 3-H)

ir spectrum : ν max CO (cm^{-1}), 2076 (m), 1991 (w), 1951 (s), 1922 (m)

uv spectrum : λ max (nm), 552 (logϵ 4.11), 382 (3.84), 247 (4.68), 226 sh (4.64)

c. 5-tert-Butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (2 mmol, 0.403 g) (40), tetraethylammonium iodopentacarbonyltungstate(0) (2.4 mmol, 1.394 g) and silver tetrafluoroborate (2.4 mmol, 0.466 g) were reacted for 15 minutes. Chromatography was on a column of silica (38 x 2.7 cm). Initial benzene eluates (100 ml) were discarded. The next fraction (700 ml) gave pentacarbonyl(5-tert-butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene)tungsten(0) (47) (0.654 g, 62.2%), as dark red microneedles from hexane-ether, m.p. 148-155° (decomp.).

Found : C 30.0; H 2.0; N 2.8

$C_{13}H_{11}NO_6S_2W$ requires : C 29.7; H 2.1; N 2.7

Mass spectrum : M^+ of complex at m/e 525 absent, but M^+ of trithiapentalene at m/e 201 evident

^{1}H nmr ($CDCl_3$, saturated) : δ 1.52 (9H, s, $(\underline{Me})_3C$- protons), 7.97 (1H, s, 4-H), 9.27 (1H, s, 3-H)

ir spectrum : ν max CO (cm^{-1}), 2074 (s), 1991 (w), 1949 sh (vs), 1940 (vs), 1921 (s)

uv spectrum : λ max (nm), 564 (log ϵ 4.21), 386 (3.78), 285 br (3.95), 242 (4.80), 228 (4.73)

d. 3,4-Propano-1-oxa-6,6aλ^4-dithia-2-azapentalene (2 mmol, 0.371 g) (41), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol 0.506 g) were reacted for 15 minutes. Chromatography was on a column of silica (40 x 2.7 cm). Initial benzene eluates (150 ml) were discarded. The next fraction (450 ml) afforded pentacarbonyl (3,4-propano-1-oxa-6,6aλ^4-dithia-2-azapentalene)chromium(0) (48) (0.601 g, 79.7%) as dark brown microrods from hexane-dichloromethane, m.p. 108-120°C (decomp.).

Found : C 38.2; H 1.6; N 3.7

$C_{12}H_7NO_6S_2Cr$ requires : C 38.2; H 1.9; N 3.7

Mass spectrum : M^+ of complex at m/e 377 absent, but M^+ of triheterapentalene at m/e 185 evident

^{1}H nmr ($CDCl_3$) : δ 2.21 (2H, quint, $4'$-H_2), 3.09 (2H, dt, $5'$-H_2), 3.32 (2H, t, $3'$-H_2), 8.97 (1H, t, 5-H), $J_{5,5'}$ 0.8 Hz

ir spectrum : ν max CO (cm^{-1}), 2068 (m), 1999 (w), 1951 (s), 1935 sh (s), 1922 (m)

uv spectrum : λ max (nm) 585 (log ϵ 3.98), 395 (3.73), 238 (4.28), 212 sh (4.12)

e. 3,4-Propano-1-oxa-6,6aλ^4-dithia-2-azapentalene (41) (2 mmol, 0.371 g), tetraethylammonium iodopentacarbonylmolybdate(0) (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol, 0.506 g) were reacted for 15 minutes. Chromatography was on a column of silica gel (45 x 2.7 cm). Initial benzene eluates (150 ml) were discarded. Further elution with benzene (550 ml) afforded pentacarbonyl(3,4-propano-1-oxa-6,6aλ^4-dithia-2-azapentalene)molybdenum(0) (49) (0.418 g, 49.8%) as brown microneedles from hexane-dichloromethane, m.p. 100-108°C (decomp.).

Found : C 34.3; H 1.6; N 3.5

$C_{12}H_7NO_6S_2Mo$ requires : C 34.2; H 1.7; N 3.3

Mass spectrum : M^+ of complex at m/e 421 absent,

^{1}H nmr ($CDCl_3$, sat.) : δ 2.23 (2H, quint, $4'$-H_2), 3.13 (2H, dt, $5'$-H_2), 3.28 (2H, t, $3'$-H_2), 9.04 (1H, t, 5-H) $J_{5,5'}$ 0.9 Hz

ir spectrum : ν max CO (cm^{-1}) 2074 (m), 2000 (w), 1953 (s), 1923 (m)

uv spectrum : λ max (nm) 546 (log ϵ 4.03), 380 (3.74), 245 (4.70), 227 sh (4.60)

Continued elution with benzene-ether (93:7, 240 ml and 80:20, 70 ml) afforded no useful material. Further elution with benzene-ether (80:20, 180 ml and 50:50, 140 ml) followed by ether (150 ml) afforded 3,4-propano-1-oxa-6,6aλ^4-dithia-2-azapentalene (41) (61.8 mg, 3.3% crude material) which was identified by comparative tlc and mass spectrometry (M^+ at m/e 185).

f. 3,4-Propano-1-oxa-6,6aλ^4-dithia-2-azapentalene (41) (2 mmol, 0.371 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.51 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 15 minutes. The residue was chromatographed on a column of silica (40 x 2.7 cm). The first benzene eluates (120 ml) were discarded. Further elution with benzene (800 ml) and benzene-ether (49:1, 150 ml and 97:3, 200 ml) gave pentacarbonyl(3,4-propano-1-oxa-6,6aλ^4-dithia-2-azapentalene) tungsten(0) (50) (0.586g, 57.6%) as brown microrods from hexane-dichloromethane, m.p. 135-142° (decomp.).

Found : C 28.3; H 1.1; N 2.7

$C_{12}H_7NO_6S_2W$ requires : C 28.3; H 1.4; N 2.8

Mass spectrum : M^+ of complex at m/e 509 absent, but M^+ of triheterapentalene at m/e 185 evident

^{1}H nmr ($CDCl_3$, sat.) : δ 2.27 (2H, quint, 4$'$-H_2), 3.16 (2H, dt, 5$'$-H_2), 3.31 (2H, t, 3$'$-H_2), 9.06 (1H, t, 5-H) $J_{5,5'}$ 0.8 Hz

ir spectrum : ν max CO (cm^{-1}) 2075 (m), 1992 (w), 1942 (s), 1921 (m)

uv spectrum : λ max (nm) 556 (log ϵ 4.09), 387 (3.63), 242 (4.80), 221 sh (4.66)

g. 3,4-Dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (42) (2 mmol, 0.346 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 20 minutes. Chromatography was on a column of silica (35 x 2.7 cm). Initial benzene eluates (120 ml) were discarded. The next fraction (320 ml) afforded pentacarbonyl(3,4-dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene)chromium(0) (51) (0.312 g, 42.7%), as brown microneedles from dichloromethane-hexane, m.p. 100-110°C (decomp.).

Found : C 36.4; H 1.8; N 3.8

$C_{11}H_7NO_6S_2Cr$ requires : C 36.2; H 1.9; N 3.8

Mass spectrum : M^+ of complex at m/e 365 absent, but M^+ of triheterapentalene at m/e 173 evident

^{1}H nmr ($CDCl_3$, sat.) : δ 2.90 (3H, s, 4-Me), 3.10 (3H, s, 3-Me), 9.08 (1H, s, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2065 (w), 1998 (vw), 1952 (s), 1942 (m), 1921 (w) uv spectrum : λ max (nm) 559 (log ϵ 3.84), 397 (3.71), 237 (4.52), 213 sh (4.43)

Continued elution with benzene (250 ml) afforded no useful products. Further elution with benzene-ether (92:8, 400 ml and 75:25, 100 ml) gave yellow eluates which yielded 3,4-dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (42) (0.105 g, 30.0%) as red platelets from cyclohexane-hexane (1:1).

Mass spectrum : M^+ at m/e 173

h. 3,4-Dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (42) (2 mmol, 0.346 g), tetraethylammonium iodopentacarbonylmolybdate(0) (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol, 0.503 g) were reacted for 8 minutes. Chromatography was performed on a column of silica (33 x 2.7 cm). Initial benzene eluates (120 ml) were discarded. The next fraction (400 ml) gave pentacarbonyl(3,4-dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene)molybdenum(0) (52) (0.183 g, 22.7%) from acetone-dichloromethane. The product was not quite tlc pure and was therefore not fully characterised.

^{1}H nmr ($CDCl_3$) : δ 2.89 (3H, s, 3-Me), 2.90 (3H, d, 4-Me), 9.05 (1H, q, 5-H), $J_{5,4}$ 0.7 Hz (all signals from starting material). 2.91 (3H, d, 4-Me), 3.10 (3H, s, 3-Me), 9.11 (1H, q, 5-H), $J_{5,4}$ 0.7 Hz (all signals from complex).

i. 3,4-Dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (42) (2 mmol, 0.346 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.510 g) and silver tetrafluoroborate (2.6 mmol, 0.504 g) were reacted for 20 minutes. Chromatography was performed on a column of silica (40 x 2.7 cm). Initial benzene eluates (120 ml) were discarded. Elution with benzene (330 ml) and benzene-ether (97:3, 200 ml) afforded pentacarbonyl(3,4-dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene)tungsten(0) (53) (0.770 g, 77.5%) as dark blue microrods from hexane-dichloromethane, m.p. 123-132°C (decomp.).

Found : C 26.5; H 1.5; N 2.8

$C_{11}H_7NO_6S_2W$ requires : C 26.6; H 1.4; N 2.8

Mass spectrum : M^+ of complex at m/e 497 absent, but M^+ of triheterapentalene at m/e 173 evident

^1H nmr ($CDCl_3$, sat.) : δ 2.90 (3H, d, 4-Me), 3.09 (3H, s, 3-Me), 9.10 (1H, q, 5-H), $J_{5,4}$ 0.7 Hz

ir spectrum : ν max CO (cm^{-1}) 2074 (m), 1990 (w), 1943 (vs), 1918 (s)

uv spectrum : λ max (nm) 542 (log ϵ 4.05), 387 (3.75), 242 (4.83), 220 sh (4.70)

Continued elution with benzene-ether (83:17, 300 ml) gave a yellow fraction which was discarded. The next fraction (250 ml) contained 3,4-dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (42) (0.017 g, 5% crude material) which was identified by comparative tlc and mass spectrometry (M^+ at m/e 173).

j. 1-Oxa-6,6aλ^4-dithia-2-azapentalene (43) (2 mmol, 0.290 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.506 g) were reacted for 14 minutes. Chromatography was on a column of silica (40 x 2.7 cm). Initial benzene eluates (120 ml) were discarded. Further elution (600 ml) gave eluates which afforded pentacarbonyl(1-oxa-6,6aλ^4-dithia-2-azapentalene)chromium(0) (54) (0.583 g, 86.4%) as brown-black microrods from hexane-dichloromethane, m.p. 116-126°C (decomp.).

Found : C 32.1; H 0.6; N 4.2

$C_9H_3NO_6S_2Cr$ requires : C 32.1; H 0.9; N 4.2

Mass spectrum : M^+ of complex at m/e 337 absent, but M^+ of triheterapentalene at m/e 145 evident

^1H nmr ($CDCl_3$) : δ 8.09 (1H, d, 4-H) $J_{4,5}$ 6.0 Hz, 9.22 (1H, d, 5-H), 9.32 (1H, s, 3-H)

ir spectrum : ν max CO (cm^{-1}), 2066 (m), 2000 (w), 1951 (s), 1927 (m)

uv spectrum : λ max (nm), 617 (log ϵ 4.10), 390 (3.79), 233 (4.63)

k. 1-Oxa-6,6aλ^4-dithia-2-azapentalene (43) (2 mmol, 0.290 g), tetraethylammonium iodopentacarbonylmolybdate (0) (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol 0.506 g) were reacted for 6.5 minutes. Chromatography was on a column of silica (40 x 2.7 cm). Initial benzene eluates (140 ml) were discarded. Further elution gave pentacarbonyl(1-oxa-6,6aλ^4-dithia-2-azapentalene)molybdenum(0) (55) (0.332 g, 43.6%). The material was not quite tlc pure and was therefore not fully characterised.

^{1}H nmr ($CDCl_3$, sat.) : δ 8.18 (1H, d, 4-H), $J_{4,5}$ 6.1 Hz, 9.32 (1H, s, 3-H), 9.33 (1H, d, 5-H)

l. 1-Oxa-6,6aλ^4-dithia-2-azapentalene (43) (2 mmol, 0.290 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.511 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 8 minutes. Chromatography was on a column of silica (43 x 2.7 cm). Initial benzene eluates (180 ml) were discarded. Further elution using benzene (920 ml) and benzene-ether (97:3, 250 ml and 70:30, 450 ml) afforded pentacarbonyl(1-oxa-6,6aλ^4-dithia-2-azapentalene)tungsten(0) (56) (0.689 g, 73.6 g) as dark yellow-brown microrods from hexane-dichloromethane, m.p. 139-146°C (decomp.).

Found : C 23.1; H 0.6; N 3.0

$C_9H_3NO_6S_2W$ requires : C 23.0; H 0.6; N 3.0

Mass spectrum : M^+ of complex at m/e 469 absent, but M^+ of triheterapentalene at m/e 145 evident

^{1}H nmr ($CDCl_3$, sat.) : δ 8.17 (1H, d, 4-H), 9.29 (1H, d, 5-H), 9.40 (1H, s, 3-H) $J_{4,5}$ 6.3 Hz

ir spectrum : ν max CO (cm^{-1}) 2072 (s), 1990 (w), 1943 (s), 1924 sh (s)

uv spectrum : λ max (nm) 583 (log ϵ 4.19), 387 (3.74), 242 (4.81), 228 (4.81)

m. 4-(N,N-dimethylamino)nitrosobenzene (2 mmol, 0.300 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.503 g) were reacted for 14 minutes. Chromatography was on a column of alumina (33 x 2.7 cm). Initial benzene eluates (120 ml) were discarded. Subsequent elution with benzene (50 ml) and benzene-ether (92:8, 70 ml) removed the complex from the column. However, the complex decomposed during evaporation of the solvent, leaving a red, basic residue. The product was not characterised further.

n. 4-(N,N-dimethylamino)nitrosobenzene (2 mmol, 0.300 g), tetraethylammonium iodopentacarbonylmolybdate(0) (1.282 g, 2.6 mmol) and silver tetrafluoroborate (2.6 mmol, 0.504 g) were reacted for 15 minutes. Tlc analysis of the reaction mixture indicated that a complex was formed. However, during chromatography using a column of silica (40 x 2.7 cm) and benzene, and subsequent removal of the solvent, complete decomposition of the complex occurred. The reaction was not investigated further.

o. 4-(N,N-dimethylamino)nitrosobenzene (2 mmol, 0.300 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.510 g) and silver tetrafluoroborate (2.6 mmol, 0.506 g) were heated for 15 minutes. Chromatography was on a column of alumina (35 x 2.7 cm). Initial benzene eluates (120 ml) and benzene-ether (98:2, 150 ml) eluates were discarded. Subsequent elution with benzene-ether (92:8, 200 ml and 50:50, 200 ml) afforded pentacarbonyl(4-(N,N-dimethylamino)nitrosobenzene)tungsten(0) (44) (0.422 g, 44.6%) as fine brown needles from hexane-dichloromethane, m.p. > 125° (decomp.).

Found : C 33.1; H 2.1; N 6.0

$C_{13}H_{10}N_2O_6W$ requires : C 32.9; H 2.1; N 5.9

Mass spectrum : M^+ of complex at m/e 474 absent, but M^+ of starting nitroso compound at m/e 150 evident

^{1}H nmr ($CDCl_3$) : δ 3.21 (6H, s, (<u>Me</u>)$_2$N-protons), 6.56 and 6.68 (2H, 2 <u>o</u>-protons), 7.94 and 8.05 (2H, 2 <u>m</u>-protons)

ir spectrum : ν max CO (cm^{-1}) 2065 (m), 1997 (vw), 1957 (m), 1948 (m), 1929 (w)

uv spectrum : not obtained

p. The thermal decomposition of pentacarbonyl(3,4-dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene)tungsten(0) (53) (0.5 mmol, 0.249 g) was effected by heating the complex in boiling xylene for 15 minutes. After cooling, the mixture was filtered through Celite. The filtrate was evaporated to a volume of 15 ml, then absorbed onto a column of alumina (25 x 2.7 cm). Elution with benzene (300 ml) gave no useful products. Continued elution with the same solvent (400 ml), followed by benzene-ether (98:2, 200 ml), gave orange eluates. These were evaporated and the residue crystallised from cyclohexane to give 3,4-dimethyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (0.059 g, 68.0%) (42). M^+ at m/e 173.

q. The thermal reaction of 5-<u>tert</u>-butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (40) (5 mmol, 1.007 g) with molybdenum hexacarbonyl (10 mmol, 0.264 g) in hot (50°C) ethanol was attempted. The mixture was stirred and heated to the point of reflux over 15 minutes, then cooled and the solvent removed. The residue was chromatographed on a column of silica (42 x 2.7 cm, column I). Initial elution with petrol-benzene (2:1, 250 ml) gave no useful products. The next fraction (750 ml) was evaporated and the residue stripped of unreacted molybdenum hexacarbonyl by alternately dissolving the material in hexane and ethanol, then removing the solvent under reduced pressure. The product was combined with the residue from the next fraction from column I (benzene, 1000 ml) and rechromatographed on a column of silica gel (20 x 2.2 cm) using benzene . After removal of the solvent, the residue was dissolved in ether (30 ml) and the solution filtered. An equivalent volume of hexane was added to the solution, which was then cooled to 0°C and slowly stripped of solvent under reduced pressure. This method yielded pentacarbonyl(5-tert-butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene)molybdenum(0) (46) (0.079 g 3.6%) as red rods, m.p. 114-118°C (decomp.).

Found : C 35.4; H 2.4; N 3.2

$C_{13}H_{11}NO_6S_2Mo$ requires : C 35.7; H 2.5; N 3.2

Mass spectrum : M^+ of complex at m/e 437 absent, but M^+ of triheterapentalene at m/e 201 evident

^1H nmr ($CDCl_3$) : δ 1.52 (9H, s, $\underline{Bu}^t$ -protons), 7.97 (1H, s, 4-H), 9.16 (1H, s, 3-H)

Further elution of column I with benzene-ether (96:4, 500 ml) afforded no useful products. The next fraction (70:30) gave a yellow residue which was rechromatographed on a column of alumina (35 x 2.2 cm). Initial benzene eluates (500 ml) were discarded. Elution with benzene-ether (98:2, 250 ml and 97:3, 400 ml) afforded 5-tert-butyl-1-oxa-6,6aλ^4-dithia-2-azapentalene (2.899 g, 58.0%) (40) as yellow-red microneedles from hexane, m.p. 72-74°. M^+ at m/e 201.

2. The Preparation of Pentacarbonylchromium(0), Molybdenum(0) and Tungsten(0) Complexes of 6,6aλ^4-Dithia-1,2-diazapentalenes

a. 5-*tert*-Butyl-1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene (64) (2.0 mmol, 0.553 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.512 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 35 minutes. A tlc examination of the reaction mixture suggested that a small amount of complex formation had occurred. However, chromatography of the reaction product on a column of silica (30 x 2.7 cm) using benzene failed to separate the complex from the starting triheterapentalene. Attempts to separate these materials on a column of alumina resulted in decomposition of the metal complex and the recovery of dithiadiazapentalene (64) (0.489 g, 88.6%). M^+ at m/e 276.

Similar results were obtained in the reactions of compound (64) with tetraethylammonium iodopentacarbonylmolybdate(0) and chromate(0). In these reactions, the quantities of recovered compound (64) were 0.529 g (95.6%) and 0.454 g (82%), respectively.

b. 1-Phenyl-3,4-propano-6,6aλ^4-dithia-1,2-diazapentalene (61) (2 mmol, 0.520 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.504 g) were reacted for 25 minutes. Chromatography was on a column of silica (26 x 2.7 cm). Initial benzene eluates (130 ml) were discarded. The next fraction contained pentacarbonyl(1-phenyl-3,4-propano-6,6aλ^4-dithia-1,2-diazapentalene)chromium(0) (65) (0.661g, 73%) as dark purple microneedles from hexane-dichloromethane, m.p. 115-138°C (decomp.).

The complex was judged impure by tlc and was therefore not fully characterised.

^{1}H nmr (CDCl$_3$) : δ 2.14 (2H, quint, 4'-H$_2$), 3.08 (2H, dt, 5'-H$_2$), 3.15 (2H, t, 3'-H$_2$), 7.23-7.56 (3H, m, 2 *m* + *p*-protons of 1-Ar), 7.71-7.78 (2 *o*-protons of 1-Ar), 8.87 (1H, t, 5-H) $J_{5,5'}$ 0.8 Hz

ir spectrum : ν max CO (cm^{-1}) 2054 (w), 1984 (vw), 1947 (m), 1926 (w)

uv spectrum : qualitative λ max (nm) 656, 453, 237, 210 sh

c. 1-Phenyl-3,4-propano-6,6aλ^4-dithia-1,2-diazapentalene (61) (1 mmol, 0.261 g), tetraethylammonium iodopentacarbonylmolybdate(0) (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 30 minutes. Chromatography was on a column of silica (25 x 2.7 cm). First benzene eluates were discarded. The next fraction (130 ml) gave pentacarbonyl(1-phenyl-2,3-propano-6,6aλ^4-dithia-1,2-diazapentalene)molybdenum(0) (66) (0.112 g) as dark green microrods from hexane-dichloromethane, m.p. 114-127°C (decomp.).

The complex was judged to be impure by tlc and was not fully characterised.

^{1}H nmr (CDCl$_3$) : δ 2.15 (2H, quint, 4'-H$_2$), 3.08 (2H, dt, 5'-H$_2$), 3.20 (2H, t, 3'-H$_2$), 7.24-7.58 (3H, 2 *m* + *p*-protons of 1-Ar), 7.77-7.90 (2H, 2 *o*-protons of 1-Ar), 9.01 (1H, t, 5-H) $J_{5,5'}$ 0.9 Hz ir spectrum : ν max CO (cm^{-1}) 2066 (w), 1990 (m), 1951 (m), 1920 (w)

uv spectrum : qualitative λ max (nm) 620, 508, 288 inf., 231, 203

d. 1-Phenyl-3,4-propano-6,6aλ^4-dithia-1,2-diazapentalene (61) (2 mmol, 0.521 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.510 g) and silver tetrafluoroborate (2.6 mmol, 0.507 g) were reacted for 40 minutes. Chromatography was on a column of silica (38 x 2.7 cm). Initial benzene eluates (100 ml) were discarded. The next fraction (700 ml) gave pentacarbonyl(1-phenyl-3,4-propano-6,6aλ^4-dithia-1,2-diazapentalene)tungsten(0) (67) (0.974 g, 83.2%) as crimson needles from hexane-ether, m.p. 131-135°C (decomp.)

Found : C 37.1; H 2.0; N 4.7

$C_{18}H_{12}N_2O_5S_2W$ requires : C 37.0; H 2.1; N 4.8

Mass spectrum : M^+ of complex at m/e 585 absent, but M^+ of triheterapentalene at m/e 260 evident

^{1}H nmr ($CDCl_3$, sat.) : δ 2.13 (2H, quint, 4'-H_2), 3.08 (2H, dt, 5'-H_2), 3.20 (2H, t, 3'-H_2), 7.33-7.65 (3H, m, 2 m + p-protons of 1-Ar), 7.70-7.88 (2H, m, 2 o-protons of 1-Ar), 9.02 (1H, t, 5-H) $J_{5,5'}$ 0.8 Hz

ir spectrum : ν max CO (cm^{-1}) 2062 (m), 1978 (vw), 1944 (s), 1919 (m)

uv spectrum : qualitative λ max (nm) 658, 456, 238, 213 inf.

e. 1-Phenyl-3,4-dimethyl-6,6aλ^4-dithia-1,2-diazapentalene (62) (2 mmol, 0.497 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.506 g) were reacted for 30 minutes. Chromatogaphy was on a column of silica (35 x 2.7 cm). Initial benzene eluates (100 ml) were discarded. The next fraction (700 ml) contained pentacarbonyl(1-phenyl-3,4-dimethyl-6,6aλ^4-dithia-1,2-diazapentalene)chromium(0) (68) (0.706 g, 80.0%) as dark brown microneedles from hexane-dichloromethane, m.p. 136-138°C (decomp.).

Found : C 46.2; H 2.5; N 6.3

$C_{17}H_{12}N_2O_5S_2Cr$ requires : C 46.4; H 2.8; N 6.4

Mass spectrum : M^+ of complex at m/e 440 absent, but M^+ of triheterapentalene at m/e 248 evident

^1H nmr ($CDCl_3$) : δ 2.92 (3H, s, 3-Me), 2.98 (3H, d, 4-Me) $J_{4,5}$ 0.7 Hz, 7.32-7.62 (3H, m, 2 m + p-protons of 1-Ar), 7.69-7.85 (2H, m, 2 o-protons of 1-Ar), 8.90 (1H, q, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2059 (m), 1988 (vw), 1948 (m), 1923 (w)

uv spectrum : qualitative λ max (nm) 642, 450, 290, 241, 207 sh.

f. 1-Phenyl-3,4-dimethyl-6,6aλ^4-dithia-1,2,-diazapentalene (62) (1 mmol, 0.248 g), tetraethylammonium iodopentacarbonylmolybdenum (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 30 minutes. Chromatography was on a column of silica (3 x 2.7 cm). First benzene eluates (100 ml) were discarded.

The next fraction gave pentacarbonyl(1-phenyl-3,4-dimethyl-6,6aλ^4-dithia-1,2-diazapentalene)molybdenum(0) (69) as microneedles from hexane-dichloromethane, m.p. > 133°C (decomp.). The complex was judged to be impure by tlc and was therefore not fully characterised.

^{1}H nmr ($CDCl_3$) : δ 2.87 (3H, s, 3-Me), 2.97 (3H, d, 4-Me) $J_{4,5}$ 0.7 Hz, 7.25-7.67 (3H, m, 2 m + p-protons of 1-Ar), 7.72-7.89 (2H, m, 2 o-protons of 1-Ar), 8.84 (1H, q, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2062 (w), 1992 (m), 1952 (m), 1922 (w)

uv spectrum : qualitative λ max (nm) 608, 496, 290 sh, 238, 206

g. 1-Phenyl-3,4-dimethyl-6,6aλ^4-dithia-1,2-diazapentalene (62) (2 mmol, 0.467 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.511 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 45 minutes. Chromatography was on a column of silica (40 x 2.7 cm). First benzene eluates (120 ml) were discarded. The next fraction (700 ml) gave pentacarbonyl(1-phenyl-3,4-dimethyl-6,6aλ^4-dithia-1,2-diazapentalene)tungsten(0) (70) (0.812 g, 70.9 %) as dark brown microneedles from hexane-dichloromethane, m.p. 139-145°C (decomp.).

Found : C 35.8; H 2.4; N 5.0

$C_{17}H_{12}N_2O_5S_2W$ requires : C 35.7; H 2.1; N 4.9

Mass spectrum : M^+ of complex at m/e 572 absent, but M^+ of triheterapentalene at m/e 260 evident

^{1}H nmr ($CDCl_3$) : δ 2.84 (3H, s, 3-Me), 2.96 (3H, d, 4-Me) $J_{4,5}$ 0.7 Hz, 7.39-7.67 (3H, m, 2 m + p-protons of 1-Ar), 7.73-7.90 (2H, m, 2 o-protons of 1-Ar), 8.94 (1H, q, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2071 (m), 1979 (vw), 1943 (s), 1922 (m)

uv spectrum : qualitative λ max (nm) 628, 432, 233, 209 inf.

h. 1-Phenyl-6,6aλ^4-dithia-1,2-diazapentalene (63) (2 mmol, 0.441 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.507 g) were reacted for 30 minutes. Chromatography was on a column of silica (34 x 2.7 cm). The first benzene eluates (100 ml) were discarded. The next fraction gave pentacarbonyl(1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene)chromium(0) (71) (0.616 g, 79%) as purple microneedles from hexane-dichloromethane, m.p. 104-114°C (decomp.).

Found : C 43.7; H 1.7; N 6.8

$C_{15}H_8N_2O_5S_2Cr$ requires : C 43.7; H 2.0; N 6.8

Mass spectrum : M^+ of complex at m/e 412 absent, but M^+ of triheterapentalene at m/e 220 evident

^{1}H nmr ($CDCl_3$) : δ 7.37-7.87 (5H, m, protons of 1-Ar), 7.72 (1H, d, 4-H) $J_{4,5}$ 7.6 Hz, 8.49 (1H, s, 3-H), 9.31 (1H, d, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2057 (w), 1989 (vw), 1949 (m), 1930 (w) uv spectrum : qualitative λ max (nm) 656, 446, 234, 210 inf.

i. 1-Phenyl-6,6aλ^4-dithia-1,2-diazapentalene (63) (1 mmol, 0.220 g), tetraethylammonium iodopentacarbonylmolybdate(0) (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 30 minutes. Chromatography was on a column of silica 23 x 2.7. Initial benzene-petrol eluates (4:1, 120 ml) were discarded. The next fraction gave pentacarbonyl(1-phenyl-6,6aλ^4-dithia-1,2-diazapentalene)molybdenum(0) (72) (0.103 g) as dark green microrods from hexane-dichloromethane, m.p. > 105° (decomp.).

The complex was not judged pure by tlc and was therefore not fully characterised.

^{1}H nmr ($CDCl_3$) : δ 7.36-7.69 (3H, m, 2 m + p-protons of 1-Ar), 7.74-7.92 (2H, m, 2 o-protons of 1-Ar), 7.87 (1H, d, 4-H) $J_{4,5}$ 7.4 Hz, 8.55 (1H, s, 3-H), 9.36 (1H, d, 5-H)

ir spectrum : ν max (CO) (cm^{-1}) 2062 (w), 1990 (vw), 1953 (m), 1927 (w)

uv spectrum : qualitative λ (max) 622, 478, 284 inf., 232, 203

j. 1-Phenyl-6,6aλ^4-dithia-1,2-diazapentalene (2 mmol, 0.441 g) (63), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.511 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 40 minutes. Chromatography was on a column of silica (33 x 2.7 cm). Initial benzene eluates (120 ml) were discarded. The next fraction (700 ml) yielded pentacarbonyl(1-phenyl-6,6aλ^4-

dithia-1,2-diazapentalene)tungsten(0) (73) (0.938 g, 86.2 %) as green microneedles from hexane-dichloromethane, m.p. 132-138°C (decomp.).

Found : C 32.9; H 1.3; N 5.1

$C_{15}H_8N_2S_2O_5W$ requires : C 33.1; H 1.5; N 5.2

Mass spectrum : M^+ of complex at m/e 544 absent, but M^+ of triheterapentalene at m/e 220 evident

^1H nmr ($CDCl_3$, sat.) : δ 7.44-7.70 (3H, m, 2 m + p-protons of 1-Ar), 7.60 (1H, d, 4-H) $J_{4,5}$ 7.4 Hz, 7.80-7.94 (2H, m, 2 o-protons of 1-Ar), 8.55 (1H, s, 3-H), 9.48 (1H, d, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2066 (m), 1981 (vw), 1946 (s), 1925 (m)

uv spectrum : not obtained

3. The Preparation of Pentacarbonylchromium(0), Molybdenum(0) and Tungsten(0) Complexes of 6,6aλ^4-Dithia-1-azapentalenes

a. 3,4-Propano-1-methyl-6,6aλ^4-dithia-1-azapentalene (76) (2 mmol, 0.395 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.508 g) were reacted for 30 minutes. Chromatography was on a column of silica (55 x 2.7 cm). Initial elution with benzene (250 ml) gave no useful product. The next fraction was eluted with benzene (550 ml) and benzene-ether (97:3, 370 ml). The residue from this fraction was rechromatographed on a column of alumina (18 x 2.7 cm). Initial benzene eluates (150 ml) were discarded. The next fraction (350 ml) gave pentacarbonyl(3,4-propano-1-methyl-6,6aλ^4-dithia-1-azapentalene)chromium(0) (79) (0.446 g, 57%) from cyclohexane-acetone, m.p. 110–122°C (decomp.).

Found : C 43.4; H 2.9; N 3.5

$C_{14}H_{11}NO_5S_2Cr$ requires : C 43.2; H 2.8; N 3.6

Mass spectrum : M^+ of complex at m/e 389 absent, but M^+ of triheterapentalene at m/e 197 evident

^{1}H nmr ($CDCl_3$) : δ 1.94 (2H, quint, $4'$-H_2), 2.82 (2H, t, $5'$- or $3'$-H_2), 2.89 (2H, t, $3'$- or $5'$-H_2), 3.82 (3H, s, 1-Me), 7.91 (2H, s, br, 2- and 5-H)

ir spectrum : ν max (CO (cm^{-1}) 2055 (w), 1980 (vw), 1941 (s), 1912 (w)

uv spectrum (MeOH) : qualitative λ max (nm) 501, 432, 382, 240, 215

b. 3,4-Propano-1-methyl-6,6aλ^4-dithia-1-azapentalene (76) (1 mmol, 0.197 g), tetraethylammonium iodopentacarbonylmolybdate(0) (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 30 minutes. Chromatography was on a column of silica (30 x 2.7 cm). Elution with benzene-ether (99:1, 110 ml) gave no useful products. The next eluates (520 ml) were evaporated and the residue crystallised from benzene. The material obtained in this way was then recrystallised to give pentacarbonyl(3,4-propano-1-methyl-6,6aλ^4-dithia-1-azapentalene) molybdenum(0) (80) (67.3 mg, 15.5%) as red-orange microrods from cyclohexane-acetone, m.p. 107-115°.

Found : C 38.7; H 2.4; N 3.2

$C_{14}H_{11}NO_5S_2Mo$ requires : C 38.8; H 2.6; N 3.2

Mass spectrum : M^+ of complex at m/e 433 absent, but M^+ of trithiapentalene at m/e 197 evident

^1H nmr ($CDCl_3$) : δ 1.95 (2H, quint, $4'$-H_2), 2.82 (2H, t, $5'$- or $3'$-H_2), 2.89 (2H, t, $3'$- or $5'$-H_2), 3.83 (3H, s, br, 1-Me), 7.94 (1H, d, 2-H), 7.99 (1H, t, 5-H) $J_{5,5'}$ 1.2 Hz

ir spectrum : ν max CO (cm^{-1}) 2057 (w), 1991 (w), 1945 (s), 1909 (w)

uv spectrum (MeOH) : qualitative λ max (nm) 490 sh, 429, 248, 233 sh, 210 sh

c. 3,4-Propano-1-methyl-6,6aλ^4-dithia-1-azapentalene (2 mmol, 0.395 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.512 g) and silver tetrafluoroborate (2.6 mmol, 0.501 g) were reacted for 30 minutes. Chromatography was on a column of silica (50 x 2.7 cm). Initial benzene eluates (270 ml) were discarded. The next fraction, benzene (800 ml) and benzene-ether (98:2, 300 ml), was evaporated and the residue rechromatographed on a column of alumina (20 x 2.7 cm) using benzene as eluant. The fraction containing the complex was evaporated. Crystallisation of the residue gave pentacarbonyl(3,4-propano-1-methyl-6,6aλ^4-dithia-1-azapentalene)tungsten(0) (81) (0.293 g, 28.1%) as brick-red needles from benzene, m.p. $>$ 60° (decomp.).

Found : C 32.5; H 2.1; N 2.8

$C_{14}H_{11}S\ O_5W$ requires : C 32.3; H 2.1; N 2.7

Mass spectrum : M^+ of complex at m/e 521 absent but M^+ of triheterapentalene at m/e 197 evident

^{1}H nmr ($CDCl_3$) : δ 1.95 (2H, quint, $4'$-H_2), 2.84 (2H, t, $5'$- or $3'$-H_2), 2.91 (2H, t, $3'$- or $5'$-H_2), 3.85 (3H, d, 1-Me) $J_{1,2}$ 0.4 Hz, 7.94 (1H, d, 2-H), 7.99 (1H, t, 5-H) $J_{5,5'}$ 1.2 Hz

ir spectrum : ν max CO (cm^{-1}) 2052 (w), 1978 (vw), 1940 (s), 1912 (m)

uv spectrum (MeOH) : qualitative λ max (nm) 486, 372, 260 sh, 230, 206 inf.

d. 1,3,4-Trimethyl-6,6aλ^4-dithia-1-azapentalene (77) (2 mmol, 0.371 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 25 minutes. Chromatography was on a column of silica (35 x 2.7 cm). Initial benzene eluates (130 ml) were discarded.

Further elution with benzene (870 ml) and then benzene-ether (93:7, 150 ml and 2:1, 180 ml) gave pentacarbonyl (1,3,4-trimethyl-6,6aλ^4-dithia-1-azapentalene)chromium(0) (82) (0.429 g, 56.8%) as orange microplatelets from hexane-dichloromethane, m.p. 115-131°C (decomp.).

Found : C 41.4; H 2.9; N 3.7

$C_{13}H_{11}NO_5S_2Cr$ requires : C 41.2; H 2.7; N 3.7

Mass spectrum : M^+ of complex at m/e 377 absent, but M^+ of triheterapentalene at m/e 246 evident

^{1}H nmr ($CDCl_3$) : δ 2.58 (3H, s, 3-Me), 2.62 (3H, d, 4-Me) $J_{4,5}$ too small to be measured, 3.77 (3H, s, 1-Me), 7.86 (1H, s, 2-H), 7.95 (1H, q, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2067 (s), 1988 (vw), 1946 (s), 1929 (s)

uv spectrum : not obtained

Further elution of the column using the same solvent system (120 ml) and ether (180 ml) gave a small quantity of 1,3,4-trimethyl-6,6aλ^4-dithia-1-azapentalene (14.5 mg, impure). M^+ at m/e 185.

e. 1,3,4-Trimethyl-6,6aλ^4-dithia-1-azapentalene (1 mmol, 0.186 g) (77), tetraethylammonium iodopentacarbonylmolybdate(0) (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol, 0.509 g) were reacted for 25 minutes. Chromatography was on a column of silica (48 x 2.7 cm). Elution with benzene (200 ml) and benzene-ether (99:1, 125 ml) gave no useful products. Further elution using the same solvent system (99:1, 230 ml; 98:2, 400 ml; and 9:1, 400 ml) gave eluates which were stripped of solvent and the residue recrystallised from benzene-hexane 9:1. Recrystallisation of the product from cyclohexane-acetone gave pentacarbonyl(1,3,4-trimethyl-6,6aλ^4-dithia-1-azapentalene)molybdenum(0) (83) (38.3 mg, 9.1%) as red microrods from cyclohexane-acetone, m.p. $>$ 133° (decomp.). This compound was judged not to be pure by tlc and was therefore not completely characterised.

^{1}H nmr ($CDCl_3$) : δ 2.60 (3H, s, 3-Me), 2.64 (3H, d, 4-Me) $J_{4,5}$ 1.0 Hz, 3.79 (3H, s, 1-Me), 7.88 (1H, s, 2-H), 8.02 (1H, q, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2057 (s), 1973 (m), 1936 (m), 1905 (w)

uv spectrum (MeOH) : qualitative λ max (nm) 484, 373, 256 sh, 230, 206 sh

f. 1,3,4-Trimethyl-6,6aλ^4-dithia-1-azapentalene (77) (2 mmol, 0.371 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.511 g) and silver tetrafluoroborate (2.6 mmol, 0.504 g) were reacted for 25 minutes. Chromatography was on a column of silica (55 x 2.7 cm). Initial benzene eluates (250 ml) were discarded. The next fraction (100 ml) was evaporated and the residue rechromatographed on a column of alumina (50 x 2.7 cm) using benzene-ether (98:2) as eluant. A slower-running impurity was removed by this process. The complex was then rechromatographed on a column of alumina (25 x 2.7 cm) using benzene. Fractions containing faster-running yellow impurities were discarded. The main fraction gave pentacarbonyl(1,3,4-trimethyl-6,6aλ^4-dithia-1-azapentalene)tungsten(0) (84) (0.250 g, 24.7%) as brick-red microrods from cyclohexane-acetone, m.p. 146-152° (decomp.).

Found : C 30.8 H 2.3; N 2.8

$C_{13}H_{11}NO_5S_2W$ requires : C 30.7; H 2.2; N 2.8

Mass spectrum : M^+ of complex at m/e 509 absent, but M^+ of triheterapentalene at m/e 185 evident

^1H nmr spectrum ($CDCl_3$) : δ 2.59 (3H, s, 3-Me), 2.63 (3H, d, 4-Me) $J_{4,5}$ 1.0 Hz, 3.80 (3H, s, 1-Me), 7.87 (1H, s, br, 2-H), 8.04 (1H, q, 5-H)

ir spectrum : ν max CO (cm^{-1}) 2047 (w), 1974 (vw), 1936 (s), 1906 (w)

uv spectrum (MeOH) : qualitative λ max (nm) 489, 375, 256 sh, 232, 207 sh

g. 1,2,5-Trimethyl-6,6aλ^4-dithia-1-azapentalene (78) (2 mmol, 0.371 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.506 g) were reacted for 35 minutes. Chromatography was on a column of silica (50 x 2.7 cm). Initial benzene eluates (320 ml) were discarded. The residue from the next fraction, which was eluted with benzene (180 ml) and then benzene-ether (98:2, 420 ml), was rechromatographed on a column of alumina (25 x 2.7 cm). Elution with benzene-ether (99:1, 70 ml) afforded no useful products. The residue from the next fraction was crystallised from cyclohexane-acetone. The product obtained in this way was then recrystallised from dichloromethane-hexane to give pentacarbonyl(1,2,5-trimethyl-6,6aλ^4-dithia-1-azapentalene)chromium(0) (85) (0.333 g, 44.1%) as red microrods from hexane-dichloromethane, m.p. > 110°C (decomp.)

Found : C 41.3; H 2.9; N 3.7

$C_{13}H_{11}NO_5S_2Cr$ requires : C 41.4; H 2.9; N 3.8

Mass spectrum : M^+ of complex at m/e 377 absent, but M^+ of triheterapentalene at m/e 213 evident

^1H nmr ($CDCl_3$) : δ 2.43 (3H, s, 2-Me), 2.52 (3H, d, 5-Me) $J_{5,4}$ 0.5 Hz, 3.62 (3H, s, 1-Me), 6.99 (1H, s, 3-H), 7.14 (1H, q, 4-H)

ir spectrum (MeOH) : λ max CO (cm^{-1}) 2054 (w), 1978 (vw), 1944 (m), 1908 (w)

uv spectrum : not obtained

h. 1,2,5-Trimethyl-6,6aλ^4-dithia-1-azapentalene (78) (2 mmol, 0.371 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.512 g) and silver tetrafluoroborate (2.6 mmol, 0.503 g) were reacted for 35 minutes. Chromatography was on a column of silica (40 x 2.7 cm). Elution with benzene (150 ml) gave eluates which were discarded. Further elution with benzene (400 ml), followed by benzene-ether (97:3, 750 ml) gave, after evaporation of the solvents, a solid which was rechromatographed on a column of alumina (25 x 2.7 cm). Elution with benzene-ether (96:4) gave two fractions. The residue from the first (180 ml) was recrystallised from cyclohexane-acetone. The mother liquors from the filtration of this product were combined with the second fraction (60 ml) and passed through a column of alumina (25 x 2.7) using benzene-ether (96:4). The eluates containing the complex were evaporated and the residue crystallised as before. This process yielded pentacarbonyl-(1,2,5-trimethyl-6,6aλ^4-dithia-1-azapentalene)tungsten(0) (86)

(0.483 g, 47.5%) as red-orange rods from cyclohexane-acetone, m.p. 143-147° (decomp.).

Found : C 30.9; H 2.2; N 2.7

$C_{13}H_{11}NO_5S_2W$ requires : C 30.7; H 2.2; N 2.8

Mass spectrum : M^+ of complex at m/e 509 not apparent, but M^+ of triheterapentalene at m/e 213 evident

^1H nmr ($CDCl_3$) : δ 2.45 (3H, s, 2-Me), 2.53 (3H, d, 5-Me) $J_{5,4}$ 0.9 Hz, 3.65 (3H, s, 1-Me), 6.99 (1H, s, 3-H), 7.09 (1H, q, 4-H)

ir spectrum : ν max CO (cm^{-1}) 2058 (w), 1975 (vw), 1936 (s), 1907 (w)

uv spectrum (MeOH) : qualitative λ max (nm) 464, 399 inf, 355, 255, 230, 210 sh

4. The Preparation of Pentacarbonylchromium(0), Molybdenum(0) and Tungsten(0) Complexes of Substituted 1,2-Dithiole-3-thiones

a. 4,5-Dimethyl-1,2-dithiole-3-thione (9) (2 mmol, 0.325 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.512 g) and silver tetrafluoroborate (2.6 mmol, 0.507 g) were reacted together for 30 minutes. Chromatography was on a column of silica (32 x 2.7 cm). Elution with benzene-petrol (1:1, 150 ml) gave eluates which were discarded. Continued elution with the same solvents (1:1, 350 ml and 2:1, 450 ml) gave pentacarbonyl(4,5-dimethyl-1,2-dithiole-3-thione)tungsten(0) (90) (0.836 g, 86%) as dark-brown microrods from hexane-dichloromethane, m.p. 155–161°C.

Found : C 24.9; H 1.1

$C_{10}H_6O_5S_3W$ requires : C 24.7; H 1.2

Mass spectrum : M^+ of complex at m/e 486 absent, but M^+ of thione at m/e 162 evident

^{1}H nmr ($CDCl_3$) : δ 2.27 (3H, q, 4-Me) $J_{4,5}$ 0.5 Hz, 2.52 (3H, q, 5-Me)

ir spectrum : ν max CO (cm^{-1}) 2067 (s), 1987 (vw), 1946 (s), 1928 (s)

uv spectrum (MeOH) : λ max (nm) 550 (log ϵ 4.03), 392 (3.69), 344 (3.94), 236 (4.76), 215 (4.75)

b. 4,5-Dimethyl-1,2-dithiole-3-thione (9) (2 mmol, 0.325 g), tetraethylammonium iodopentacarbonylmolybdate(0) (2.6 mmol, 1.282 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 30 minutes. Chromatography was on a column of silica (33 x 2.7 cm). Initial benzene-petrol eluates (7:3, 120 ml) were discarded. The next fraction gave pentacarbonyl(4,5-dimethyl-1,2-dithiole-3-thione)molybdenum(0) (91) (0.565 g, 70.9%) as red-brown microneedles from hexane-dichloromethane, m.p. 124-135°.

The product was impure by tlc and was therefore not fully characterised.

^{1}H nmr ($CDCl_3$) : δ 2.26 (3H, q, 4-Me), 2.53 (3H, q, 5-Me) $J_{5,4}$ 0.7 Hz

ir spectrum : ν max CO (cm^{-1}), 2072 (m), 1996 (vw), 1956 (s), 1932 (m)

uv spectrum (MeOH) : qualitative λ max (nm) 480, 405, 247, 218

c. 5-Phenyl-1,2-dithiole-3-thione (38) (2 mmol, 0.403 g), tetraethylammonium iodopentacarbonylchromate(0) (2.6 mmol, 1.168 g) and silver tetrafluoroborate (2.6 mmol, 0.505 g) were reacted for 20 minutes. Chromatography was on a column of silica (30 x 2.7 cm). Benzene-petrol (2:1, 120 ml) gave no useful products. The next fraction (800 ml) afforded pentacarbonyl(5-phenyl-1,2-dithiole-3-thione)chromium(0) (92) (0.742 g, 92%) as dark red microneedles from cyclohexane-acetone, m.p. 145-155°.

Found : C 41.4; H 1.3

$C_{14}H_6S_3O_5Cr$ requires : C 41.8; H 1.5

Mass spectrum : M^+ of complex at m/e 402 absent, but M^+ of thione at m/e evident

^{1}H nmr ($CDCl_3$) : δ 7.50-7.76 (5H, m, 2 o + 2 m + p-protons of 5-Ar), 7.71 (1H, s, 4-H) ir spectrum : ν max CO (cm^{-1}) 2052 (m), 1992 (vw), 1953 (s), 1933 (m)

uv spectrum (MeOH) : λ max (nm) 550 (log ϵ 3.99), 320 (4.23), 235 (4.59) inf., 214 (4.59)

5. The Attempted Preparation of Pentacarbonyl(5-tert-butyl-1-oxa-6,6a λ^4-dithiapentalene)tungsten(0)

a. 5-*tert*-Butyl-1-oxa-6,6a λ^4-dithiapentalene (98) (2 mmol, 0.400 g), tetraethylammonium iodopentacarbonyltungstate(0) (2.6 mmol, 1.512 g) and silver tetrafluoroborate (2.6 mmol, 0.506 g) were reacted for 15 minutes to give an orange-coloured solution. Chromatography was on a column of silica (25 x 2.7 cm). Initial benzene eluates (120 ml) were discarded. The next fraction (150 ml) contained the complex. However, on evaporation of the solvent only a tarry residue remained. The product was not investigated further.

REFERENCES

1. F. Arndt, P. Nachtwey, and J. Pusch, Chem. Ber. 1925, 58, 1633.
2. M. Mammi, S. Bezzi and C. Garbuglio, Nature, 1958 182, 247.
3. N. Lozac'h, Adv. Het. Chem., 1971, 13, 161.
4. N. Lozac'h, "Comprehensive Heterocyclic Chemistry", Pergammon Press, Oxford, 1983, 6, 1049.
5. E. Klingsberg, Quart. Rev., 1969, 23, 537.
6. D. H. Reid, "Organic Compounds of Sulphur, Selenium and Tellurium", The Chemical Society, London, 1970, 1, 321.
7. R. J. S. Beer, ibid., 1972, 2, 497.
8. R. J. S. Beer, ibid., 1975, 3, 494.
9. R. J. S. Beer, ibid., 1977, 4, 300.
10. D. Leaver, ibid., 1979, 5, 306.
11. M. Davis, ibid., 1981, 6, 299.
12. L. K. Hansen and A. Hordvik, Acta Chem. Scand., 1973, 27, 411.
13. A. Hordvik, ibid., 1966, 20, 1885.
14. L. Pauling, "The Nature of the Chemical Bond", 3rd edition, Cornell University Press, Ithaca, New York, 1960.
15. D. W. J. Cruickshank, Acta Cryst., 1970, B26, 1260.
16. F. Leung and S. C. Nyburg, Chem. Comm., 1969, 137.
17. B. Birknes, A. Hordvik, and L. J. Saethre, Acta Chem. Scand., 1972, 26, 2140.
18. A. Hordvik, O. Sjølset and L. J. Saethre, ibid., 1973, 27, 379.
19. A. Hordvik, ibid., 1971, 25, 1583.
20. B. Birknes, A. Hordvik and L. J. Saethre, ibid., 1973, 27, 382.
21. P. L. Johnson and I. C. Paul, Chem. Comm., 1969, 1014.

22. A. Hordvik and L. J. Saethre, Acta Chem. Scand., 1972, 26, 1729.

23. A. Hordvik, O. Sjølset and L. J. Saethre, ibid., 1972, 26, 1279.

24. A. Hordvik and K. Julshamn, ibid., 1971, 25, 1835.

25. A. Hordvik and L. J. Saethre, ibid., 1972, 26, 3114.

26. M. Mammi, R. Bardi, G. Traverso and S. Bezzi, Nature, 1961, 192, 1282.

27. A. Hordvik, E. Sletten and J. Sletten, Acta Chem. Scand., 1969, 23, 1377.

28. P. L. Johnson, K. I. G. Reid and I. C. Paul, J. Chem. Soc. (B), 1971, 946.

29. E. C. Laguno and I. C. Paul, Tet. Lett., 1973, 1565.

30. F. C. Leung and S. C. Nyburg, Can. J. Chem., 1971, 49, 167.

31. F. C. Leung and S. C. Nyburg, ibid., 1972, 50, 324.

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

33. L. K. Hansen and K. Tomren, Acta Chem. Scand. (A), 1977, 31, 292.

34. L. P. Darmo and L. K. Hansen, ibid., 1977, 31, 412.

35. A. Hordvik and L. J. Saethre, Israeli J. Chem., 1972, 10, 239.

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. H. G. Hertz, G. Traverso and W. Waltern, Annalen, 1959, 625, 43.

39. J. G. Dingwall, PhD Thesis, University of St. Andrews, 1968.

40. R. Gleiter and R. Gygax, Top. Curr. Chem., 1976, 63, 49.

41. S. McKenzie and D. H. Reid, J. Chem. Soc. (C), 1970, 145.

42. R. K. Mackie, S. McKenzie, D. H. Reid and R. G. Webster, J.C.S. Perkin I, 1973, 657.

43. R. Pinel, Y. Mollier and N. Lozac'h, Bull. Soc. Chim. France, 1966, 856.

44. D. H. Reid and R. G. Webster, J.C.S. Perkin I, 1975, 775.

45. D. H. Reid, J. Chem. Soc. (C), 1971, 3187.

46. A. S. Ingram, D. H. Reid and J. D. Symon, J.C.S. Perkin I, 1974, 242.

47. R. M. Christie, D. H. Reid, R. G. Walker and R. G. Webster, J.C.S. Perkin I, 1978, 195.

48. K. Maeda, Bull. Chem. Soc. Jap., 1961, 34, 781.

49. H. Behringer and J. Falkenberg, Chem. Ber., 1969, 102, 1580.

50. D. Paquer, M. Perrier and J. Vialle, Bull. Soc. Chim. France, 1970, 4517.

51. C. Pedersen and K. Schaumburg, Org. Mag. Res., 1974, 6, 586.

52. R. D. Lapper and A. J. Poole, Tet. Lett., 1974, 2783.

53. B. Lindberg *et al*, Chem. Scripta, 1971, 1, 183.

54. D. T. Clark, D. Kilcast and D. H. Reid, Chem. Comm, 1970, 638.

55. L. J. Saethre *et al*, Chem. Phys., 1977, 20, 431.

56. L. J. Saethre *et al*, J. Am. Chem. Soc., 1980, 102, 1783.

57. D. Festal and Y. Molier, Tet. Lett., 1970, 1259.

58. R. M. Christie and D. H. Reid, J.C.S. Perkin I, 1976, 880.

59. T. Pedersen, S. Skaarup and C. Pedersen, Acta Chem. Scand., 1977, 31B, 711.

60. E. M. Shustorovich, J. Gen. Chem., U.S.S.R., 1959, 29, 2424.

61. R. J. S. Beer, D. Cartwright, R. J. Gait, R. A. W. Johnstone, and S. D. Ward, Chem. Comm., 1968, 688.

62. K. Maeda, Bull. Chem. Soc. Jap., 1960, 33, 1466.

63. K. Maeda, ibid., 1961, 34, 1166.

64. C. C. Price and S. Oae, "Sulphur Bonding", Ronald Press, New York, 1962.

65. R. A. W. Johnstone and S. D. Ward, Theor. Chem. Acta, 1969, 14, 420.

66. R. Gleiter and R. Hoffmann, Tet., 1968, 24 5988.

67. R. Gleiter, D. Werthemann and H. Behringer, J. Am. Chem. Soc., 1972, 94, 651.

68. K. Hansen, A. Hordvik and L. J. Saethre, Chem. Comm, 1972, 222.

69. D. T. Clark, Int. J. Sulphur Chem., 1972, C7, 11.

70. R. H. Findlay and M. H. Palmer, Tet. Lett., 1972, 4165.

71. R. H. Findlay and M. H. Palmer, J.C.S. Perkin II, 1974, 1885.

72. C. A. Coulson, Nature, 1969, 221, 1106.

73. J. I. Musher, Ang. Chem. Int. Ed., 1969, 8, 54.

74. R. C. L. Mooney and J. C. Slater, Acta Cryst., 1959, 12, 187.

75. O. Foss, Pure Appl. Chem., 1970, 24, 31.

76. G. Traverso, Ann. Chim. (Rome), 1954, 44, 1018.

77. N. Lozac'h and M. Stavraux, Bull. Soc. Chim. France, 1967, 2028.

78. H. Behringer, M. Ruff and R. Weidenmann, Chem. Ber., 1964, 97, 1732.

79. D. H. Reid and R. G. Webster, J.C.S. Perkin I, 1972, 1447.

80. J. G. Dingwall, D. H. Reid and J. D. Symon, J. Chem. Soc. (C), 1970, 2412.

81. H. Hartmann and R. Mayer, Z. Chem., 1966, 6, 312.

82. E. I. G. Brown, D. Leaver and D. M. McKinnon, J. Chem. Soc. (C), 1970, 1202.

83. J. G. Dingwall, A. S. Ingram, D. H. Reid and J. D. Symon, J.C.S. Perkin I, 1973, 2351.

84. E. Klingsberg, J. Org. Chem., 1968, 33, 2915.

85. D. Leaver, D. M. McKinnon and W. A. H. Robertson, J. Chem. Soc., (1962), 5104.

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

87. G. Duguay, D. H. Reid, K. O. Wade and R. G. Webster, J. Chem. Soc. (C), (1971), 2829.

88. R. M. Christie and D. H. Reid, J.C.S. Perkin I, 1976, 228.

89. A. G. Briggs, J. Czyzewski and D. H. Reid, J.C.S. Perkin I, 1979, 2340.

90. R. J. S. Beer and A. J. Poole, Tet. Lett., 1972, 1835.

91. M. Perrier and J. Vialle, Bull. Soc. Chim. France, 1979, 2, 199.

92. R. M. Christie, D. H. Reid and R. Wolfe-Murray, J.C.S. Perkin I, 1979, 926.

93. D. H. Reid, R. Walker and R. G. Webster, J.C.S. Perkin I, 1981, 1596.

94. M. Perrier and J. Vialle, Bull. Soc. Chim. France, 1979, 2, 205.

95. E. Klingsberg, J. Am. Chem. Soc., 1963, 85, 3244.

96. O. Coulibaly and Y. Mollier, Bull. Soc. Chim. France, 1969, 3208.

97. N. Lozac'h, Y. Mollier, and F. Terrier, Bull. Soc. Chim. France, 1963, 157.

98. R. J. S. Beer, D. Cartwright and D. Harris, Tet. Lett, 1967, 11, 953.

99. R. J. S. Beer, D. Cartwright, R J. Gait and D. Harris, J. Chem. Soc. (C), 1971, 963.

100. J. Bignebat and H. Quiniou, Compt. Rend., 1969, 269C, 1129.

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

102. H. Behringer, H. Reimann and M. Ruff., Ang. Chem., 1960, 72, 415.

103. R. M. Christie, A. S. Ingram, D. H. Reid and R. G. Webster, Chem. Comm., 1973, 92.

104. R. M. Christie and D. H. Reid, J.C.S. Perkin I, 1977, 848.

105. D. H. Reid and R. G. Webster, J.C.S. Perkin I, 1977, 854.

106. D. H. Reid and R. G. Webster, J.C.S. Perkin I, 1975, 2097.

107. A. Furuhashi, Bull. Chem. Soc. Jap., 1970, 43, 3604.

108. B. Bogdanović, C. Kruger and O. Kuzmin, Ang. Chem., 1979, 18, 683.

109. B. Bogdanović, C. Kruger and P. Locatelli, Ang. Chem., 1979, 18, 684.

110. P. J. Pogorzelec and D. H. Reid, Chem. Comm., 1982, 289.

111. C. Glidewell, D. C. Liles and P. J. Pogorzelec, Acta Cryst., 1983, (C)39, 542.

112. D. H. Reid and R. Wolfe-Murray, unpublished results.

113. R. Wolfe-Murray, PhD Thesis, University of St. Andrews, 1977.

114. H. Zollinger, Accounts Chem. Res., 1973, 6, 335.

115. R. A. Abramovitch and J. G. Saha, Tet., 1965, 21, 3297.

116. J. March, "Advanced Organic Chemistry", 2nd Ed., McGraw-Hill, London, 1977.

117. D. F. DeTar and T. Kosuge, J. Am. Chem. Soc., 1958, 80, 6072.

118. H. Zollinger, "Azo and Diazo Chemistry", Interscience Publishers Inc., New York, 1961.

119. A. G. Briggs, MSc Thesis, University of St. Andrews, 1978.

120. R. G. W. Gingerich and R. J. Angelici, J. Am. Chem. Soc., 1979, 101, 5604.

121. R. G. W. Gingerich and R. J. Angelici, J. Organomet. Chem., 1977, 132, 377.

122. T. A. Manuel, Adv. Organomet. Chem., 1965, 3, 181.

123. J. A. Connor, E. M. Jones and G. K. McEwan, J. Organomet. Chem., 1972, 43, 357.

124. E. W. Abel, I. S. Butler and J. G. Reid, J. Chem. Soc., 1963, 2086.

125. D. B. Chambers, F. Glocking and J. R. C. Light, Quart. Revs. 1968, 22.

126. I. W. Stoltz, G. R. Dobson and R. K. Sheline, Inorg. Chem., 1963, 2, 323.

127. A. Roe, Org. Reactions, 1949, 5, 204.

128. E. B. Starkey, Organic Synthesis, 1943, 2, 225.

129. J. Vialle and A. Thuiller, Bull. Chem. Soc. France, 1962, 2187.

130. E. Klingsberg, J. Am. Chem. Soc., 1961, 83, 2934.

131. E. Klingsberg, J.O.C., 1977, 132, 377.

132. Lange's "Handbook of Chemistry", 11th Edition, J. A. Dean (Ed.), McGraw-Hill, New York.

133. P. S. Braterman, Structure and Bonding, 1972, 10, 57.

134. P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, J. C. S. Dalton, 1973, 1027.

135. H. Fischer, S. Zeuner and J Riede, Ang. Chem. Int. Ed. 1984, 23, 726.

136. M. Kilner, Adv. Organomet. Chem., 1972, 10, 115.