To my wife

1,6-Dioxa-6a-thiapentalenes and Related Hypervalent Heterocyclic Compounds

being a Thesis presented by

ROBERT GORDON WEBSTER

to the University of St. Andrews in

application for the degree of Ph.D.

3rd Copy

DECLARATION

I hereby declare that the following thesis is a record of the results of experiments carried out by me, and further that the thesis is my own composition and has not previously been presented for a higher degree.

The research was carried out in the Department of Chemistry, University of St. Andrews, under the direction of Dr. D.H. Reid.

December 1973

CERTIFICATE

I certify that Robert Gordon Webster has spent nine terms at research under my direction, that he has fulfilled the conditions of Ordinance No 12 (St. Andrews) and is qualified to submit the accompanying thesis in application for a degree of Ph.D.

December 1973 Director of Research

CAREER

I entered Robert Gordon's Institute of Technology, Aberdeen in October 1966 and subsequently graduated with a Higher National Diploma, with Distinction, in Chemistry in June 1969.

I was admitted as a Research Student in the Department of Chemistry, University of St. Andrews in October 1969 and subsequently graduated with a Master of Science degree in June 1972.

I continued as a Research Student from July 1971 in the same Department.

I was awarded a Research Studentship by the University of St. Andrews for the whole of my period as a research student.

ACKNOWLEDGEMENTS

I am sincerely grateful to Dr. D.H. Reid of the Department of Chemistry, University of St. Andrews, for the counsel, assistance and guidance given to me during the prosecution of the work embodied in this thesis.

I should like to thank Professor J.M. Tedder for permission to use the facilities of the Research Laboratories of the Department of Chemistry, University of St. Andrews, where this work was carried out.

I should also like to thank the University of St. Andrews for the award of a Research Studentship.

Thanks are also due to the technical staff of the aforementioned laboratories who so ably coped with the requirements of a demanding customer.

EXPLANATORY NOTE

This thesis is divided into three sections, Parts I, II and III. Each part is divided into a number of principal sections, each prefixed by a capital letter.

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

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

Part III is devoted to a description of the experimental details and is complementary to Part II.

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

CONTENTS

Summary

A new rapid synthesis of 1-oxa-6,6a-dithiapentalene and 1,6,6a-trithiapentalene has been developed, starting from δ-pyrone.

Studies of oxidative coupling reactions led to the discovery of a method of forming sulphur-oxygen and selenium-oxygen bonds. Using this procedure a series of 1,6-dioxa-6a-thiapentalenes and 1,6-dioxa-6a-selenapentalenes was isolated. The reactivity of 1,6-dioxa-6a-thiapentalenes was investigated; results indicate that electrophilic substitution occurs at position 3. Protonation of 1,6-dioxa-6a-thiapentalenes and 1,6-dioxa-6a-selenapentalenes has been shown to occur at C-3. A mechanism for electrophilic substitution in trithiapentalenes and analogues has been enunciated.

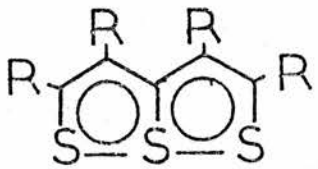
1,6-Dioxa-6a-thia-2-azapentalenes have been synthesised.

A new route to 3-nitromethylene-3H-1,2-dithioles has been developed.

Methylation and protonation of trithiapentalene and analogues have been investigated.

Note on Nomenclature

The compounds to be described in this thesis have given rise to a unique problem in nomenclature. Various names have been suggested for compound (1): 6a-thiathiophthen[10,18], 6a-thiothiophthene[12,13], and meribicyclo-3,5-epidithio-2,4-pentadien-1-thial[21]. Chemical Abstracts indexes compounds of type (1) under [1,2]-dithiolo-[1,5,b][1,2]-dithiole-7S[IV]. However none of these names can be modified to allow for the numerous oxygen, selenium and nitrogen analogues of this compound which are known. Lozac'h[66,3] has suggested 1,6,6a-trithiapentalene as a name for compound (1) and, although this name has been criticised[231] the nomenclature system which can be based on this name has the advantage that all trithiapentalene analogues can be named easily. This latter system of nomenclature will be employed throughout this thesis.



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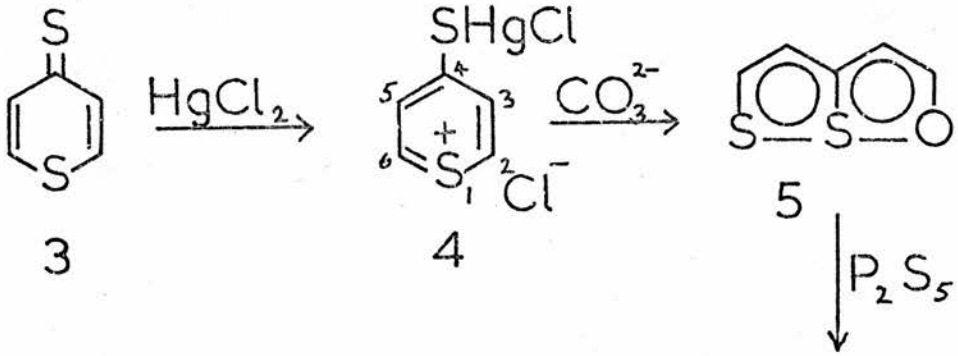

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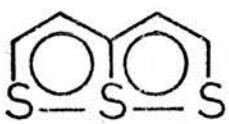
Scheme I



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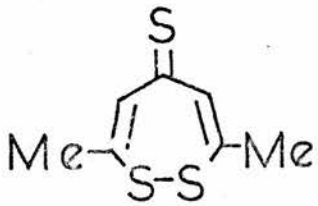

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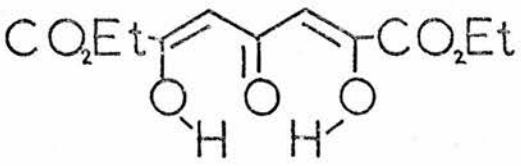
The subject matter for this thesis is a study of the protonation of trithiapentalenes (1) and of the synthesis and properties of oxygen, nitrogen and selenium analogues of this system. This introduction serves to indicate the type of work which has preceded the present study. Particular attention will be drawn towards the oxygen analogues of trithiapentalenes since one of the more important parts of this thesis describes the synthesis of the simplest analogues of trithiapentalenes, namely 1,6-dioxa-6a-thiapentalenes (2).

A. Synthetic Routes to 1,6,6a-Trithiapentalene

Trithiapentalenes (1) have been the subject of numerous reviews, by Breslow and Skolnik[1], Lozac'h and Vialle[2], Lozac'h[3], Beer[4], Klingsberg[5] and Lozac'h[6]. The latter's review embodies all all that has been written previously and contains much spectral information. These reviews are backed by the appearance of chapters[7,8] in the biennial Chemical Society Specialist Periodical Reports edited by Reid. Since trithiapentalenes have been reviewed so extensively this section will be restricted to the parent system (1, R=H).

The first synthetic route to 1,6,6a-trithiapentalene (Scheme I) involved reaction of aqueous sodium carbonate on the mercuric chloride complex of 4H-thiopyran-4-thione (4) which gave the 1-oxa-6,6a-dithiapentalen (5). Subsequent thionation of this compound with phosphorus pentasulphide in benzene gave 1,6,6a-trithiapentalene (6) in unspecified yield.

The compound originally thought[11] by Arndt to have structure (7) and later shown[12,13] to be the trithiapentalene (8) was prepared by thionation of heptan-2,4,6-trione with phosphorus pentasulphide



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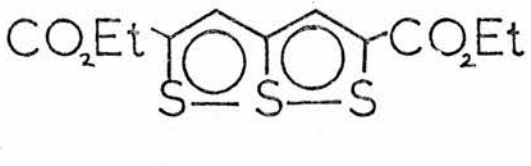

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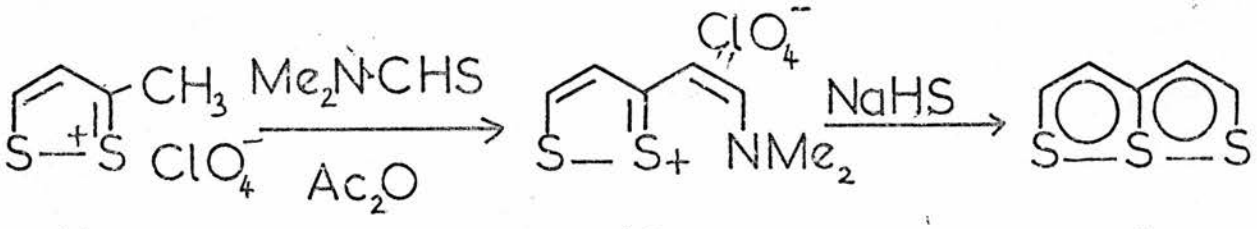
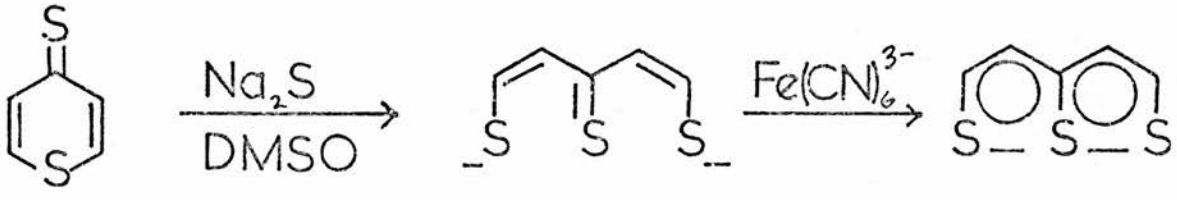


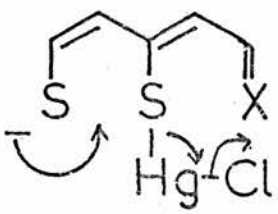
11 12 6

Scheme II



3 13 6

Scheme III



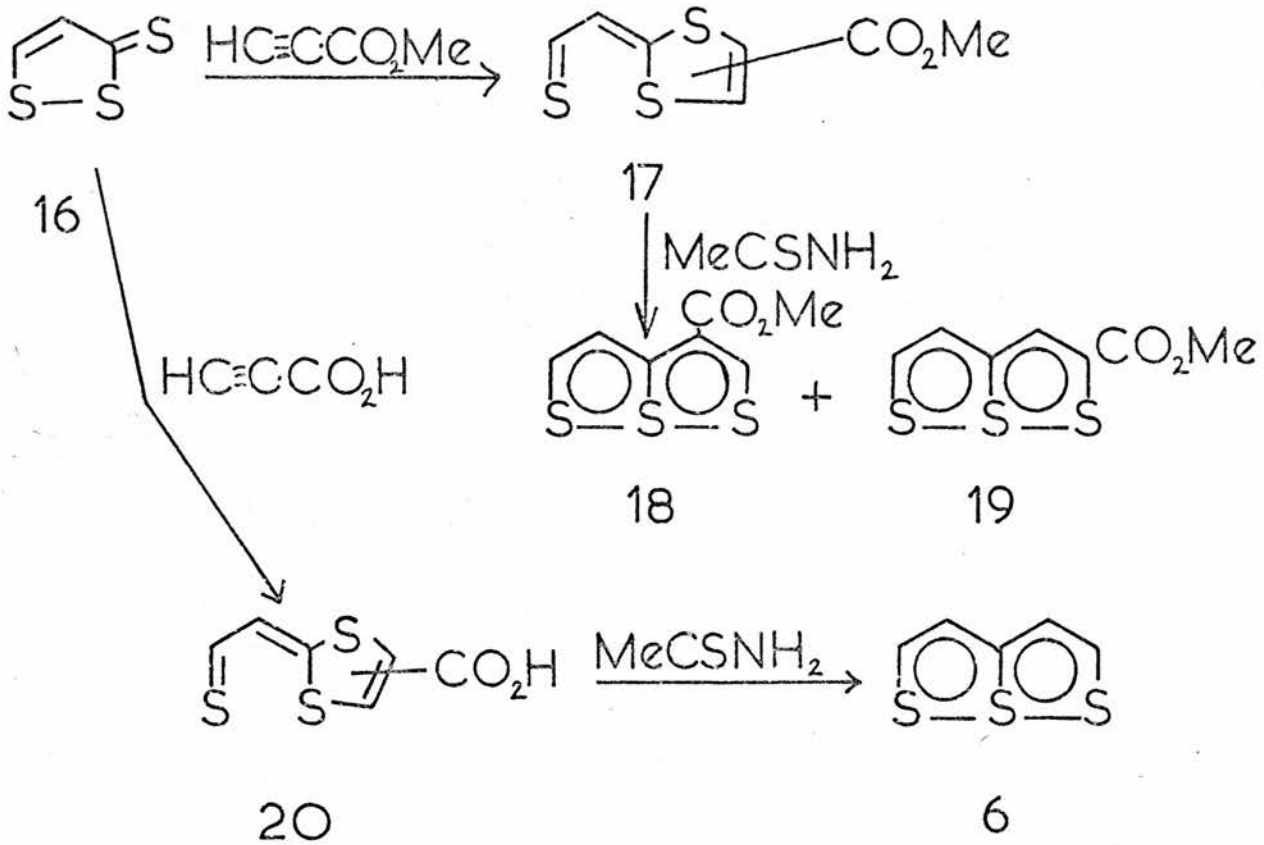
14 X=O

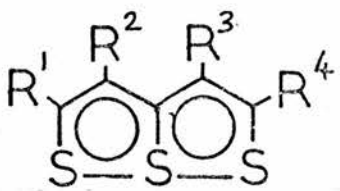
15 X=S

in benzene. Diethoxalylacetone (9) was converted by this procedure[14] into the diester (10) in low yield. The foregoing diester was hydrolysed and decarboxylated to give the trithiapentalene (6).

3-Methylene-1,2-dithiolium salts (eg 11) condense readily with N,N-dimethylthioformamide in boiling acetic anhydride to give Vilsmeier salt intermediates, exemplified by 12, which are readily solvolysed by sodium hydrogen sulphide to give trithiapentalenes[14] - in this example 1,6,6a-trithiapentalene (6). This route has been used[14-17] to prepare numerous simple alkyl trithiapentalenes and is perhaps the most versatile synthesis of trithiapentalenes. Regrettably it does not give a high yield when applied to the parent system (Scheme II).

An elegant synthesis of 1,6,6a-trithiapentalene appeared in 1970 when Reid and co-workers demonstrated[10] that 4H-thiopyran-4-thione (3) could be converted into the parent compound (6) (Scheme III). The anion (13), which is readily prepared by ring-opening of the thione (3) in dimethylsulphoxide with aqueous sodium sulphide, is oxidised to the bicyclic compound by aqueous potassium ferricyanide. Other oxidants such as iodine and oxygen were less successful. The role of the solvent is very important. Dipolar aprotic solvents, such as dimethylformamide and dimethylsulphoxide, enhance the nucleophilicity of the sulphide ion, thereby causing more facile attack on the ring. In contrast the use of ethanol gave a low yield of 1,6,6a-trithiapentalene. Another method of this type[18] will be discussed in Part II. In Traverso's synthesis (Scheme I) attack at the 2-position of the salt (4) probably leads to an intermediate of type (14). The mercury then acts as an internal oxidant and leads to the 1-oxa-6,6a-dithiapentalene (5).





Cpd	R^1	R^2	R^3	R^4
21	H	H	H	H
22	Me	H	H	H
23	H	Me	H	H
24	Bu^t	H	H	H
25	Me	H	H	Me
26	H	Me	Me	H
27	H	$-CH_2-CH_2-$		H
28	H	$-CH_2CH_2CH_2-$		H

An attempted modification of this synthesis by Reid and co-workers[10] used sodium hydrogen sulphide in place of carbonate in the hope that an intermediate of type (15) might occur. Ring-opening was not observed and the thione (3) was regenerated in high yield either by attack at position 4 in the ring or at the mercury atom.

A synthesis claimed to be "more simple and more rapid" than the preceding routes has been described[19] by Davy and Vialle. Condensation of 1,2-dithiole-3-thione (16) with methyl propiolate yielded a mixture of esters (17) which on treatment with thioacetamide in boiling naphthalene gave the trithiapentalene esters (18) and (19). Use of propiolic acid gave the acids (20) which likewise underwent rearrangement and decarboxylated to give 1,6,6a-trithiapentalene (6) in 45% yield. This method is to be recommended if large quantities of the thione (16) are available. The cited preparation of this compound[20] gives no details except the yield (70%). Full experimental details concerning the preparation of this compound would be useful.

B. Structural Studies on Trithiapentalenes

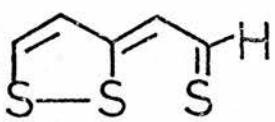
Since the discovery that three sulphur atoms in trithiapentalenes had a linear arrangement, these compounds have been subjected to numerous spectroscopic studies.

1H Nuclear Magnetic Resonance Spectra

The symmetry of 2,5-dimethyl-1,6,6a-trithiapentalene (25) was observed in the earliest nmr study by Bothner-By and Traverso[21]. Since then much data have appeared in numerous papers[14,22-29]. However the usefulness of the data to be gleaned from the compounds cited in these papers[22-29] is limited due to the number of aryl, S-methyl and ester groupings which appear as substituents. A

Proton Signal δ

Cpd	2-H	3-H	4-H	5-H	Other	Ref.
21	9.18	7.96				14
22		7.72	7.77	9.13	2.67	14
23	8.58		7.83	9.43	2.53	30
24		7.87	7.86	9.32	1.43	15
25		7.53			2.60	23
26	8.83				2.80	10
27	8.59				3.35	30
28	8.78				1.99,2.99	16



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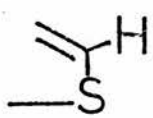

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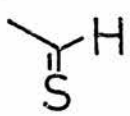

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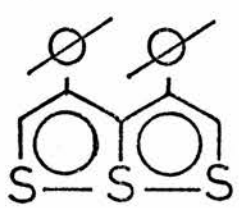

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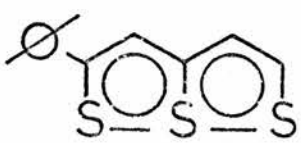
considerable number of simpler, more useful compounds are known whose chemical shift data are shown opposite.

The formulation of trithiapentalenes as monocyclic structures (29), on the basis of spectral information[31], appears to be unfounded in the light of much chemical shift data for 2-H in trithiapentalenes. The chemical shift of 2-H in simple trithiapentalenes (21-28) lies in the range δ8.58-9.43. Data on heterocyclic thioaldehydes (R-CHS)[32-34] show that the chemical shift of the thioformyl proton in the most polarised ($R^+ = CH-S^-$) thioaldehydes does not occur at higher field than δ10.2. This would seem to imply that 2-H in the trithiapentalenes is in environment (30) and not (31). It has also been suggested[14] that the deshielding of the ring protons in trithiapentalenes relative to those in 1-oxa-6,6a-dithiapentalene (32) is to be attributed to a larger ring current and hence greater aromaticity in the trithiapentalenes. It has been estimated[24] that the ring current in 2,5-dimethyl-1,6,6a-trithiapentalenes (25) is about 65% of that in naphthalene. Symmetrically substituted trithiapentalenes give nmr spectra which show magnetic equivalence of substituents at the pairs of positions 2 and 5 and 3 and 4. These results which show symmetry for compounds in solution, where intermolecular forces are minimised, will not necessarily be the same as that obtained from the same compounds by Xray crystallography. Intermolecular forces are at a maximum and localised in the solid state but are averaged in solution. 3,4-Diphenyl-1,6,6a-trithiapentalene (33) is a case in point which shows a symmetrical structure in solution[30] (by nmr spectroscopy) and an unsymmetrical structure[38] (by Xray crystallography) in the crystal. Lozac'h in his review[6], has tabulated nmr data for numerous trithiapentalenes.

Cpd	λ_{nm}	log ε	λ_{nm}	log ε	λ_{mn}	log ε	Ref.
21	230	4.20	254	4.69	472	3.68	14
22	235	4.18	262	4.68	470	3.72	14
23	232	4.18	258	4.63	476	3.64	30
24	235	4.25	256	4.69	472	3.78	15
25			261	3.74	474	3.85	28
26	236	4.28	264	4.69	492	3.73	17
27	238	4.30	260	(4.66)	524	(3.66)	30
28	233	4.33	260	4.72	492	(3.72)	16
34	249	(4.61)	270sh	(4.56)	322 (4.11)	487	3.94	30
35	230	3.25	259	4.23	480	3.25	14



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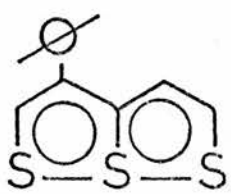

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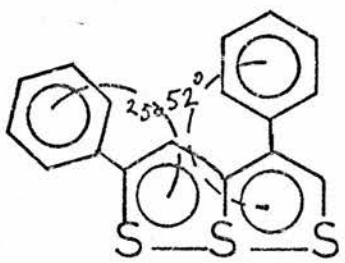

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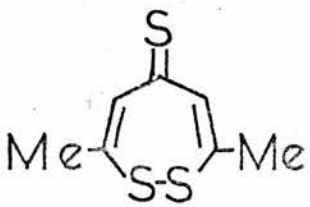

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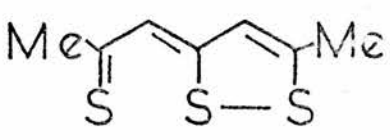

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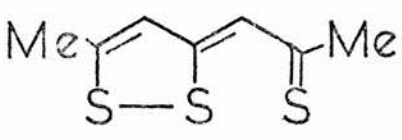

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UV and Visible Spectra

Simple trithiapentalenes show one band in their visible spectra (ca 470 nm) which is responsible for their orange-red colour. In the ultraviolet region of the spectrum two more bands are observed around 235 and 260 nm. Data for the simpler compounds are tabulated opposite with appropriate references. Lozac'h has tabulated[6] UV data for a wide range of compounds. Deviations from the regular pattern observed for the simple alkyl compounds are seen in the spectra of 3,4-disubstituted trithiapentalenes (26-28). Two effects are operative. The first is shown by the spectra of the dimethyl (26) and propano bridged trithiapentalenes (28) where a bathochromic shift (ca 20 nm) in the long wavelength transition is observed. This cannot be due to an electronic effect since 3-methyl-1,6,6a-trithiapentalene fits into the regular pattern. The shift can be attributed to steric clash of the methyl groups. Any strain which might thus be present will most likely be alleviated by adjustment of the bond angles. This could result in a shorter S_1-S_6 distance and this has been observed in Xray measurements on a closely related molecule. An opposite and larger effect may be adduced from the spectrum of 3,4-ethano-1,6,6a-trithiapentalene (27). The bathochromic shift (ca 50 nm) has been attributed[30] to strain in the bicyclic ring system due to the presence of the ethano bridge. This has been confirmed by Xray measurements on the crystal[35] (see section on Xray data).

The two aryl compounds (34) and (35) have quite different spectra. Substitution in the 3-position has little effect on the electronic spectrum; substitution in the 2-position however introduces a new band at 322 nm. This indicates that the ring system undergoes conjugation with the 2-aryl group, but not the 3-aryl group. Xray

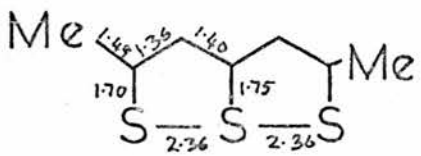
crystallographic data[36,37] for compound (36) indicates that a 3-aryl group is less likely to conjugate with the ring system than a 2-aryl group. This is due to the larger deviation from coplanarity for the 4-phenyl group compared to the 2-phenyl group.

Infrared Spectra

Infrared spectroscopy has been of little use in the elucidation of the structures of trithiapentalenes, but has found considerable application in the determination of the structures of 1-oxa-6,6a-dithiapentalenes (32) (Section E). A study[39] in 1966 indicated that trithiapentalenes had spectra similar to those obtained from substituted thiophenes, and concluded that the spectra showed trithiapentalenes to be 10π-electron aromatic systems. Aromatic character was also concluded to be present by Pietra and co-workers[40], who also noted that replacement of a terminal sulphur atom by selenium had little effect on the infrared spectrum.

Xray Crystallographic Data

In 1925 Arndt, Nachtwey and Pusch isolated an orange compound which analysed for $C_7H_8S_3$ and to which they assigned structure (37). It was over thirty years later that the structure was corrected, by Bezzi and co-workers, by Xray crystallography. Since then many compounds of the trithiapentalene type have been synthesised and during the past four to five years an increasing number of these have been analysed in the same way. The structure determination (40) revealed[41] that the sulphur atoms were colinear and that the sulphur-sulphur bond distances were equal (2.36 Å). This bond length is considerably shorter than the Van der Waals distance between two sulphur atoms (3.70 Å)[42], but longer than a sulphur-sulphur single bond in, for example, a cis-planar



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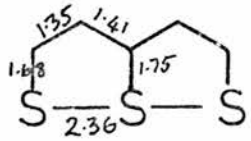

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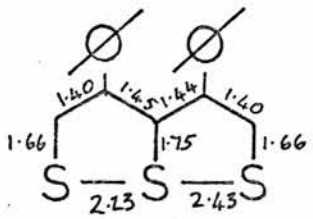

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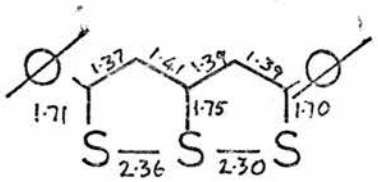

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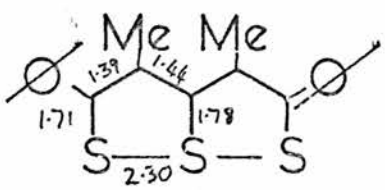

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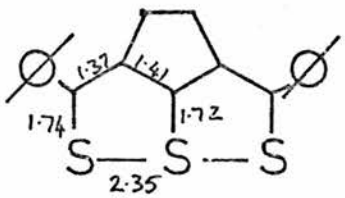

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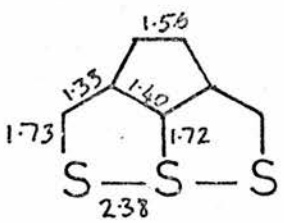

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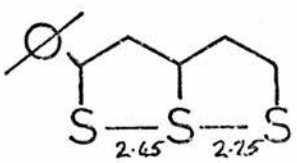

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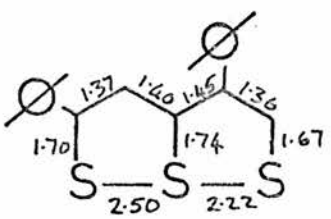

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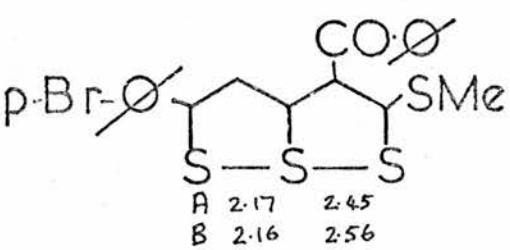

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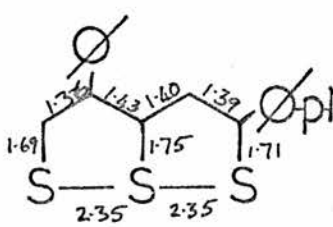

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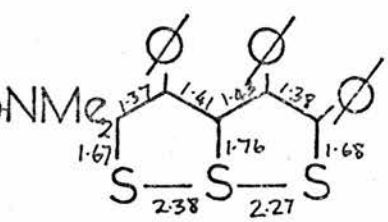

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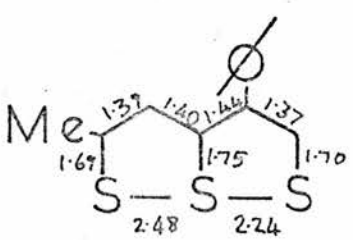

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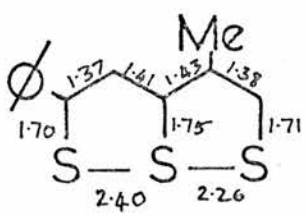

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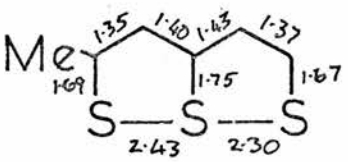

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disulphide (2.10 Å)[43]. Some degree of bonding is thus indicated. The suggestion[44] that the equal bond lengths in this compound might be due to the compound being a statistically disordered mixture of (38) and (39) has been refuted[41] within the limits of detection by Xray structural analysis. Since this first analysis numerous symmetrical structures, (41)[45], (42)[38], (43)[46], (44)[47], (45)[48], (46)[35] and unsymmetrical structures, (47)[49], (48)[50], (49)[51], (50)[52], (51)[53], (52)[54], (53)[55], (54)[56] and (55)[57] have been determined.

Equal sulphur-sulphur bond distances have been observed in the parent compound (41) and the dimethyl-diphenyl derivative (44). Similar symmetrical structures have been found for the ethano bridged compounds (45) and (46) but variations in bond lengths require some explanation. The distances between the outer sulphur atoms and between the bridging carbon atoms are longer than usually found. The S-1 - S-6 distance in compound (46) is the longest yet observed. Furthermore the bridgehead angle between C-3 and C-4 [114° for compound (45)] is considerably smaller than that found in many of the compounds, eg the parent system (41), 123°. Hence these ethano bridged compounds may be presumed to be under strain, a possibility suggested previously[30] by UV data. An opposite but smaller effect can be observed in compound (44) where the bridgehead angle is larger (126°) and the S-1 - S-6 distance is the shortest yet recorded. This may be due to the proximity of the methyl groups to each other causing strain in the opposite sense. UV data are consistent with this interpretation. The 3,4-diphenyl-1,6,6a-trithiapentalene (42)[38] shows a marked deviation from equality of sulphur-sulphur bond lengths, presumably due to clash of the bulky phenyl groups. The planes of the phenyl groups form angles of about 70° with the plane of the trithiapentalene, indicating that conjugation

is unlikely. The 2,5-diphenyl-1,6,6a-trithiapentalene (43)[46] is almost symmetrical. The small deviation from equality of S-S bond lengths in this compound is possibly due to the different "twist" angles which the phenyl groups make with the trithiapentalene.

Numerous papers[49-57] have appeared which deal with unsymmetrically substituted compounds (47-55). Only one of these compounds (50) shows equal sulphur-sulphur bonds. The differences in S-S bond lengths can be as much as 0.4 Å, the S-S bonds varying in length from 2.16 Å to 2.56 Å. The S-S bonds are thus very susceptible to the substitution pattern and their susceptibility to differences in molecular environment is illustrated forcibly by the case of 3-benzoyl-5-(p-bromophenyl)-2-methylthio-1,6,6a-trithiapentalene (49). This compound showed the presence of two crystallographically independent molecules in the crystal unit. There are numerous bond length differences between the molecules especially in the disubstituted ring. Although large variations may occur in the S-S bond lengths in any trithiapentalene, the other bonds (C-1(6) - S; C-2(5) - C-3(4); C-3(4) - C-3a) vary by no more than 0.05 Å and the central C-S bond by only 0.04 Å. Furthermore, although the differences between S-S bonds may be as much as 0.4 Å the S-1 - S-6 distance is much more constant, being in the range 4.66-4.73 Å. This excludes compounds which may introduce strain, eg. 3,4-disubstitution or may have groups with strong electronic effects, eg. benzoyl or p-dimethylaminophenyl groups as in (49) and (50).

Hordvik has undertaken a theoretical study which accounts for the effects of methyl and phenyl groups on the S-S bonds. The initial results of these CNDO/2 calculations show[58] the following:

a) A 2-methyl group lengthens the S-1 - S-6a bond

b) A 3-methyl group shortens the S-1 - S-6a bond

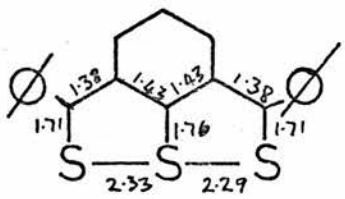
c) A 2-phenyl group lengthens the S-1 - S-6a bond, depending on the twist angle of the phenyl group. The effect is minimised for a twist angle of 0^{o} and is at a maximum for 90^{o}.

d) A 3-phenyl group causes slight shortening of the S-1 - S-6a bond, independently of the twist angle. This calculation does not conflict with any published data.

Miscellaneous Methods

Several authors[24,59,60] have published dipole moment data for trithiapentalenes. These data have been more useful in providing reference data for comparison with dipole moment data for 1-oxa-6,6a-dithiapentalenes.

Molecular core binding energies for several trithiapentalenes have been measured by Xray photoelectron spectroscopy[61]. 2,5-Dimethyl,3,4-diphenyl and the parent 1,6,6a-trithiapentalenes all give results in accord with previously published Xray crystallographic data. The prediction that 2-methyl-1,6,6a-trithiapentalene would have an unsymmetrical structure has since been confirmed by Hordvik[56]. The molecular core binding energy for S-6a in trithiapentalenes appears to be about 228.5 eV whereas the lateral sulphur atoms appear 1-2 eV lower. Lindberg, using the same technique has come to a different conclusion[153]. Examination of the Xray photoelectron spectra of symmetrically substituted trithiapentalenes has led to the conclusion that the compounds examined may have unequal S-S bonds. Unfortunately, this proposal can be neither confirmed nor denied since Xray crystallographic data are not available for the compounds which they have examined. It should be noted that the



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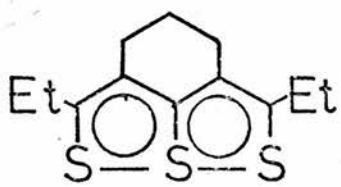

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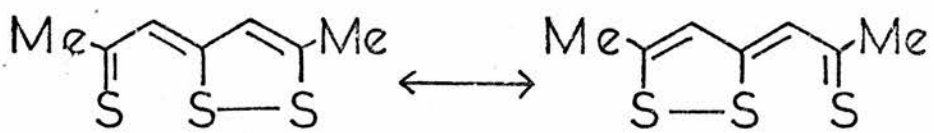

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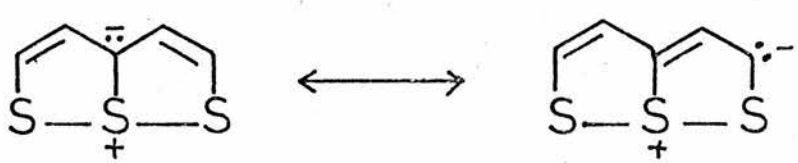

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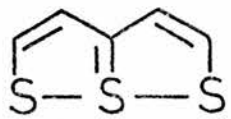
results published by both groups have been obtained by deconvolution of broad curves and may be of dubious value .

Electron spin resonance spectra have been obtained[62] for the trithiapentalene derivatives (10), (56) and (43). The spectra were obtained either by electrolytic reduction in N,N-dimethyl-formamide or by reaction with potassium in dimethoxyethane. The results are consistent with trithiapentalenes having C2V symmetry and are in accord with the M.O. model proposed by Gleiter and Hoffmann[63].

Bonding in 1,6,6a-Trithiapentalenes

The unexpected collinearity of the three sulphur atoms in 2,5-dimethyl-1,6,6a-trithiapentalene produced a structure which was not readily explained in terms of simple bonding theories. The data available show that the carbon-carbon bond lengths are of the same order as those in benzene (1.397 Å)[42], and the carbon-sulphur bonds are all shorter than single bonds (1.82 Å)[42] but longer than the hypothetical carbon-sulphur double bond length of 1.61 Å[42]. Thus some degree of π delocalisation must be present in the molecule. Giacometti and Shustarovich[65] using the one bond-no bond resonance concept (57) suggested a model with a π carbon skeleton and σ bonds between the sulphur atoms. It seems likely that this model would result in low sulphur-sulphur bond strength and hence in a none too stable molecule. Using s and p orbitals only, Lozac'h suggested[66] a contribution from the 10π electron sulphonium ylid structure (58). Delocalisation of the negative charge in this structure (59) would tend to indicate electrophilic substitution at position 2, in direct conflict with chemical evidence[15].

Use of a double bond between C-3a and S-6a introduces a quadricovalent sulphur atom (60) which may or may not require use of



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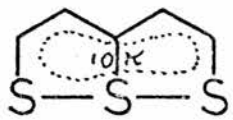

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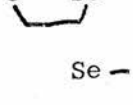
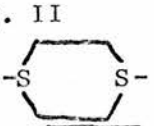
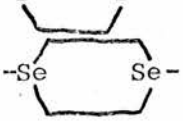
R-I-I

Fig. I	R-I	I-I	Ref.
a) R = Me_3N-	2.27	2.83	90
b) R = $(\phi CH_2)_2S$-	2.78	2.82	91
c) R = 	2.76	2.96	92
d) R = 	2.76	2.91	93

I-I-R-I-I

Fig. II	R-I	I-I	Ref.
a) 	2.87	2.79	94
b) 	2.83	2.87	95

d orbitals. Maeda[67] confirmed that σ bonding could result from hybrid pd orbitals on the central sulphur atom in the non-alternant heterocycle, trithiapentalene. Further evidence for use of d orbitals came from Johnstone and Ward[68] who obtained a measure of confirmation of their calculations by examination of the UV spectra of trithiapentalenes. Gleiter and Hoffmann[63] have considered trithiapentalenes as having an electron rich three centre bond linking the sulphur atoms, with superimposed π bonding. This type of bonding had been described previously for interhalogen compounds[69]. Calculations on potential energy functions for a model trithiapentalene were examined with and without d orbitals. The inclusion of d orbitals gave a markedly different result from that obtained without d orbitals. The authors remark that calculations on second row element molecules of unusual geometries (eg SF_4, PF_5) have shown little difference whether or not d orbitals are included. Nonetheless they believe their calculations to be reliable. The curve obtained for lateral displacement of the central sulphur atom, with d orbitals showed a broad flat minimum when the molecule is symmetrical. Indeed lateral displacement of this atom by as much as 0.1 Å had little effect on the potential energy of the system. Exclusion of the d orbitals gave a curve which showed that the molecule would have a strong preference for an unsymmetrical structure. Structure (61) would thus appear to be the best approximation for trithiapentalene.

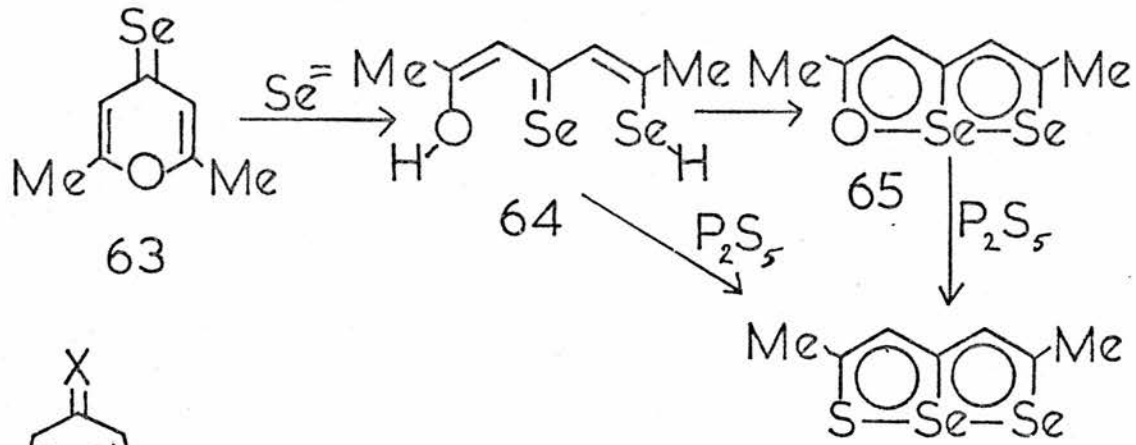
Since the bonding in these compounds has been compared to that in trihalide ions it would seem to be in order to look briefly at the data available for some of these compounds. In the trihalide ions Br_3^- [84,85] or I_3^- [86-88], the halogen atoms are arranged collinearly with equal bond distances. The bonds are longer than halogen-halogen single bonds, as in molecular bromine or iodine, but are well within

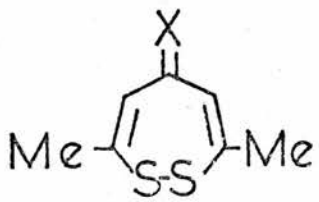
the Van der Waals contact distances. The "pseudo-halogens" thiocyanogen and selenocyanogen also form analogous salts, trithiocyanates, $(SCN)_3^-$ and triselenocyanates, $(SeCN)_3^-$ but only the latter have been found suitable for Xray crystallography[81-83]. Discussion of the triselenocyanates will be found more relevant when compared to data for 1,6,6a-triselenapentalenes (section D). Halogens have also been found to form addition compounds with electron donors such as amines, sulphides and selenides. Some of these are shown with references in figures I and II. These compounds show the interhalogen bond lengths and the donor-halogen bond lengths to be longer than the usually accepted single bond lengths but within the Van der Waals contact distances for these atoms. Series of complexes of Te(II) and (IV) with halogen, thiosulphate and thiocarbonyl and selenocarbonyl compounds have been reviewed by Foss.[89]

All these compounds have been formulated as having electron-rich three centre bonds. The question of d orbital participation has not yet been resolved, although spectral data (Mossbauer[96], nuclear quadrupole resonance[97-99]) have been cited[89] and interpretation of these spectra does not require the use of d orbitals.

D. Substitution of Selenium for Sulphur in Trithiapentalenes

The replacement of sulphur by selenium in trithiapentalenes has been of interest for several years. The first work in this field was done by Traverso[70] but interpretation of his work is hindered since at that time the correct structure for trithiapentalenes was not known and structure assignments were made on the basis of the seven-membered ring formula (62). Using the bicyclic formulae for trithiapentalene derivatives it is possible to interpret





X:O, S, Se

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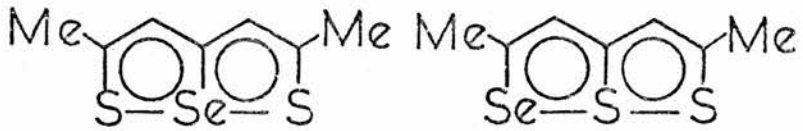

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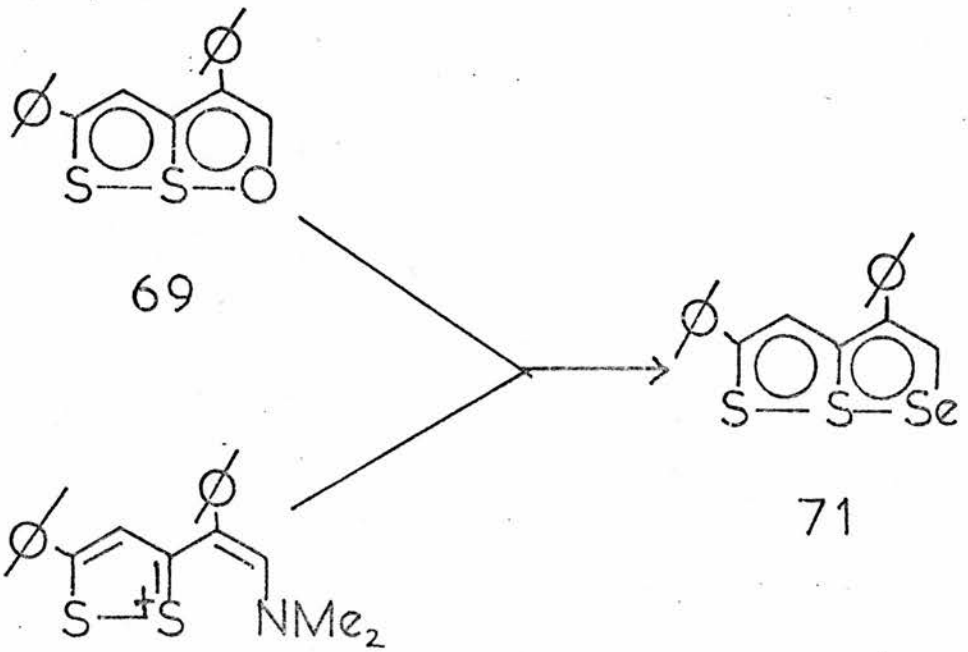

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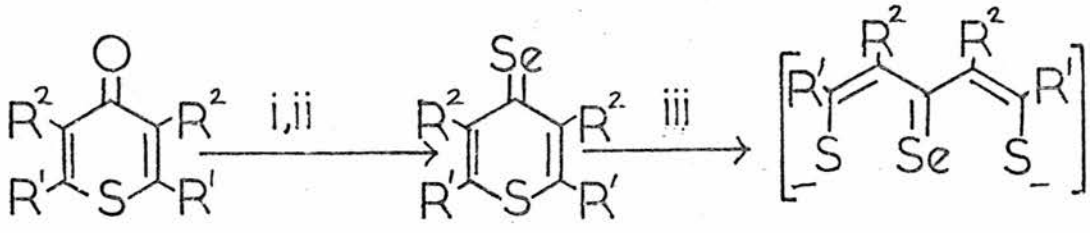
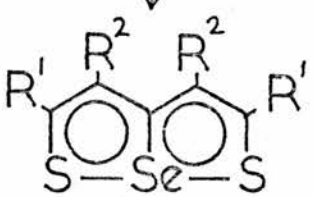


72 73 74

a) R¹: H, R²: H
b) R¹: H, R²: Me
c) R¹: ∅, R²: H

i) $POCl_3$/D.M.F.
ii) K_2SeSO_3
iii) Na_2S / D.M.S.O.
iv) $K_3Fe(CN)_6$



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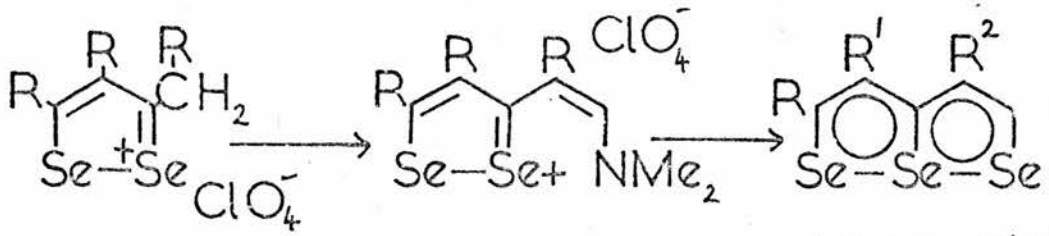
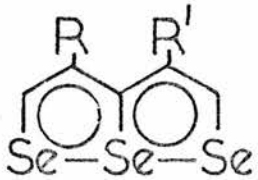


76 77

a) R: Me; R¹,R²: H
b) R: H ; R¹,R²: Me
c) R: ∅; R,R: H

78

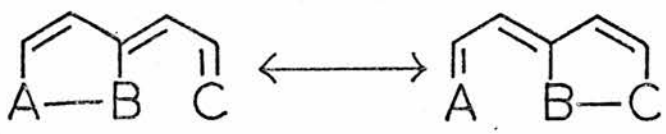


a) R, R¹: H
b) R-R¹: $-CH_2CH_2CH_2-$

79

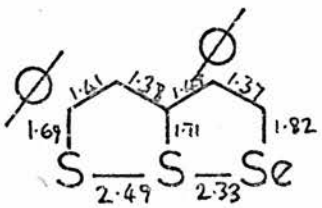
this early work. Ring opening the 4H-pyran-4-selenoketone (63) with sodium selenide gave the intermediate (64) which was isolated by careful acidification. Aerial oxidation of this compound gave 2,5-dimethyl-1-oxa-6,6a-diselenapentalene(65). Thionation of compounds (64) or (65) gave a pentalene derivative containing two selenium atoms, formulated here as (66). This compound was purified by crystallisation. Later workers[40,60] have isolated a monoselenium analogue from thionation of (65) which they formulated as the unsymmetrical structure (68) in view of its IR spectrum. This result must be held in doubt since exchange of the central selenium atom would be very unlikely under the reaction conditions. Structure (67) is more likely.

Klingsberg[71] and Reid[14] have both synthesised 2,4-diphenyl-1,6a-dithia-6-selenapentalene (71); the former from the oxygen compound (69) with phosphorus pentaselenide; the latter from the Vilsmeier salt (70) with sodium hydrogen selenide. Since then Reid has modified his synthetic route to 1,6,6a-trithiapentalene (Scheme III) to give the symmetrical 1,6-dithia-6a-selenapentalenes (75). Treatment of 4H-thiopyran-4-ones (72) with phosphoryl chloride in dimethyl formamide and then aqueous potassium selenosulphate gave the unstable selenoketones (73), which were used without isolation and purification. Ring opening the selenoketones (73) in dimethyl-sulphoxide with aqueous sodium sulphide gave deep purple solutions of the anions (74) which were readily oxidised to the dithiaselena-pentalenes (75). Yields were good for compounds (75a) and (75b) (ca 35%) but poor for the diphenyl compound (75c) (14%) due to the instability of the selenoketone (73c). 3-Methylene-1,2-diselenolium salts (76) condense[73] with dimethylthioformamide in acetic anhydride in the same manner as dithiolium salts[14], to give Vilsmeier salt



A,B,C : S,Se

80 81



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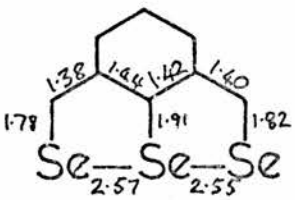

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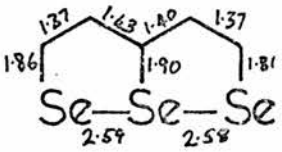

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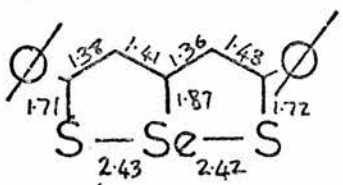

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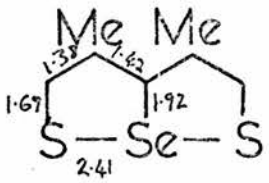

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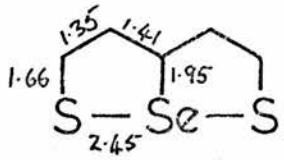
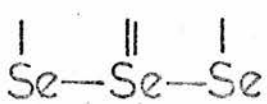


86

Cpd		Se^1-Se^3 Å	Se-Se
87	$K(SeCN)_3 \cdot \frac{1}{2}H_2O$	5.34	2.67
88	$Rb(SeCN)_3 \cdot \frac{1}{2}H_2O$	5.32	2.66
89	$Cs(SeCN)_3$	5.30	2.65
90	$[SeC(NH_2)_2]_3Cl_2 \cdot H_2O$	5.32	2.66
91	$[SeC(NH_2)_2]_3Br_2 \cdot H_2O$	5.33	2.67



92

intermediates (77). These, on hydrolysis with sodium hydrogen selenide, gave the 1,6,6a-triselenapentalenes (78) in low yield. In a similar synthesis Jackson has also prepared[73] the parent compound (79a) and the bridged compound (79b).

Nmr spectral data for these compounds indicates a close structural similarity to the trithiapentalenes, the main difference being the deshielding of ring protons relative to the corresponding protons in the sulphur compounds. For the dithiaselenapentalenes (75), the ring protons are moved downfield by about 0.35 ppm compared to the sulphur compounds. 5-H in compound (71) has moved even further downfield (by 0.78 ppm) but this is still more than 2 ppm upfield of the selenoformyl proton resonance in the most polarised selenoaldehyde yet observed[74] (δ11.97). The equivalent protons, 2-H or 5-H, in the triselenapentalenes(78 and 79) resonate in the range δ10.1-10.4. The spectra also show magnetic equivalence of identical protons. No evidence for one bond-no bond resonance (80 $\rightleftharpoons$ 81) has been obtained and indeed the spectra of the dithiaselenapentalenes are unchanged down to -60°C.

Xray crystallographic data are available for a number of these selenium compounds, (71)[71], (82)[75], (83)[76], (84)[77], (85)[78] and (86)[79]. Data for the dithiaselenapentalene (71) shows that the effect of substitution of selenium for sulphur in this molecule is small. This contrasts what will be seen for the oxygen compound (87) (section E). The carbon-carbon and carbon-sulphur bond lengths in the dithiaselenapentalenes(84) and (86) are almost identical to those in the corresponding sulphur compounds. Comparative data for the triselenapentalenes is not readily available. However it can be noted that the selenium-selenium bond lengths (ca 2.58 Å) are longer than the normal single bond (2.34 Å)[42] but are still

considerably shorter than the Van der Waals contact distance (3.80 Å)[42]. The interaction of three selenium atoms arranged in a linear sequence has been investigated, as previously mentioned, in inorganic pseudohalogen salts such as the triselenocyanates (87)[81], (88)[82] and (89)[83] and in the oxidation products of selenoureas (90) and (91)[83]. These compounds have all been observed to have the structure type shown in (92), and Foss has described these compounds as having four electron three centre bonds. The triselenapentalenes have close structural similarity to these compounds but with the added stability from a superimposed π system. The π system has the effect of reducing the distance between the selenium atoms (ca 0.4 Å) thereby increasing the overlap and hence the bonding between the selenium atoms. It is perhaps unfortunate that this type of correlation cannot be observed for the trithiapentalenes due to the trithiocyanate ion never having been isolated.

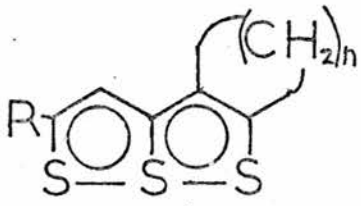
E. Analogues of Trithiapentalenes

The first reaction of a trithiapentalene to be investigated[11] was the ready replacement of one sulphur atom by oxygen. Since then, in the light of the correct formula, it has been of interest to prepare analogues of trithiapentalenes in which the terminal sulphur atoms are replaced by oxygen or nitrogen. 3-Aza and 3,4-diaza trithiapentalenes are now known and the thiocarbonyl group of the so-called one bond-no bond resonance formula has been replaced by a nitroso group. Since the main part of this thesis will be concerned with oxygen analogues of trithiapentalenes these will receive more detailed attention than the nitrogen compounds.

93

R: Ø, p-Cl-Ø, p-MeOØ.

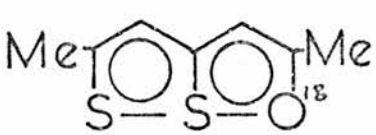
94



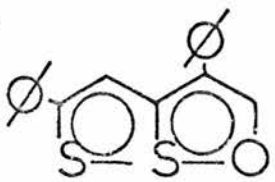
R: Ø; n: 3,4

95

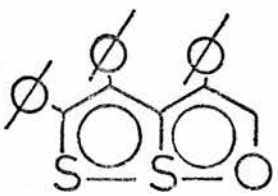
96



97



69



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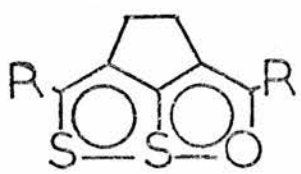
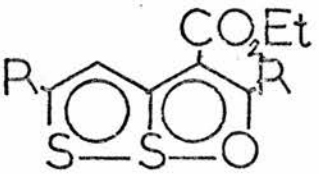


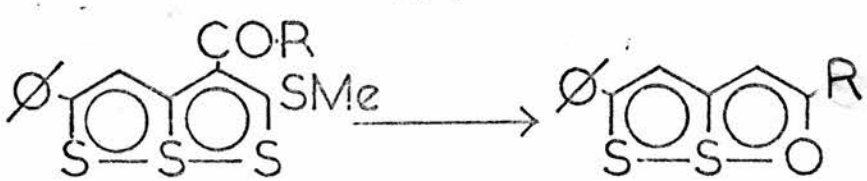
R, aryl

99



R, aryl

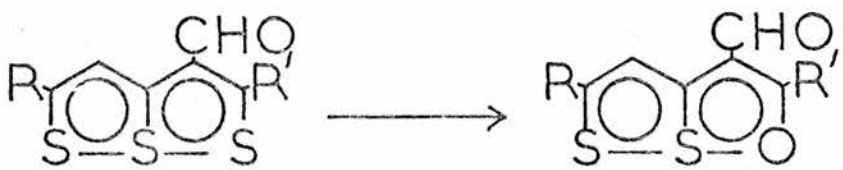
100



R: Ø, OEt

101

102



a) R, R′: aryl

b) R: Ø, t-Bu ; R′, H

103

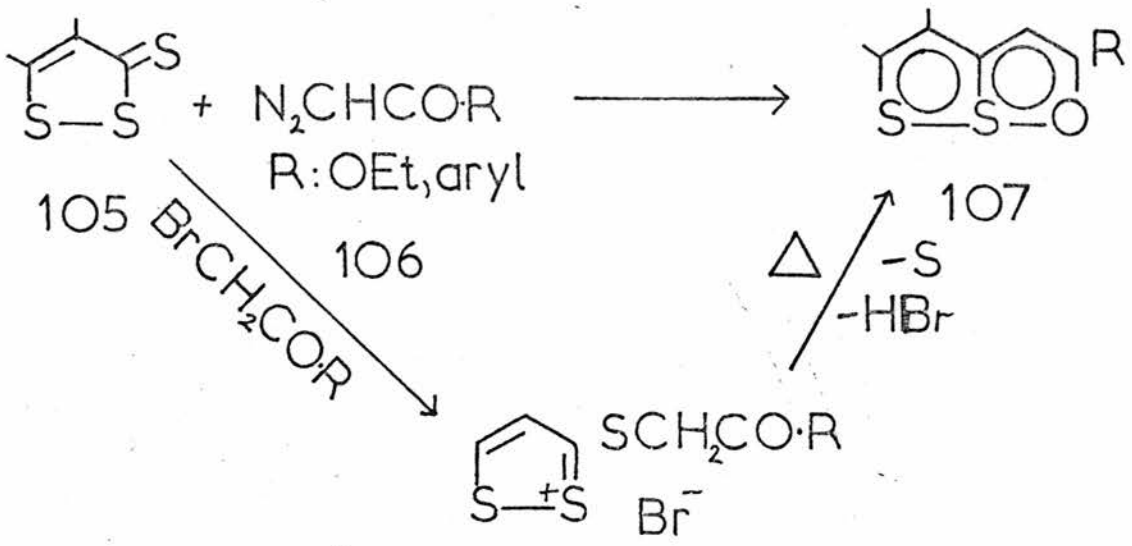
104

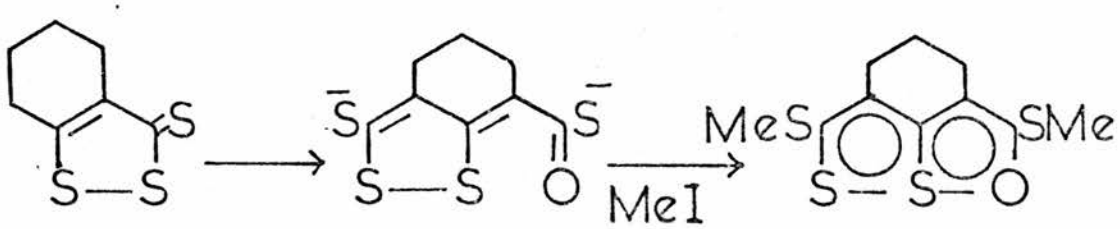
(i) 1-Oxa-6,6a-dithiapentalenes

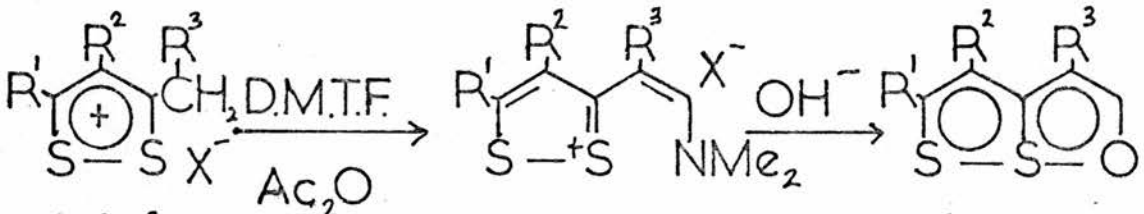
Numerous routes to 1-oxa-6,6a-dithiapentalenes are known, since these compounds have often been intermediates in synthetic routes to 1,6,6a-trithiapentalenes. These compounds together with trithiapentalenes have been reviewed[6] by Lozac'h. Since the subject of this thesis is concerned mainly with oxygen analogues of trithiapentalenes it is in order to examine routes to 1-oxa-6,6a-dithiapentalenes.

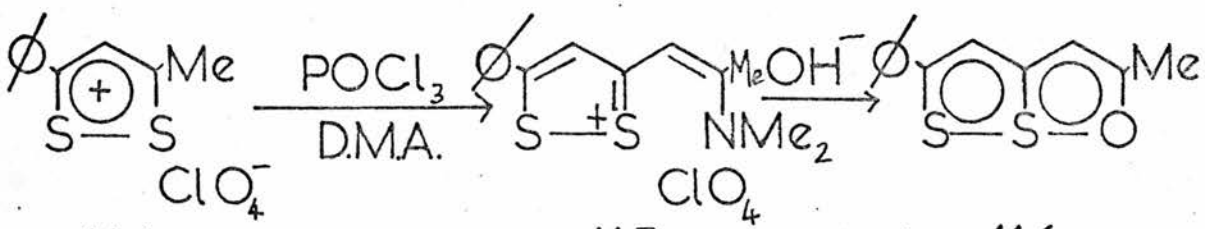
Desulphurisation of trithiapentalenes, by three main routes, has received much attention. These involve strong acids, mercuric acetate or per-acids. Arndt prepared[11] the first oxygen analogue (93) by treatment of 2,5-dimethyl-1,6,6a-trithiapentalene with concentrated sulphuric acid. Use of this reagent or 70% perchloric acid is effective in desulphurising numerous diaryl (94)[102,103] or aryl-alkyl (95)[104] trithiapentalenes. Recently the method has been used[105] to prepare the O^{18} oxadithiapentalenes (96) and (97) for an infrared study. Mercuric acetate has found more general use than acid. Most compounds examined by desulphurisation tend to be highly substituted aryl derivatives; the following have been prepared: 3,5-diphenyl-[106], 3,4,5-triphenyl-[107], 2,5-diaryl-3,4-ethano-[108] and 2,5-diaryl-3-carbethoxy-1-oxa-6,6a-dithiapentalenes[109]. Desulphurisation[27] of 3-acyl-2-methylthio-1,6,6a-trithiapentalenes (101) by mercuric acetate is unusual in that a dithioester group is lost and the acyl group moves into the linear sequence (102). 3-Formyl-1,6,6a-trithiapentalenes (103) have been desulphurised[15,111] in good yield by mercuric acetate to give 3-formyl-1-oxa-6,6a-dithiapentalenes (104). Per-acid has also been used to desulphurise 2,5-diaryl[112] and 3-formyl-2,5-diaryl-1,6,6a-trithiapentalenes.

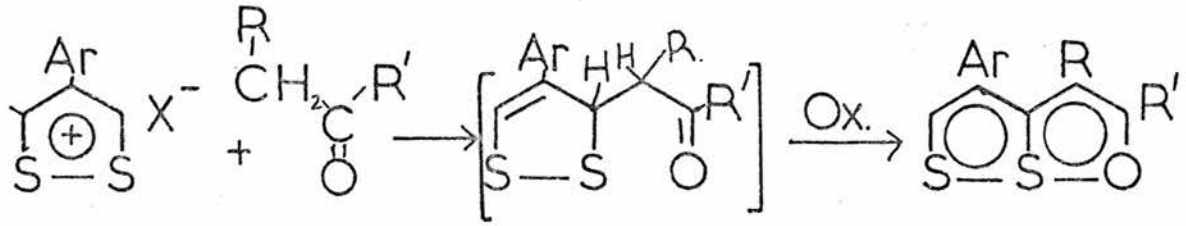
Derivatives of the 1,2-dithiole system have provided a


+ N2CHCO·R
R: OEt, aryl
105
106
107
BrCH2CO·R
Δ
-S
-HBr
SCH2CO·R
Br⁻
108

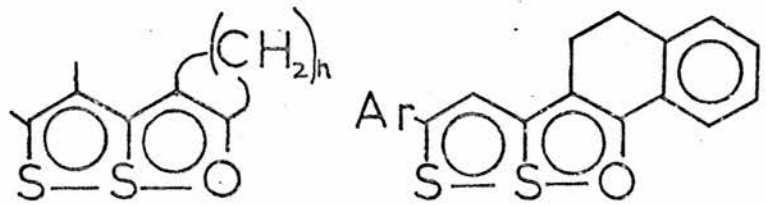

MeI
109
110


D.M.T.F.
Ac2O
OH⁻
R', R², R³, alkyl or aryl
111
112
113


POCl3
D.M.A.
ClO4⁻
114
115
116

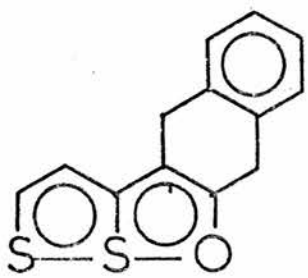


117 118 119



n: 3,4,5,6

120 121



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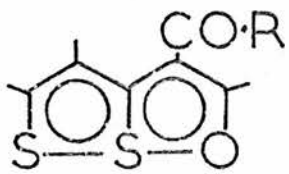

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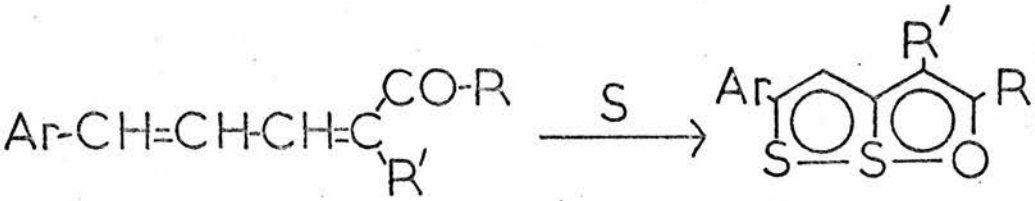
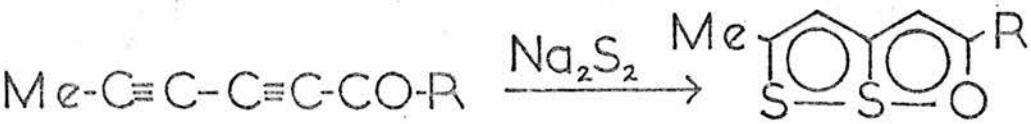


R, alkyl, aryl, OMe

R′, H, alkyl, aryl

124

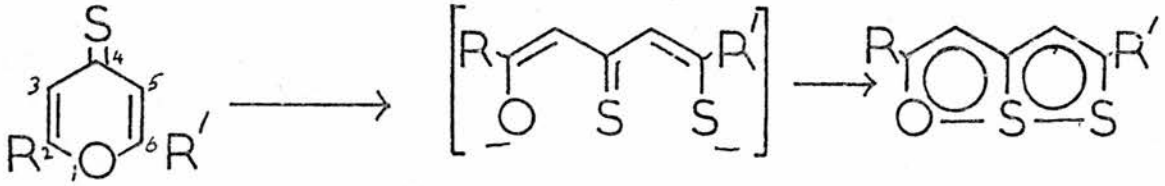


R: H, Me, Ø

125

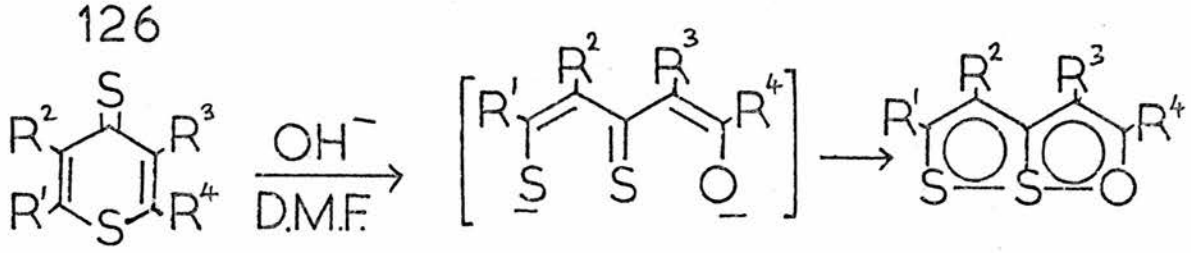
number of routes to 1-oxa-6,6a-dithiapentalenes. 1,2-Dithiole-3-thiones (105) react with α-diaza-acyl compounds (106) at 150°C to give oxadithiapentalenes (107). The quaternary salt (108) formed[115] by reaction of a 1,2-dithiole-3-thione (105) with an α-haloketone[114,116] undergoes loss of hydrogen bromide and sulphur to give an oxadithiapentalene (107) in good yield. The acidic nature[117] of a 5-methylene group in 1,2-dithiole-3-thiones facilitates its condensation with carbon oxysulphide, in the present of base, in dimethylsulphoxide, leading to the dianion (109) which gives the oxadithiapentalene (110) on treatment with methyl iodide. The reactivity of a methylene group in the same position of 1,2-dithiolium salts (111) has been utilised[14], as previously mentioned for trithiapentalenes, in the synthesis of a series of Vilsmeier salts (112). Hydrolysis with hydroxide[14] gives the oxadithiapentalenes (113) in good yield. Similarly[102] 3-phenyl-5-methyl dithiolium perchlorate (114) has been condensed with dimethylacetamide to give the intermediate Vilsmeier salt (115) which was hydrolysed to the oxadithiapentalene (116).

The condensation between a 1,2-dithiolium salt (117) and an activated methylene group has been investigated[119,120] by Klingsberg and shown to give intermediates of the type (118). With a simple substrate such as acetone this intermediate is stable and isolable, but with aryl substrates such as acetophenone the intermediate dehydrogenates spontaneously to the product (119). Where no internal oxidation takes place use of chloranil smoothly converts the intermediate (118) into the oxadithiapentalene (119). This reaction has been extended to include cyclic ketones; this leads to intermediates which dehydrogenate spontaneously giving the following products: (120)[121,122], (121)[123] and (122)[113]. Use has



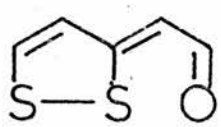
R, aryl
R', H, Me

126 128 127

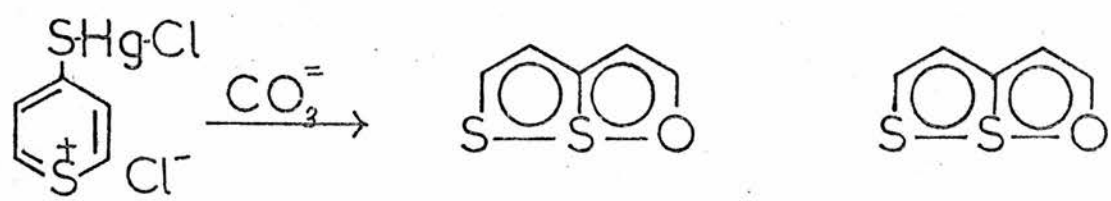


129 130 131

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



134



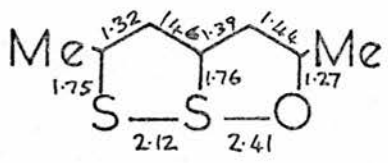
132 133 135

also been made[124,125] of compounds with active methylene groups and these lead to acyl oxadithiapentalenes (123). 3-Methylthio-1,2-dithiolium cations also condense with active methylene groups and lead to a variety of products. However the products obtainable by this route are more easily prepared[121] by the ketone/dithiolium salt method usually in better yield.

Aliphatic, unsaturated ketones or esters (124) provide an entirely different route to oxadithiapentalenes by a high temperature reaction with sulphur[124,126-129]. α,γ-Diacetylenic carbonyl compounds (125) react readily with sodium disulphide to give oxadithiapentalenes in good yield.

4H-Pyran-4-thiones and 4H-thiopyran-4-thiones have both served as starting materials for the synthesis of oxadithiapentalenes. Treatment of 4H-pyran-4-thiones with potassium hydrogen sulphide gives[23,131-133] oxadithiapentalenes with an aryl group at position 2. This must arise from nucleophilic attack in the ring at position 6. Further evidence for this comes from the ring opening of 2-phenyl-4H-pyran-4-thione (126, R = Ø, R' = H) with sodium hydrogen sulphide in DMF, ie under conditions of enhanced nucleophilicity for the sulphide ion, to the anion (128, R = Ø, R' = H). Use of 4H-thiopyran-4-thiones[10] leads to the other isomers. Nucleophilic attack on thiopyranthiones (129)[10] in DMF by hydroxide led to the anions (130) which were oxidised by ferricyanide to the oxadithiapentalenes (131). This method failed in the case of the parent system (129, $R^{1,2,3,4}$ = H)[134]. However Traverso in his synthesis of trithiapentalene did obtain this compound (133) in 28% yield by treatment of the mercuric chloride complex (132) with sodium carbonate.

Two formulations are possible for these compounds, a monocyclic (134) or a bicyclic (135) structure. From the previous



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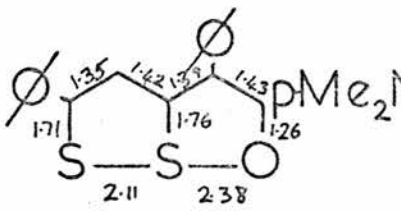

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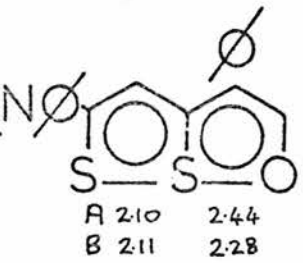

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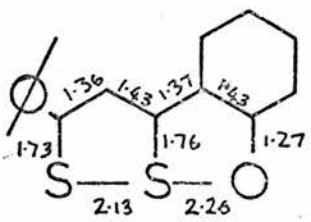

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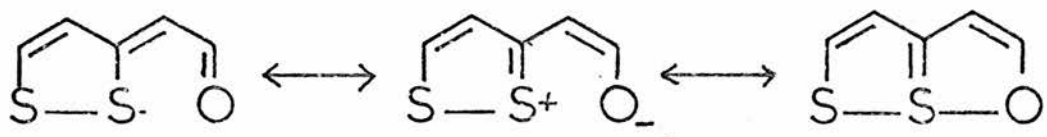
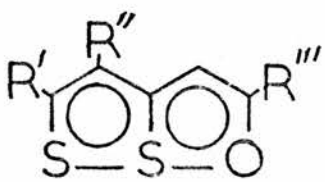


a b c

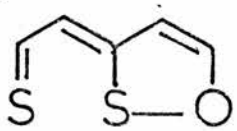
140

141

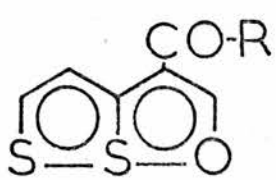


R′,R″: alkyl, aryl

142



d



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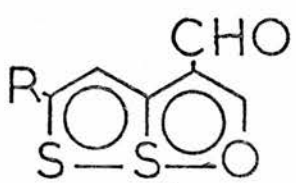


R: Bu^t, Ø

144

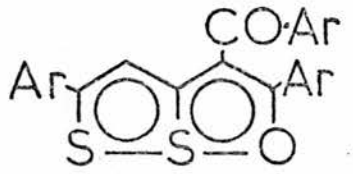
discussion on the structure of trithiapentalenes Xray crystallography would appear to be a good starting point for a discussion of the structure of the oxadithiapentalenes. Several compounds have been examined, including 2,5-dimethyl (136)[135], 3,5-diphenyl (137)[136], 2-(p-dimethylaminophenyl)-4-phenyl (138)[137] and 2,3-butano-5-phenyl-1-oxa-6,6a-dithiapentalene (139)[138]. Before discussing the data obtained for these compounds it is important to point out that the length of a sulphur-sulphur single bond varies with its molecular environment[139]. Taking the value of 2.10 Å for a sulphur-sulphur single bond as found in a cis-planar disulphide[43] as the normal length for this type of bond it must be noted that the sulphur-sulphur bond lengths found in the oxygen compounds (2.10-2.13 Å) are very close to this value and when compared to normal S-S bonds cannot be called long bonds of the type found in the trithiapentalenes. Examination of the resonance forms (140) which may be considered to contribute to the structures of these molecules, a monocyclic structure requires the molecule to have a dithiole ring (140a, b). The S-S bond lengths in dithiolium salts have been found[140-142] to lie in the range of 2.02 Å and on this basis the S-S bonds in oxadithiapentalenes can be called long bonds.

Furthermore the sulphur-oxygen Van der Waals contact distance (3.25 Å)[42] is considerably longer than any of the S-O bond lengths found for the oxygen compounds (136-139) (2.26-2.44 Å) which implies some degree of bonding interaction. Leung and Nyburg have suggested[143] that in a molecule of this type (141) the larger the difference in electronegativity between the sulphur atom and the heteroatom (X) the shorter will be the S-S bond length. Since oxygen is very much more electronegative than sulphur this may account for the S-S distance being less than the S-S distance in trithiapentalenes. It can also be noted that carbon-sulphur

bond lengths are very similar to the bond lengths found in trithia-pentalenes but that in the "oxathiole" ring there is a variation in the carbon-carbon bond lengths. The C-2 - C-3 bond is longer and the C-3 - C-3a is shorter than corresponding bonds in trithiapentalenes. This would seem to imply that formula (140a) might still make a contribution to the ground state of the molecule.

The infrared spectra of the oxadithiapentalenes have provided evidence of a sulphur-oxygen interaction. These compounds do not show a normal carbonyl stretching frequency. Indeed there is generally no absorption in the range 1600-1750 cm^{-1}. The range 1530-1590 cm^{-1} has been suggested[124,125,144,146] as that in which the "carbonyl" stretching frequency occurs. This has been confirmed[105,145,148] by examination of the infrared spectra of O^{18} enriched oxadithiapentalenes. This generally showed one new band occurring 10-12 cm^{-1} lower than the supposed carbonyl stretching band in the O^{16} compound. Aryl compounds (142, R''' = aryl)[105,124,125,144,145] have a lower CO stretching frequency range (1530-1560 cm^{-1}) than alkyl compounds (142, R''' = H, alkyl)[105,138,145,148] (1570-1590 cm^{-1}). The suggestion[130] that νCO for compound (136) occurs at 1460 cm^{-1} is thus invalid. It is apparent that a carbonyl stretching frequency in this range means that the carbonyl group is extremely polarised, ie has considerable single bond character. It has been suggested[145] that there is only about 35% double bond character in the "carbonyl" group of these compounds and this has led to interpetation as evidence of a S-O interaction, ie formula (140c).

Numerous dicarbonyl compounds (143) are known and it is interesting to note that two carbonyl stretching frequencies can be observed. The 3-formyl-1-oxa-6,6a-dithiapentalenes (144) show



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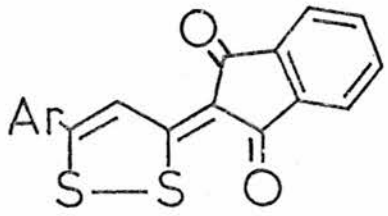

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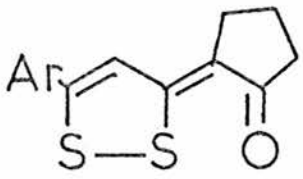

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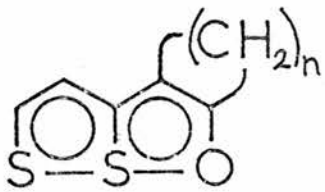
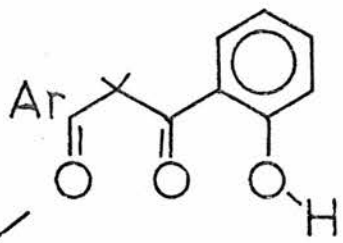


(n:4,5,6)

148

152



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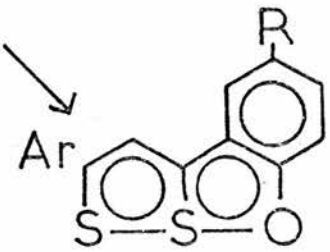

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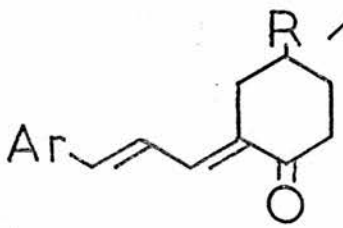

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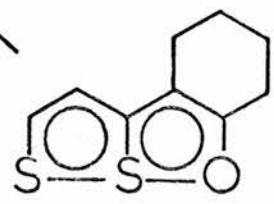

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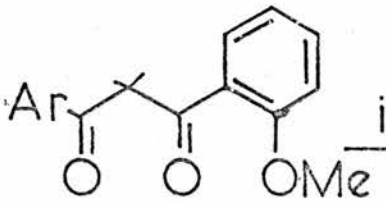

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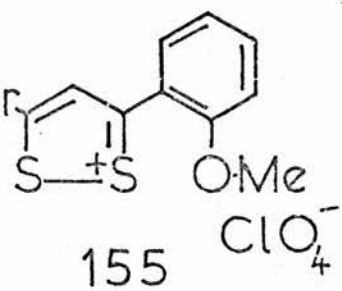


155

S 190°

S

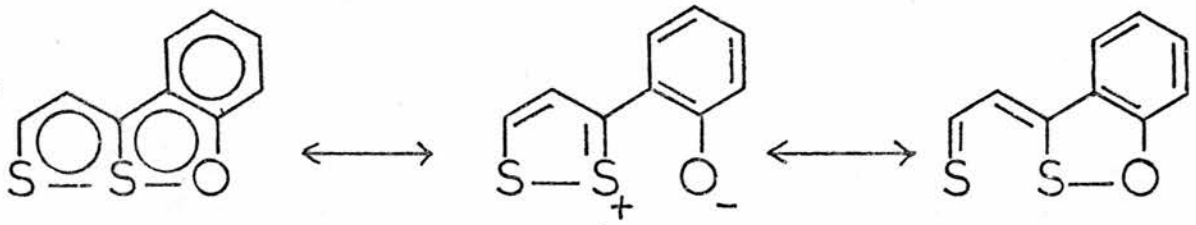
Py.

i

(i. H_2S_2 / $HClO_4$)

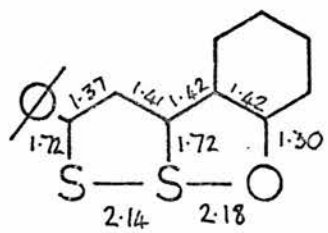
bands at 1660 cm^{-1} and 1575 cm^{-1} corresponding to the stretching mode of the formyl group and the ring CO respectively. The 3-aroyl-1-oxa-6,6a-dithiapentalenes (145) also show bands due to two stretching modes at 1635 cm^{-1} and 1540 cm^{-1} assigned as above. Abnormal stretching frequencies in dicarbonyl compounds of this type are observed[144] in the indanedione derivative (146). Here a monocyclic structure must be favoured since the ring CO stretch occurs at 1640 cm^{-1} indicating a carbonyl group which is only slightly polarised and hence allows little S-O interaction. Another compound with an abnormal ring CO stretching frequency (1630 cm^{-1}) is (147)[146]. Other members of this series (148) have normal (ca 1570 cm^{-1}) stretching frequencies. The only explanation for the abnormalities in these compounds is strain due to the presence of the five-membered ring.

An interesting series of compounds within the oxadithiapentalene class of compounds are the benzo[b]-1-oxa-6,6a-dithiapentalenes (149). Four main methods have been used for their synthesis: heating cinnamylidene cyclohexanones (150) with sulphur at 190°C; dehydrogenating tetrahydrobenzo-[b]-1-oxa-6,6a-dithiapentalenes (151) with sulphur[24] (essentially the same method); condensation of a methylthiodithiolium salt (152) and phenoxide ion[24]; treatment of 1-aryl-3(o-hydroxyphenyl)-propan-1,3-dione (153) with phosphorus pentasulphide in pyridine. This latter method suffers the disadvantage that considerable quantities of 2-aryl-benzo[b]-4H-pyran-4-thiones are produced. This side-product can be avoided by using Vialles method[147] in which a 1-aryl-3-(o-methoxyphenyl)-propan-1,3-dione (154) is condensed with hydrogen disulphide to give a dithiolium salt (155) which on being boiled in pyridine yielded the product (149).



a b c

156



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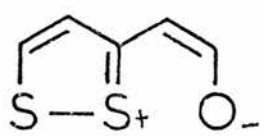

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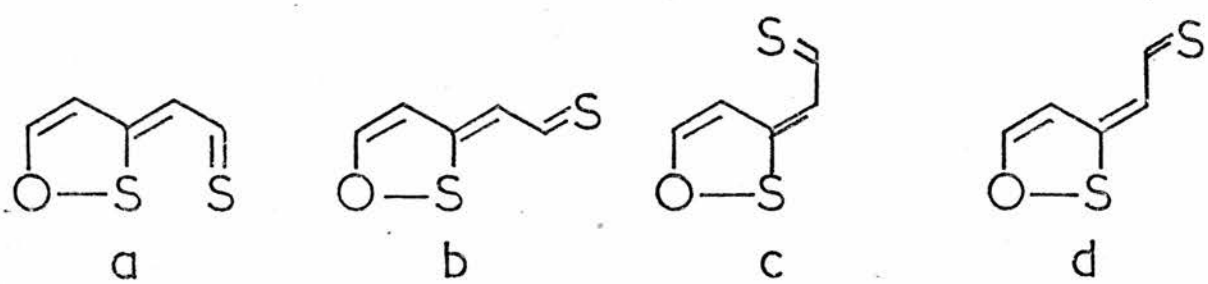
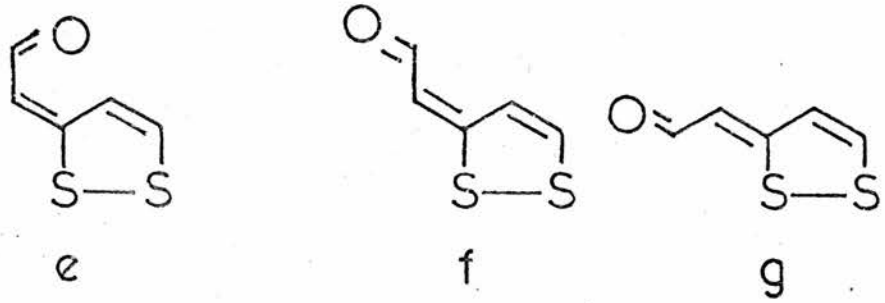
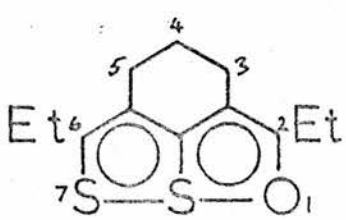


a b c d



e f g

159



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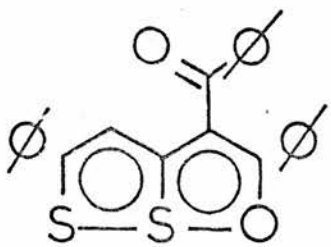


161

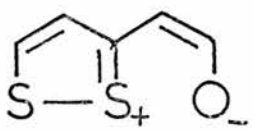
Replacement of O^{16} by O^{18} in compound (156) showed[148] that only one band was moved in the infrared spectrum. This was the band which occurred at 1284 cm^{-1} and is believed to be due to coupled vibrations with the phenolic ring. Only the structures (156a,b,c) can contribute to the ground state of the molecule and thus a short S-O bond distance was anticipated before the structure determination (157)[148] was performed. The sulphur-oxygen distance is the shortest seen for a compound of this type and must add weight to the infrared spectroscopic evidence for a considerable contribution from structure (156a). Furthermore the dipole moment of this compound is only 4.40 D which is much lower than the dipole moment of 13 D, calculated for the ionic form (156 b)[24]. Dipole moments for simple oxadithiapentalenes also occur in this range (3.8 - 4.7 D)[29,59,60,146] and hence ionic structures such as (158) are unlikely to contribute greatly to the ground states of these molecules.

Whereas nmr spectroscopy has been used with much success in showing magnetic symmetry and aromaticity for trithiapentalenes, the technique has not provided really useful information for the oxadithiapentalenes. Sulphur-oxygen interaction can be deduced from nmr spectroscopy since the 2-H signal resonates at higher field (δ9.27-9.38)[14,16,30] than what is considered normal for aldehydes (δ9.5-10.0). Xray photoelectron spectroscopy[153] also adds little to what has already been stated except that structure (140d) can contribute very little to the ground state of the molecule. No definite information about sulphur-oxygen interaction can be obtained by this method. UV and visible spectra show close similarities[14,16,18,119] to the trithiapentalenes, the visible band having undergone a hypsochromic shift (470 to 420 nm), the

short wavelength band being unchanged and the remaining band having undergone a bathochromic shift (260 to 395 nm). Again this spectroscopic technique gives little new or useful information.

Oxadithiapentalenes have been observed[149-152] to undergo a photochemically induced isomerisation. Seven structures are possible for this isomer (159a-g). Gleiter and co-workers[151] have gone to some trouble to eliminate some of the isomeric possibilities. Their spectroscopic investigation of this isomer was possible due to its stability ($t_{\frac{1}{2}}$ ca 6 hours). Large differences between the nmr spectra of the isomer and the starting material rule out a, b and g. These isomers, together with f, are also ruled out since the oxadithiapentalene (160) is photo-stable, and the only transitions possible for this molecule are rotation about either of the bonds 2-3a or 5a-6. The infrared spectra of the photoproduct and the O^{18} photoproduct indicated the presence of a free carbonyl group which can only occur for isomer e. Pedersen and Lohse are more direct in their approach and note that in a matrix of poly-methylmethacrylate the photoisomer is readily formed but reverts to the starting material only reluctantly. This rules out O-S bonded isomers (a,b) since these would not be so affected by a viscous medium. Furthermore, the photostability of compound (161) rules out the other O-S bonded isomers (c,d) and the known[125] trans structure of the starting material precludes the cis isomers (f,g). The structure must therefore be (159e).

The oxadithiapentalenes have received little theoretical treatment compared with the trithiapentalenes. An extended Hückel molecular orbital calculation shows[154] sulphur-oxygen overlap and hence covalent bonding between these atoms to be small or nonexistent. A more sophisticated CNDO/2 calculation[153]



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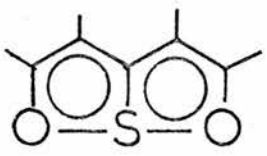

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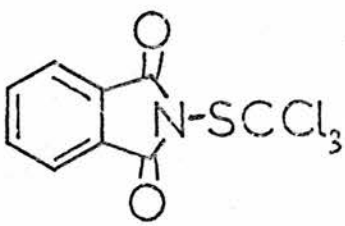

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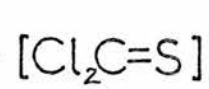

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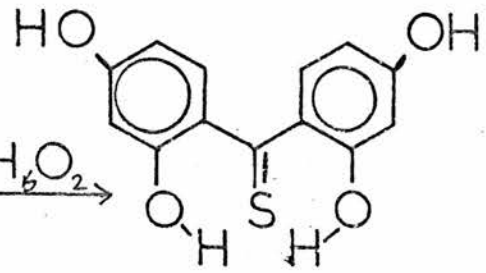

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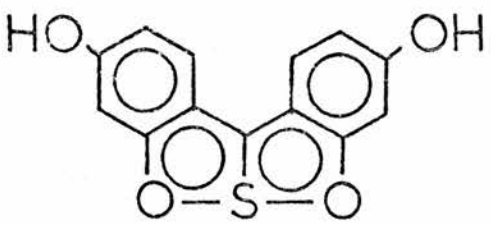

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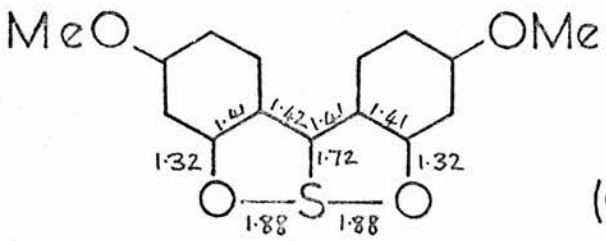

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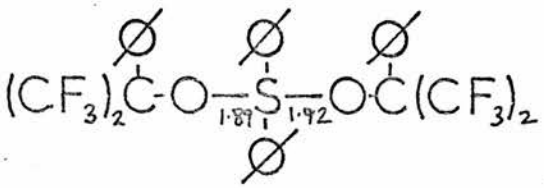


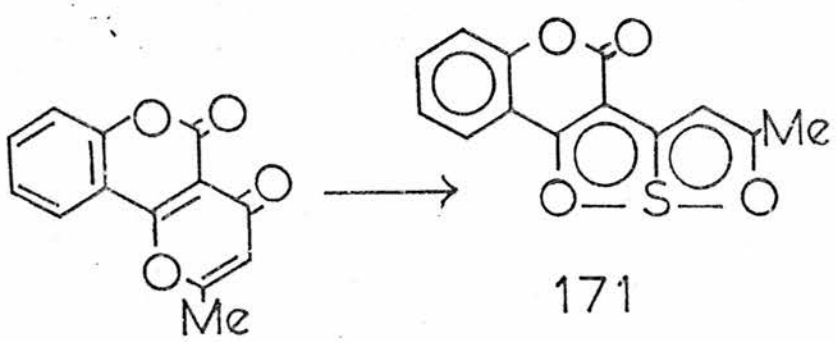
170

suggests that there is a "non-bonding" interaction between the dithiole ring and the carbonyl oxygen simply due to electrostatic interaction between oppositely charged parts of the molecule. This result must be held in doubt since experimentally a charged structure with a considerable contribution from (162) seems unlikely.

The evidence thus presented indicates that oxadithiapentalenes may be represented as bicyclic structures (163). However in these compounds the sulphur-oxygen interaction cannot be regarded as being as strong as the sulphur-sulphur interaction in trithiapentalenes, but it must be noted that the preferred conformation for the oxadithiapentalenes is the linear sequence of atoms and that energy (eg light) is required to break this sequence.

(ii) 1,6-Dioxa-6a-thiapentalenes

1,6-Dioxa-6a-thiapentalenes (164) have received comparatively little attention until recently when the first derivative (165) was obtained[155,156] by fusion of captan (166) with resorcinol at 120-130°C. It is suggested[158] that the captan decomposed to form thiophosgene (167) which thioacylates resorcinol. The resulting intermediate (168) then undergoes oxidative coupling to yield the product (165). The structure was determined[157] by Xray crystallographic techniques using the dimethyl ether (169). The sulphur-oxygen bonds (1.88 Å) are considerably longer than the sum of the covalent radii for sulphur and oxygen (1.70 Å)[42] and much shorter than the Van der Waals contact distance (3.25 Å)[42] for these atoms. Comparable sulphur-oxygen bond lengths have also been observed[159] in a diaryl-dialkoxysulphurane (170). Pomerantz observes that these dibenzodioxathiapentalenes cannot be described by the



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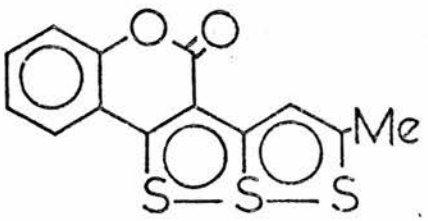

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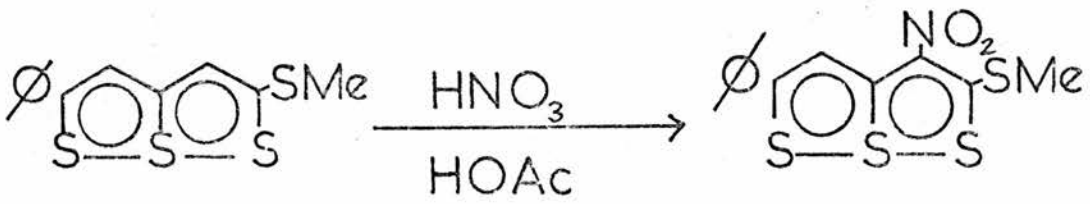

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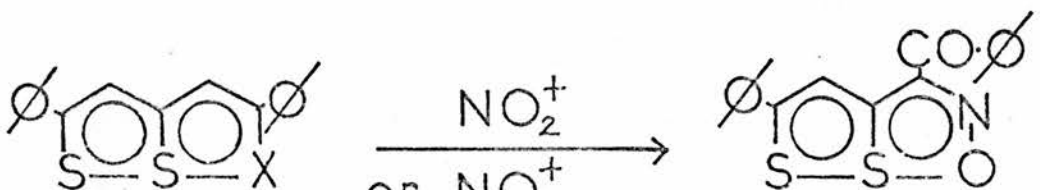

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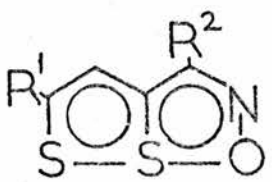
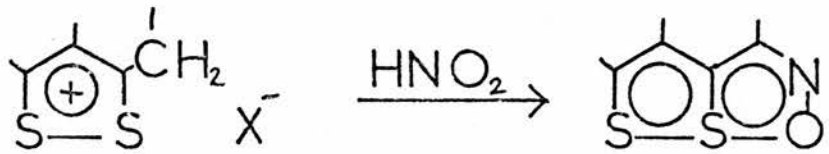


179

	R^1	R^2
a	Ø	ØCO
b	Ø	CS_2Me
c	Ø	$CSNMe_2$
d	MeS	CS_2Me
e	Ø	H



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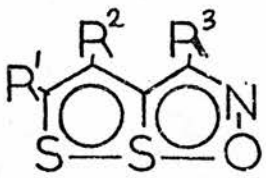
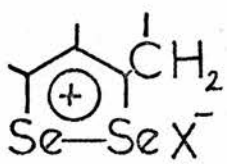
Scheme IV



181

	R^1	R^2	R^3
a	H	H	H
b	Bu^t	H	H
c	Ø	H	H
d	H	Me	Me
e	H	$-[CH_2]_3-$	



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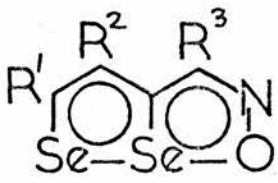


183

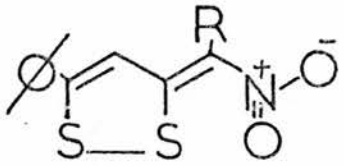
	R^1	R^2	R^3
a	Me	H	H
b	Ø	H	H
c	H	Me	Me

"one bond-no bond" resonance concept and a bicyclic formulation must be accepted. The only other known derivative of dioxathiapentalenes (171) was obtained[160] by thionation of the coumarin (172) with silicon disulphide. The oxadithiapentalene (173) and the trithiapentalene (174) were also isolated from the same reaction.

No derivatives other than those derived from the work described in this thesis[161] are known. Further discussion will be continued in Part II.

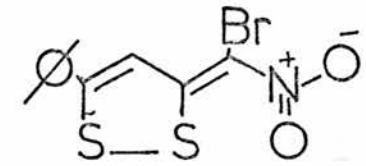
(iii) 1-Oxa-6,6a-dithia-2-azapentalenes and 3-Nitromethylene-3H-1,2-dithioles

2-Methyl-5-phenyl-1,6,6a-trithiapentalene (175) has been nitrated[25] to give the nitro derivative (176). Nitration of 2,5-diphenyl-1,6,6a-trithiapentalene (177, X = S) did not proceed in the expected fashion. Instead the first derivative of the 1-oxa-6,6a-dithia-2-azapentalenes was isolated (178)[162,163]. This product was also obtained by nitrosation[162,163] of the trithiapentalene and by nitration or nitrosation of the oxadithiapentalene (177, X = O)[162,163]. Nitrosation of several trithiapentalenes led to the isolation of a series of these compounds (179a-d)[162,163]. Desulphurisation of the dithioester (179b) with mercuric acetate with loss of the ester group gave the simpler compound (179e)[25]. A preparatively more useful synthesis[16] involves reaction of 3-methylene-1,2-dithiolium salts with nitrous acid (Scheme IV). This route has led to the isolation of a series of simply substituted 1-oxa-6,6a-dithia-2-azapentalenes (181) and is the simplest route to these compounds. All are obtained in good yield. Use of 3-methylene-1,2-diselenolium salts (182) in place of the dithiolium salts led to the isolation of a series of selenium analogues of these compounds (183).



a) R: H
b) R: Me

184



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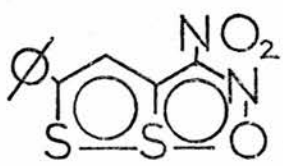

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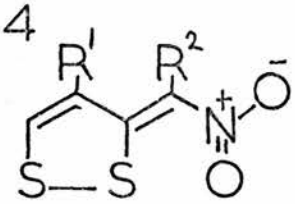
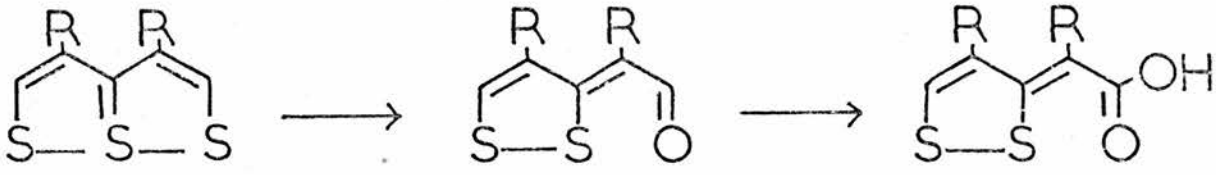


a) $R^1 = R^2$: Me
b) R^1–R^2: $[CH_2]_3$

187



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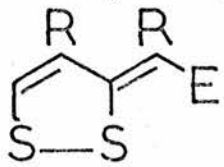
189

Scheme V

E^+ (E NO or NO_2)



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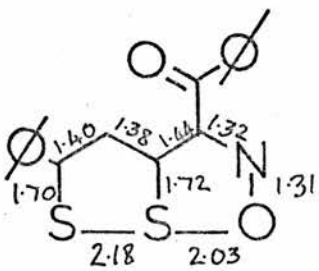

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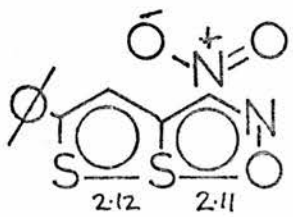
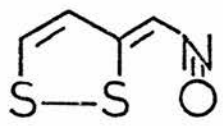


192

Condensation of 3-methylthio-5-phenyl-1,2-dithiolium methosulphate with nitromethane or nitroethane gave[162] the nitro compounds (184a,b) which are related structurally to the oxadithiaazapentalenes. Compounds of this type (184a) appear to be fairly reactive; they brominate readily[162] and undergo nitrosation leading to the products (185) and (186). Nitrosation of compound (184a) leads to the rearranged product (186). Rearrangements of this type will be discussed in Part II. Nitromethylene dithioles (187a,b) have been isolated[16] from nitration of 3,4-disubstituted trithiapentalenes with tetranitromethane. Scheme V shows the suggested route to this compound and other products (monocyclic structures are used for convenience). The carboxylic acid (189) was not isolated and its intermediacy must be held in doubt since further electrophilic substitutions on 3,4-disubstituted trithiapentalenes[168] have shown that a formyl or thioformyl group is readily eliminated under relatively mild conditions. The oxadithiapentalene (188) and the oxadithiaazapentalene (190, E = NO) were also isolated with the main product.

The structure of these compounds is of interest in relation to the question of sulphur-oxygen interactions. Crystal structure determinations have been performed[163] on the "nitroso" compounds (191) and (192). However the bond lengths in compound (192) have not been determined since crystals of this compound are invariably "twinned". The general shape of the molecule was determined and showed the proximity of the nitroso group and not the nitro group to the sulphur-sulphur sequence. The only bond lengths given, 2.12 Å for sulphur-sulphur and 2.11 Å for sulphur-oxygen should not be relied heavily upon. In compound (191) the S-S distance (2.18 Å) is longer and the S-O distance (2.03 Å) is shorter than the



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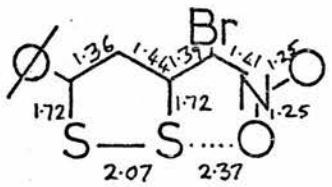

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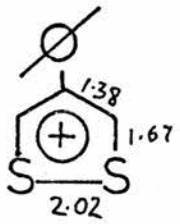

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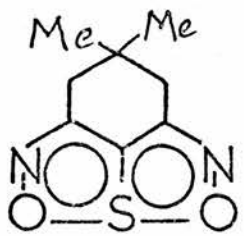

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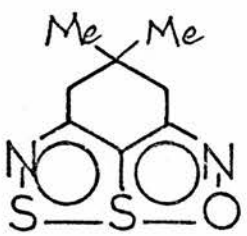


197

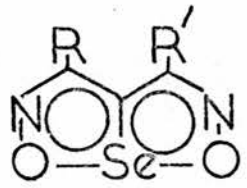
corresponding bond distances in the oxadithiapentalenes. This is indicative[165] of a bicyclic formulation for these compounds.

A monocyclic formulation for the nitro-methylene dithioles has been suggested[167] on the basis of the crystallographic data from the bromo compound (194). The lengths of the S-S (2.07 Å) and C-S (1.72 Å) bonds, being shorter[167] than in the oxadithiapentalenes have been taken as indicating that the compound has the monocyclic structure. Lack of information about other members of this series precludes making this statement final, since the S-O distance is still within the range found for the oxadithiapentalenes. Furthermore formulation of the compound as a dithiole derivative still leaves the S-S and C-S bond distances longer than those already found for this type of compound (195)[140-142]. Comparison of nmr spectral data for the "nitro" and "nitroso" compounds has led to the conclusion[16] that there is a larger ring current and hence more π electron delocalisation in the "nitroso" compounds.

In conclusion it seems likely that the "nitroso" compounds can be formulated with certainty as 1-oxa-6,6a-dithia-2-azapentalenes, ie as bicyclic entities. However in the absence of further data all that can be said about the "nitro" compounds is that their formulation as 3-nitromethylene-3H-1,2-dithioles seems likely but that a sulphur-oxygen interaction is present which is weaker than in the oxadithiapentalenes.

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

The first compound of this type has recently been synthesised by Beer and Poole[169]. Reaction of dimedone dioxime with sulphur dichloride gave the 1,6-dioxa-6a-thia-2,5-diazapentalene (196) and a small amount of a compound tentatively suggested to be the



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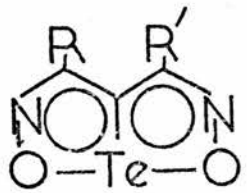
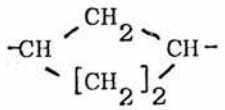
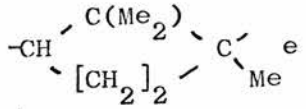
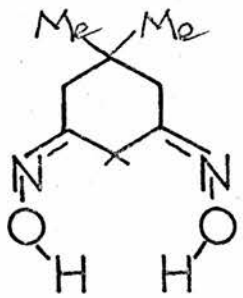


199

	R	R^1	Ref
a	H	H	a
b	Me	Me	b
c	$-[CH_2]_3-$		c
d	$-CH_2C(Me)_2CH_2-$		d
e	Ar	H	
f			
g			e



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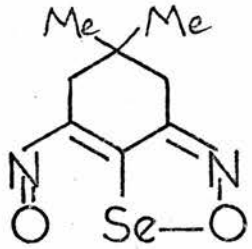

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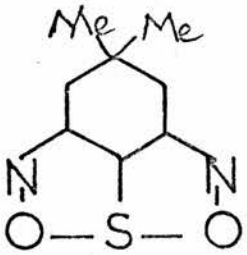

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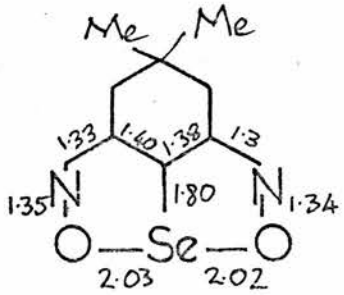
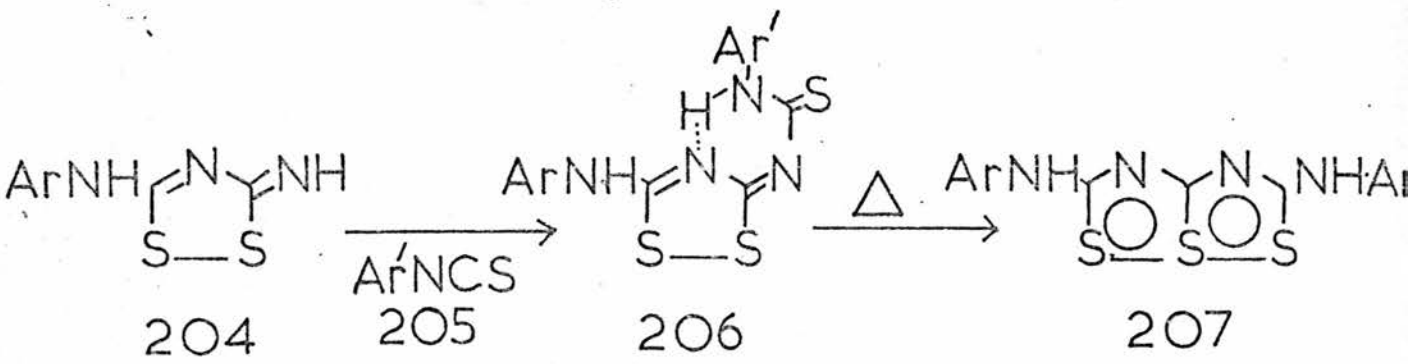


203

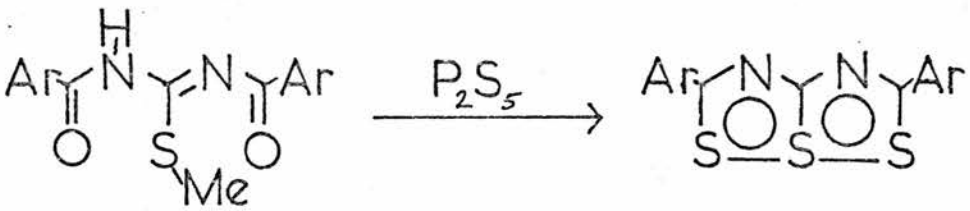
1-oxa-6,6a-dithia-2,5-diazapentalene (197). The nmr spectrum of compound (196) suggests a symmetrical structure.

Previously the only known members of this type of compound were selenium analogues. Reinvestigation[171-173] of work by King and Felton[170] led to the characterisation of a series of 1,6-dioxa-6a-selena-2,5-diazapentalenes (198). The selenium compounds were discovered by King and Felton in an investigation of the oxidation of dimedone dioxime (200) with selenium dioxide. They formulated the products as monocyclic compounds (201). The symmetry of these compounds was recognised[171] by Vialle and co-workers from the simple nmr spectra. Beer further added[173] that the spectrum of compound (198d) was unchanged down to -60^{o} except for broadening of the signals of the methyl groups. The spectrum of the simplest member of the series (198a) is unchanged from $+40^{o}$ to -60^{o} [171]. Use of a variety of oximes of β-diketones led to a variety of products of this type (198)[171,172]. Use of tellurium dioxide instead of selenium dioxide gave a series of tellurium analogues[172], the first compounds incorporating tellurium in the three centre bond.

Xray crystallographic data have been obtained for the sulphur[218] and selenium[173,186] compounds; the data are shown in diagrams (202) and (203). It is immediately apparent that the compounds show a high degree of symmetry and that the sulphur or selenium and oxygen atoms are well within their Van der Waals contact distances (S-O, 3.25 Å; Se-O, 3.40 Å)[42] but outwith the expected covalent single bond lengths (S-O, 1.70 Å; Se-O, 1.83 Å)[42]. The NO bond lengths are similar to that found in the "nitroso" compound (191). These data indicate that, taken with previously discussed spectroscopic data, the compounds can safely be described by a bicyclic formula.

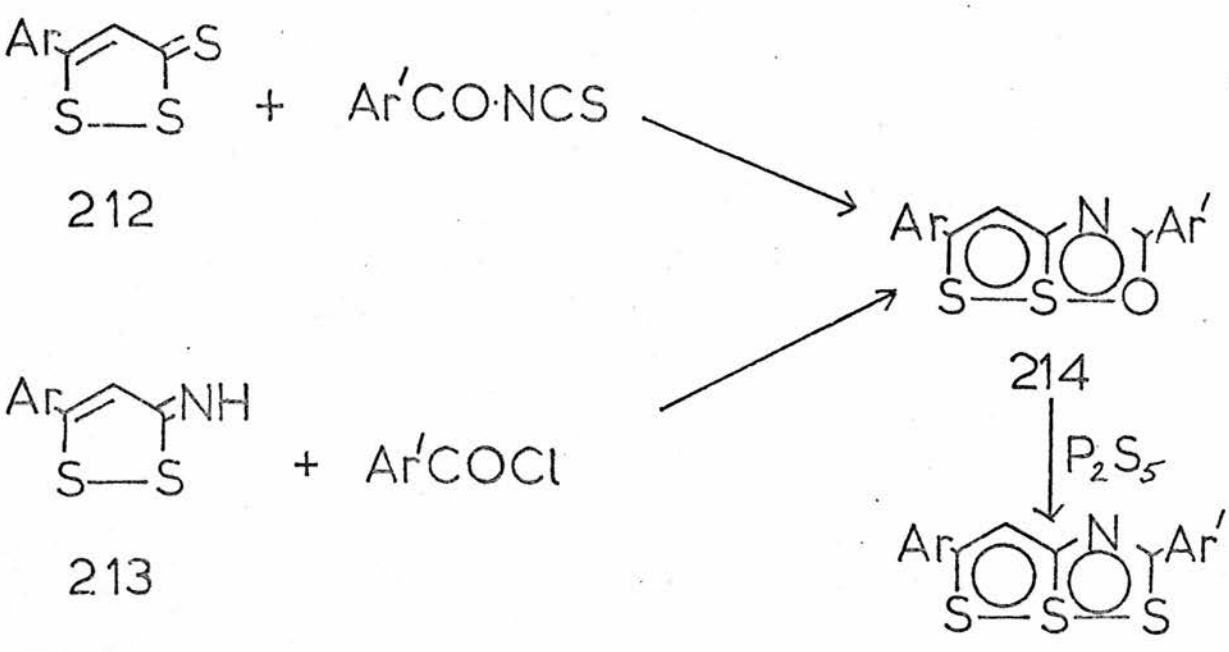


204 205 206 207



208 209

210 211



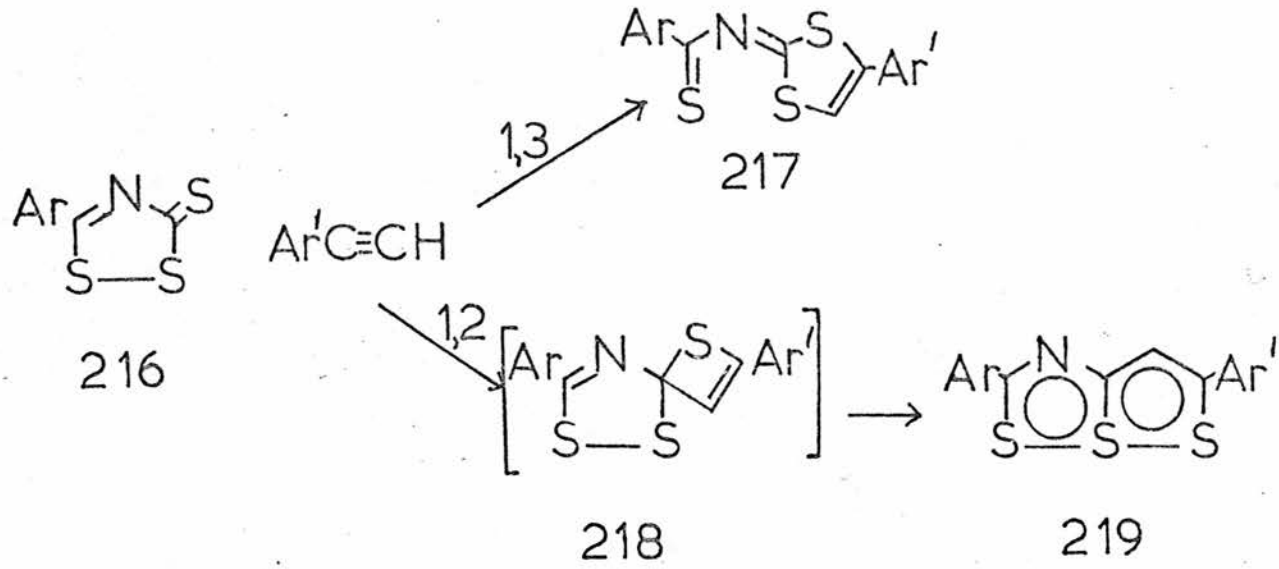
212 213 214 215

(v) 3-Aza and 3,4-Diaza-1,6,6a-trithiapentalenes

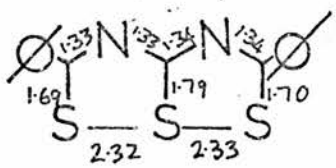
These compounds are perhaps the simplest aza analogues of trithiapentalenes in that there is no disturbance of the elements which comprise the three centre bond. Reaction of 1,2,4-dithiazol-3-imines (204) with isothiocyanates (205) in pyridine yield the trans intermediates (206) which readily isomerise on heating to give the trithiapentalenes (207)[174]. Use of isomeric starting materials (ie 204, Ar → Ar' and 205 Ar' → Ar) leads[174] to the same trithiapentalene. N,N-Diaroyl-S-methylisothioureas (208) react readily[174,176,177] with phosphorus pentasulphide in boiling xylene to give 1,6,6a-trithia-3,4-diazapentalenes (209) in good yield.

Behringer has modified his synthesis of 3,4-diaza compounds to give 3-aza compounds (211)[175], by reacting 3-amino-1,2-dithiolium salts (210) with aryl isothiocyanates. 1,2-Dithiol-3-thiones (212) or 3-imines (213) react with aroyl isothiocyanates or aroyl halides respectively to give the same products, a 1-oxa-6,6a-dithia-3-aza-pentalene (214). These latter compounds are readily thionated to give 1,6,6a-trithia-3-azapentalenes (215). Aryl acetylenes can be added to 1,2,4-dithiazol-3-thiones (216)[179]. 1,3-Addition gives the 1,3-dithiole derivatives (217) but 1,2 addition gives intermediates (218) which rearrange to the trithiapentalenes (219).

Formulation of the "aza" compounds as trithiapentalenes would seem to be justified since Xray crystallographic data for two of the symmetrical structures show close similarities to the trithiapentalenes. 2,5-Diphenyl-1,6,6a-trithia-3,4-diazapentalene has the structure shown (220)[180]. The C-S and S-S bond lengths are in the same range as found for the trithiapentalenes and the molecule is almost symmetrical. The C-N bond lengths are similar to those found in pyridine (1.34 Å)[181]. As in trithiapentalenes the S-S-S



216 217 218 219



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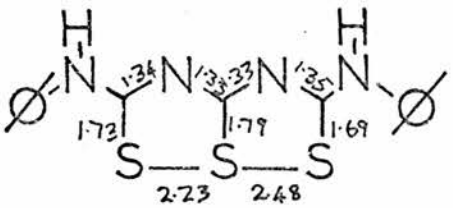

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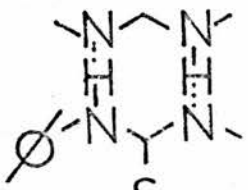

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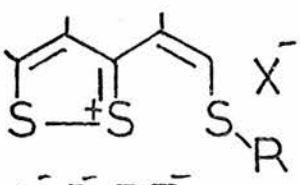
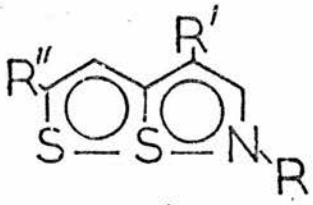
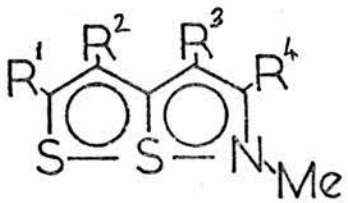


X: I^-, BF_4^-
R: Me, Et
223



R,R',R'': aryl
224



225

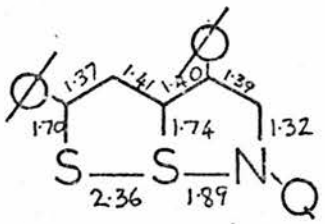
	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	Me
c	H	Me	Me	H
d	Me	H	H	H
e	Bu^t	H	H	H
f	H	$-[CH_2]_3-$		H

sequence of bonding is readily perturbed, as seen in the structure of the symmetrical hydrogen bonded derivative (221)[182]. The pattern of bond lengths are in accord with those already found for trithiapentalenes and no special comment is required except to point out that the asymmetry of the molecule may be due to the intermolecular hydrogen bonding (222) or to the different "twist" angles of the phenyl groups.

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

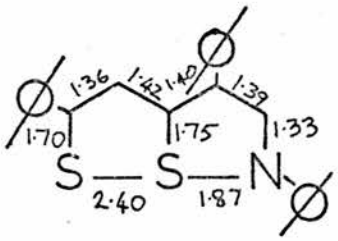
Alkylation of trithiapentalenes with methyl iodide[107] or triethyloxonium fluoroborate[183] gives 3-[2-alkylthiovinyl]dithiolium salts (223). These salts[107,183] or 1-oxa-6,6a-dithiapentalenes[107] react with primary aromatic amines to give 1,6a-dithia-6-azapentalenes (224). These syntheses are, unfortunately, limited to yielding highly substituted aryl derivatives. Treatment of Vilsmeier salts with primary alkyl amines serves as a good route[17] to simple alkyl 1,6a-dithia-6-azapentalenes (225a, c-f). In the same paper, trithiapentalenes have also been shown to react with methylamine to give the same series of aza compounds (225 a-f). This is a good synthesis of the simplest member of the series, namely (225a). The reaction is interesting in that it reveals potential thioaldehyde character in trithiapentalenes.

The structures of two derivatives have been determined by Xray crystallography (226)[143] and (227)[184]. The S-N bond lengths (1.87, 1.89 Å) are longer than a normal S-N bond, say in a thiadiazole (228)[185]. The S-S bonds (2.36, 2.40 Å) are of the same magnitude as those in trithiapentalenes. These compounds appear to be related more closely to the trithiapentalenes than to the oxadithiapentalenes. A bicyclic formulation (224) would seem to



Q : 3-quinolyl

226



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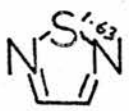

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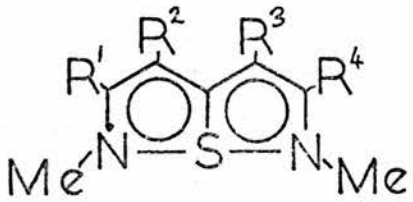
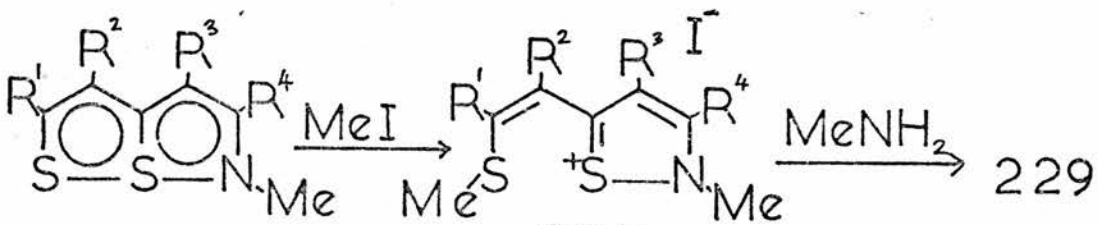


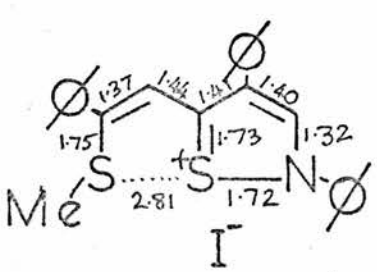
229

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	Me	Me	H
c	Me	H	H	Me
d	H	$[CH_2]_3$		H

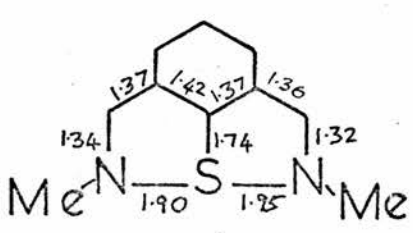


230

Scheme VI



231a

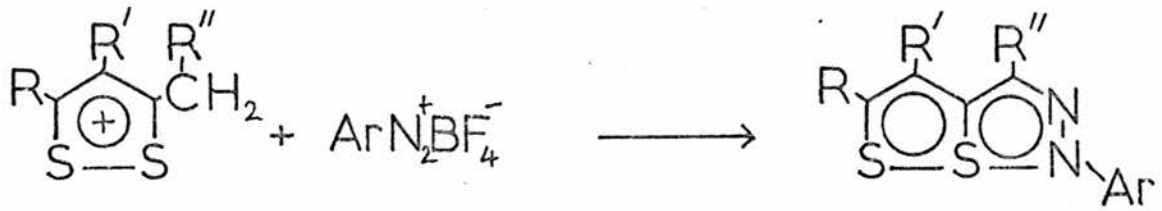


231

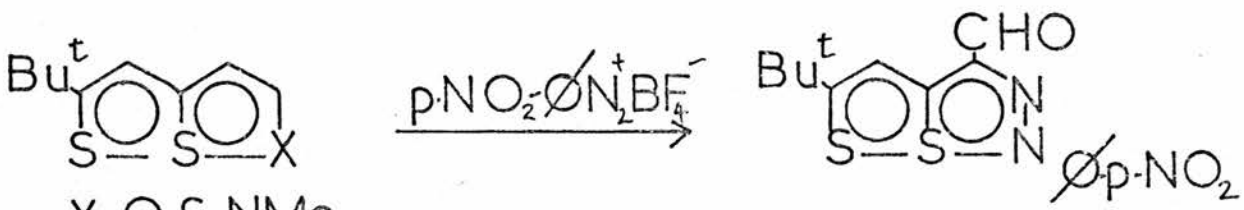
be in order for these compounds. The nmr spectra of trithiapentalenes have been cited[14] as evidence in support of trithiapentalenes being bicyclic aromatic systems with larger ring currents than the oxadithiapentalenes. The nmr spectra of the aza compounds have now been presented[17] and have been taken as indicative of the compounds having larger ring currents and greater aromaticity than the 1-oxa-6,6a-dithiapentalenes. The spectra also indicate that ring currents and aromaticity are greater in the trithiapentalenes than in the 1,6a-dithia-6-azapentalenes. On the evidence available the 1,6a-dithia-6-azapentalenes can be formulated with certainty as bicyclic structures.

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

A series of 6a-thia-1,6-diazapentalenes (229) have been synthesised by Reid and Symon (scheme VI)[134,187,188]. 1,6a-Dithia-6-azapentalenes have been shown[107,134,187] to methylate at sulphur giving isothiazole derivatives (230). This has been confirmed in one case (231) by Xray crystallography[184]. Treatment of the salts (230) with methylamine gave the 6a-thia-1,6-diazapentalenes (229). The nmr spectra of these compounds are consistent with them having C2V symmetry. The spectrum of the tetramethyl derivative (229b) is consistent with a bicyclic formulation, a frozen, monocyclic structure (232a,b) being precluded since the spectrum is unchanged (in CS_2) down to -70°C. Further evidence for the bicyclic nature of these compounds comes from the Xray crystallographic study of compound (229d) [diagram (231)]. In this structure the sulphur and nitrogen atoms lie well within their Van der Waals contact distance (3.35 Å)[42] but the S-N bond (1.90 Å) is still long [cf isothiazolium S-N, (231), 1.72 Å[184]]. It is also noteworthy that this

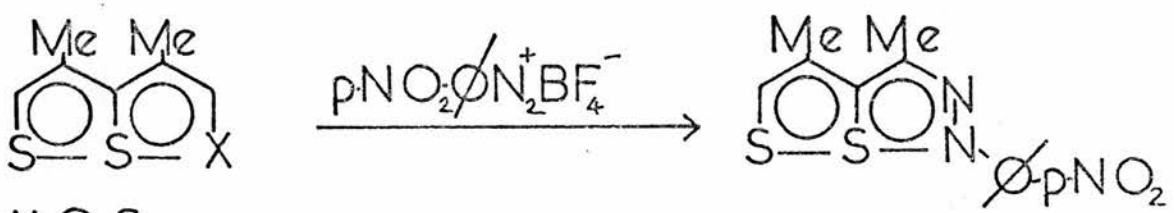


232 233



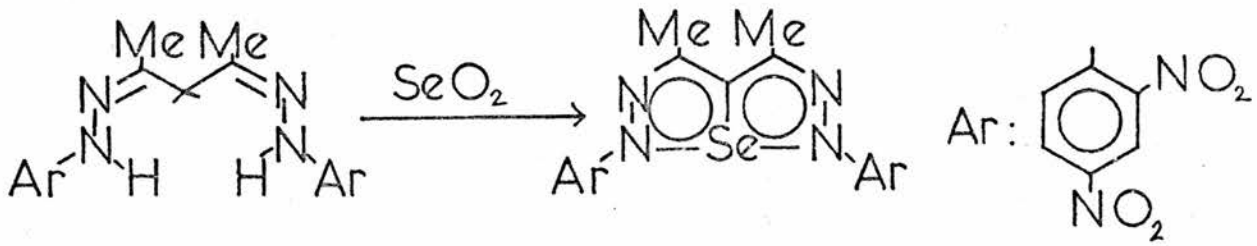
X:O,S,NMe

234 235



X:O,S

236 237



238 239

sulphur-nitrogen distance (1.90-1.95 Å) is very similar to that in the 1,6a-dithia-6-azapentalenes [(226), 1.89 Å; (227), 1.87 Å]. The carbon-nitrogen bonds also have similar lengths (1.32, 1.34 Å) to the aromatic C-N bonds in pyridine (1.34 Å)[185].

(viii) 1,6a-Dithia-5,6-diazapentalenes and Related Compounds

Reid and co-workers in a preliminary communication[168] have observed that 3-methylene-1,2-dithiolium salts (232) couple with arene-diazonium salts in ethanol to give a series of 1,6a-dithia-5,6-diazapentalenes (233). A bicyclic structure has been presumed for these compounds since the trithiapentalene derivatives (234) on reaction with p-nitrobenzenediazonium fluoroborate all rearrange to 1,6a-dithia-5,6-diazapentalene derivatives (235). Furthermore, if the reactive position (3) is blocked (236), a formyl or thioformyl group is eliminated leading to the diazo derivative (237). Further data on these compounds are awaited with interest.

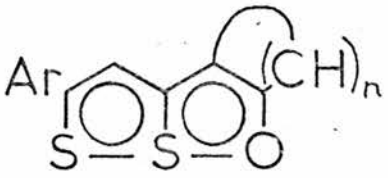
Vialle has prepared[172] a symmetrical derivative related to these compounds. Oxidation of the hydrazone (238) with selenium dioxide gave a 6a-selena-1,2,5,6-tetraazapentalene (239). This compound, a golden green solid, shows a high degree of symmetry (nmr spectroscopy) but no further details are given.

F. Reactions of 1,6,6a-Trithiapentalenes and Isosteres

Since a section in the main part of this thesis will be devoted to reactions of various trithiapentalene isosteres, a review of reactions already performed may be useful. Some will have been mentioned already.

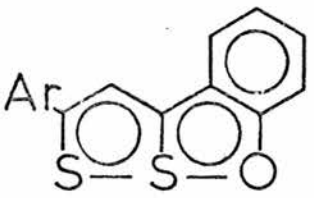
R : H, Me

240

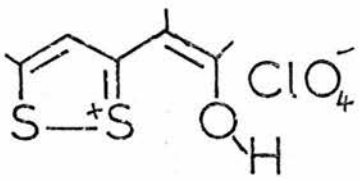


n : 3, 5, 6

241



242



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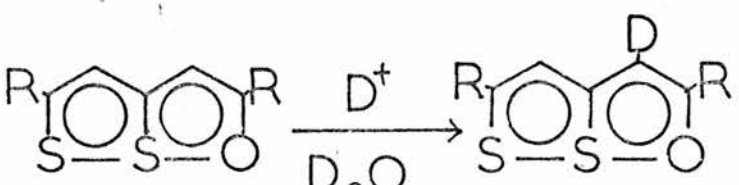
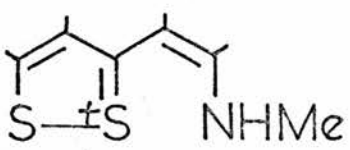


a) R : Me

b) R : Ø

244



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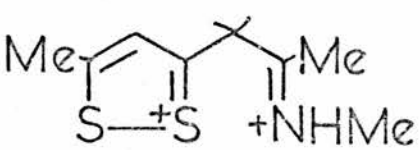

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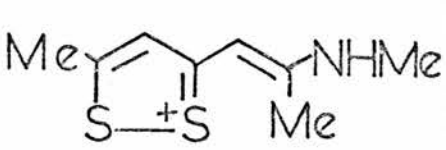

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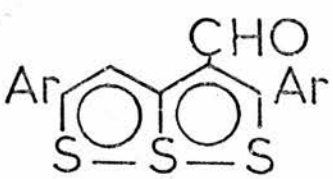

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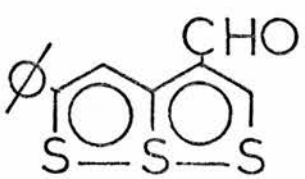

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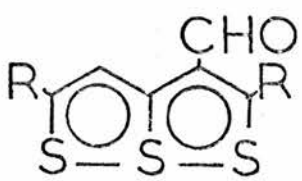
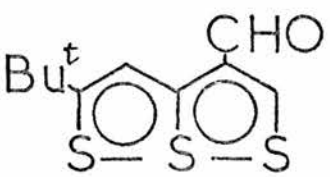


a) R : H

b) R : D

250



251

(i) Carbonyl or Thiocarbonyl Reactions

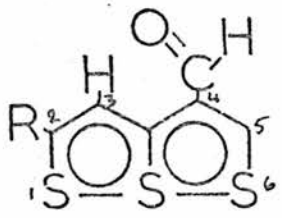
The first reaction of this type to be described was the formation[22] of 2,4-dinitrophenylhydrazones by the oxadithiapentalenes (240). Trithiapentalenes did not react under the same conditions[22]. Previously Traverso and Sanesi had observed[190] the liberation of hydrogen sulphide and the production of a yellow-brown solution on addition of hydroxylamine to a trithiapentalene; they did not attempt to isolate the product. Klingsberg observed[106] that 2-aryl-1-oxa-6,6a-dithiapentalenes did not undergo carbonyl reactions but that oxadithiapentalenes with a free 2 position did. Klingsberg also found[107] that oxadithiapentalenes react readily with a variety of primary aromatic amines forming imines, which have since been described as the bicyclic 1,6a-dithia-6-azapentalenes. Potential thioaldehyde character is revealed by trithiapentalenes in their facile reaction with methylamine[17] which leads to the 1,6a-dithia-6-azapentalenes as already described. Alkylation of trithiapentalenes with methyl iodide[107,121] and triethyloxonium fluoroborate[183] has already been described. The latter reagent was found to alkylate alkyl substituted trithiapentalenes. Only mild conditions have been found necessary to alkylate 1,6-dithia-6-azapentalenes[107,134,187]. Alkylation of 1-oxa-6,6a-dithiapentalenes has received no attention.

(ii) Electrophilic Reactions

The simplest electrophilic reaction is protonation but this has raised comparatively little interest. No protonation studies on trithiapentalenes have been reported. 1-Oxa-6,6a-dithiapentalenes (241)[24] and (242)[191] have been shown to form stable perchlorates (243). The significance of the hydrogen-deuterium exchange in compounds (244a,b) went unnoticed[105]. The exchange at

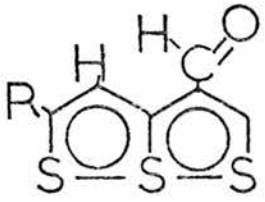
position 3 can only arise from protonation at position 3. Protonation of the nitrogen analogues has received much more detailed and useful analysis[17]. 1H nmr spectral studies show that protonation of 1,6a-dithia-6-azapentalenes in trifluoroacetic acid occurs predominantly at nitrogen, forming the 3-(2-methylaminovinyl)-1,2-dithiolium ion (245). 2,5,6-Trimethyl-1,6a-dithia-6-azapentalene gave comparable amounts of two species, resulting from protonation both at C-4 (246) and at nitrogen (247). The presence of a 4-C protonation species in other members of the series was established by H/D exchange experiments using deuteriotrifluoroacetic in place of trifluoroacetic acid. This resulted in the disappearance of the signal attributed to 4-H in the spectra of other members of the series.

Formylation has been studied in a little more detail. Formylation of 2,5-diaryl-1,6,6a-trithiapentalenes yields the 3-formyl compounds (248)[110-112]. Formylation of 2-phenyl-1,6,6a-trithiapentalene[192] led to the 4-formyl compound (249) for which the position of substitution was determined by 1H nmr spectroscopy. The position of formylation of 1,6,6a-trithiapentalene has been determined unambiguously by comparing the nmr spectrum of the product with that from the formylation product of 2,5-dideuterio-1,6,6a-trithiapentalene[15]. The latter reaction product shows only two signals in its nmr spectrum thus establishing retention of the deuterium atoms and hence to the conclusion that the product is 3-formyl-2,5-dideuterio-1,6,6a-trithiapentalene (250b). Formylation of 1,6,6a-trithiapentalene must therefore lead to 3-formyl-1,6,6a-trithiapentalene (250a). In the same manner 2-t-butyl-1,6,6a-trithiapentalene was deduced to formylate at the 4-position giving (251). Two structures are possible for these formyl compounds

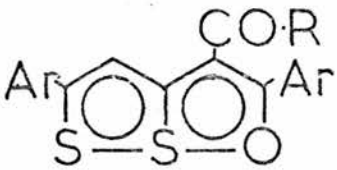


a

252

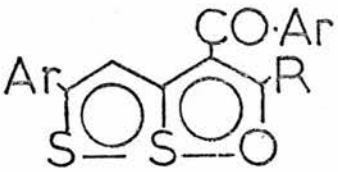


b



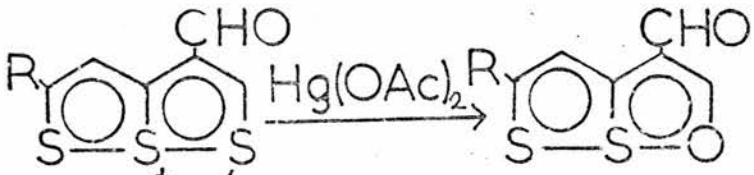
a) R:H
a') R:D

253



b) R:H
b') R:D

253



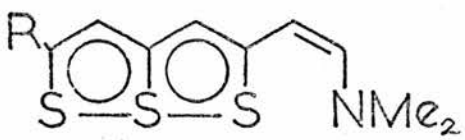
R:Bu^t, Ø

254

255

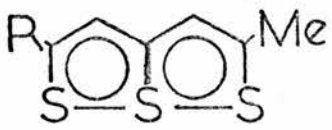
R:H, Me

256



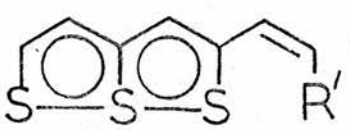
R:H, Me

257



+ R'CHO

R', aryl

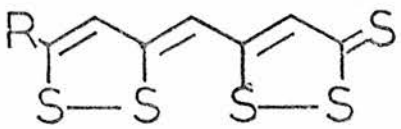


258

Scheme VII

+ CS_2

R, aryl



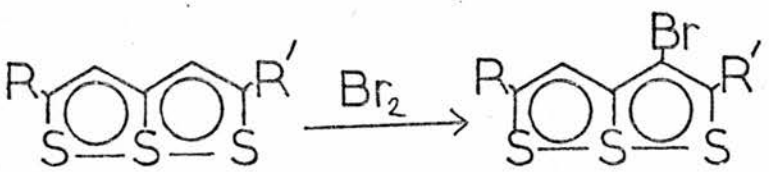
259

Scheme VIII

(252a,b). Structure (252a) is to be preferred since the proton in the other ring (3-H) has undergone a downfield shift (1.66-1.74 ppm) which can be attributed to the diamagnetic anisotropy of the formyl group.

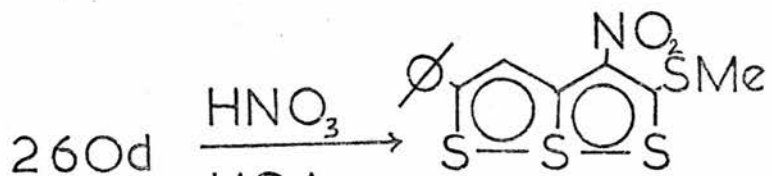
Formylation of 2,5-diaryl-1-oxa-6,6a-dithiapentalenes[110] occurs at the 3-position. This reaction is interesting in that a mixture of isomers (253a,b) was obtained. Two sets of signals were observed in the 1H nmr spectra of the formylation products and assignment of these signals was made by comparison with the spectra of the deuterioformylation products (253a',b'). These signals were apparent at room temperature but at 140°C only 1 pair of signals is apparent, intermediate between the positions of the two sets observed at room temperature. Rotation about the C-3 - C-1' bond accounts for this. Other 3-formyl-1-oxa-6,6a-dithiapentalenes (255) have been obtained[15] by desulphurising the corresponding sulphur compounds (254). These compounds provide further evidence for the bicyclic nature of 1-oxa-6,6a-dithiapentalenes since a normal C=O stretching frequency (ca 1660 cm^{-1}) is observed for the formyl group, together with the abnormal stretching frequency (ca 1575 cm^{-1}) for the ring C⋯O.

Attempted formylation of 2-methyl and 2,5-dimethyl-1,6,6a-trithiapentalenes (256) produced the enamines (257). This result further demonstrates the side chain reactivity in trithiapentalenes which has already been investigated by Stavaux and Lozac'h[193-195]. These workers found that 2-methylene groups in trithiapentalenes are reactive and condense readily with aromatic aldehydes[193] to give styryl compounds (258) (Scheme VII) or with carbon disulphide[194,195] to give the dithiole derivative (259) (Scheme VIII).

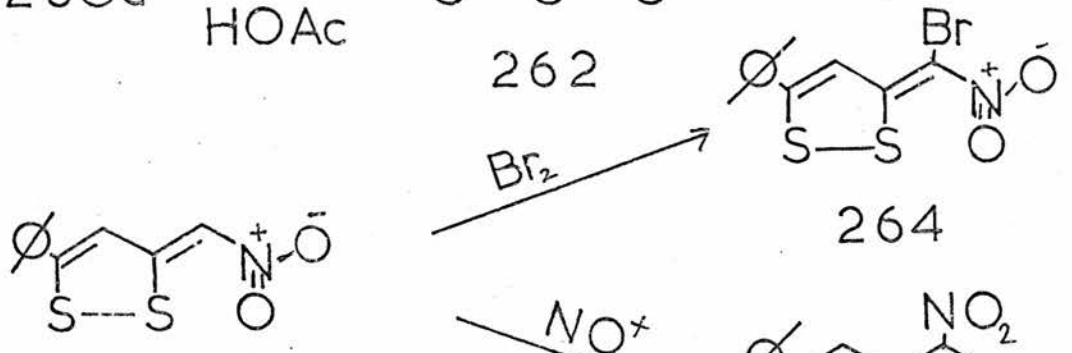


260 261

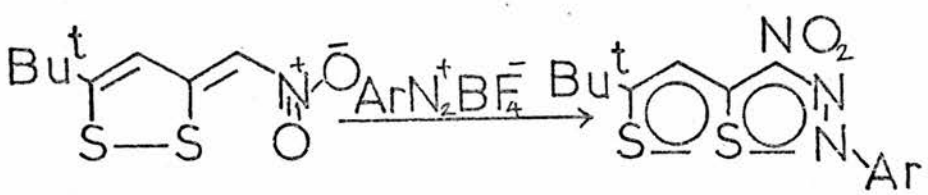
a. R = R', Me
b. R = R', Ø
c. R,Ø; R',Me
d. R,Ø; R',SMe



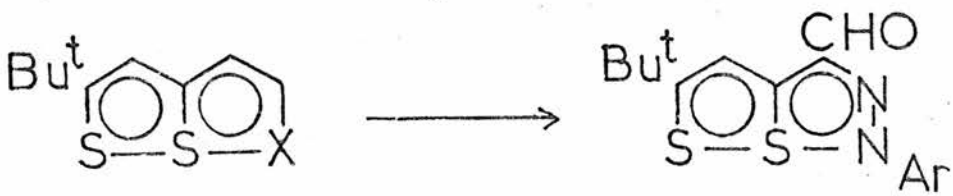
260d 262



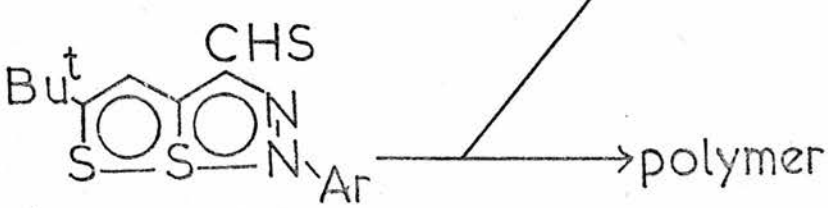
263 264 265



266 267



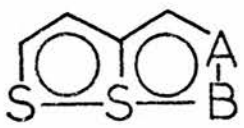
234 235



268 polymer

2,5-Disubstituted trithiapentalenes (260) have been brominated under mild conditions to give high yields of the 3-bromo compounds (261). 1H nmr spectroscopy has been used to assign the structures (261a-d). The position of substitution is in accord with charge densities calculated for some of these compounds[25]. Nitration of 2-methylthio-5-phenyl-1,6,6a-trithiapentalene (260d) with nitric acid in hot acetic acid produced[25] the 3-nitro compound (262) whose structure was determined unambiguously by synthesis. Attempted nitration of trithiapentalenes with tetranitromethane failed[16] to produce 3-nitro-1,6,6a-trithiapentalenes but did give numerous other products which have been discussed already [Section E, (iii)]. Nitrosation of trithiapentalenes also does not give 3-nitroso-1,6,6a-trithiapentalenes but is accompanied by desulphurisation and rearrangement to the 3-acyl-1-oxa-6,6a-dithiapentalenes as discussed previously [Section E, (iii)]. The 3-nitromethylenedithiole (263) is observed to be highly reactive[162] and on treatment with bromine in benzene gives the bromo compound (264) and with nitrous acid gives the rearranged product (265) [Section E, (iii)]. The 3-nitro-methylenedithiole (266) undergoes a similar type of rearrangement on treatment with an arenediazonium fluoroborate[168] to 4-nitro-2-t-butyl-1,6a-dithia-5,6-diazapentalene (267). As already mentioned [Section E, (viii)], the trithiapentalene and its derivatives (234) undergo similar rearrangements[168] when treated with arenediazonium fluoroborates. The thioaldehyde intermediate (268) not only hydrolyses to the aldehyde (236) but also gives some thioaldehyde polymer, in the well known fashion of thioaldehydes.

The results of the electrophilic substitution reactions can be correlated and with other results already obtained can be used to set up an order of preference for interaction of an AB group in



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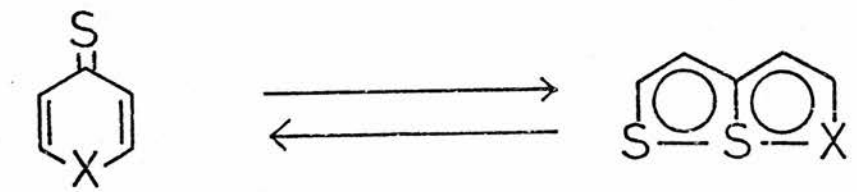
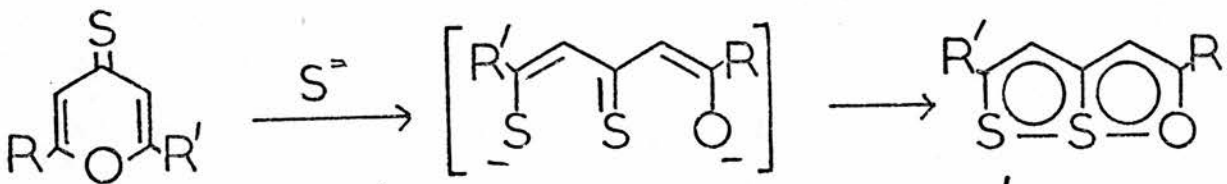


X:O,S

270

271



272

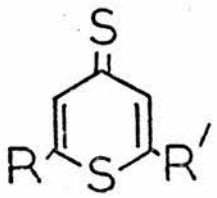
274

273

$S^{=}$

$S^{=}$

	R	R^1
a	Ø	H
b	Ø	Me
c	Ø	CO_2Et
d	Me	Me



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the hypervalent[197] heterocycle (269). The order is $NO_2 > < CHO < CHS > < CHNR < NO > < NNAr$. Further work is evidently required to settle the order for the "nitroso" and "diazo" groups, the "thioformyl" and "imine" groups and the "nitro" and formyl" groups. The following reasons can be given for setting out the order as shown.

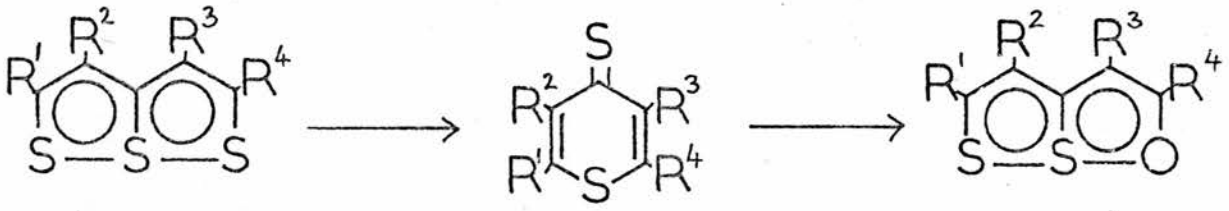
a) The "diazo" and "nitroso" groups will have a stronger interaction than the "formyl", "thioformyl" and "imine" (not certain for nitrosation) since these groups are readily displaced by the "diazo" and "nitroso" groups.

b) The "imine" and "thioformyl" interaction will be greater than that of the "formyl" and "nitro" groups on the basis of Xray crystallographic evidence.

c) The "formyl" and "nitro" groups interact less than the "thioformyl" group since formylation and nitration produce formyl and nitro trithiapentalenes.

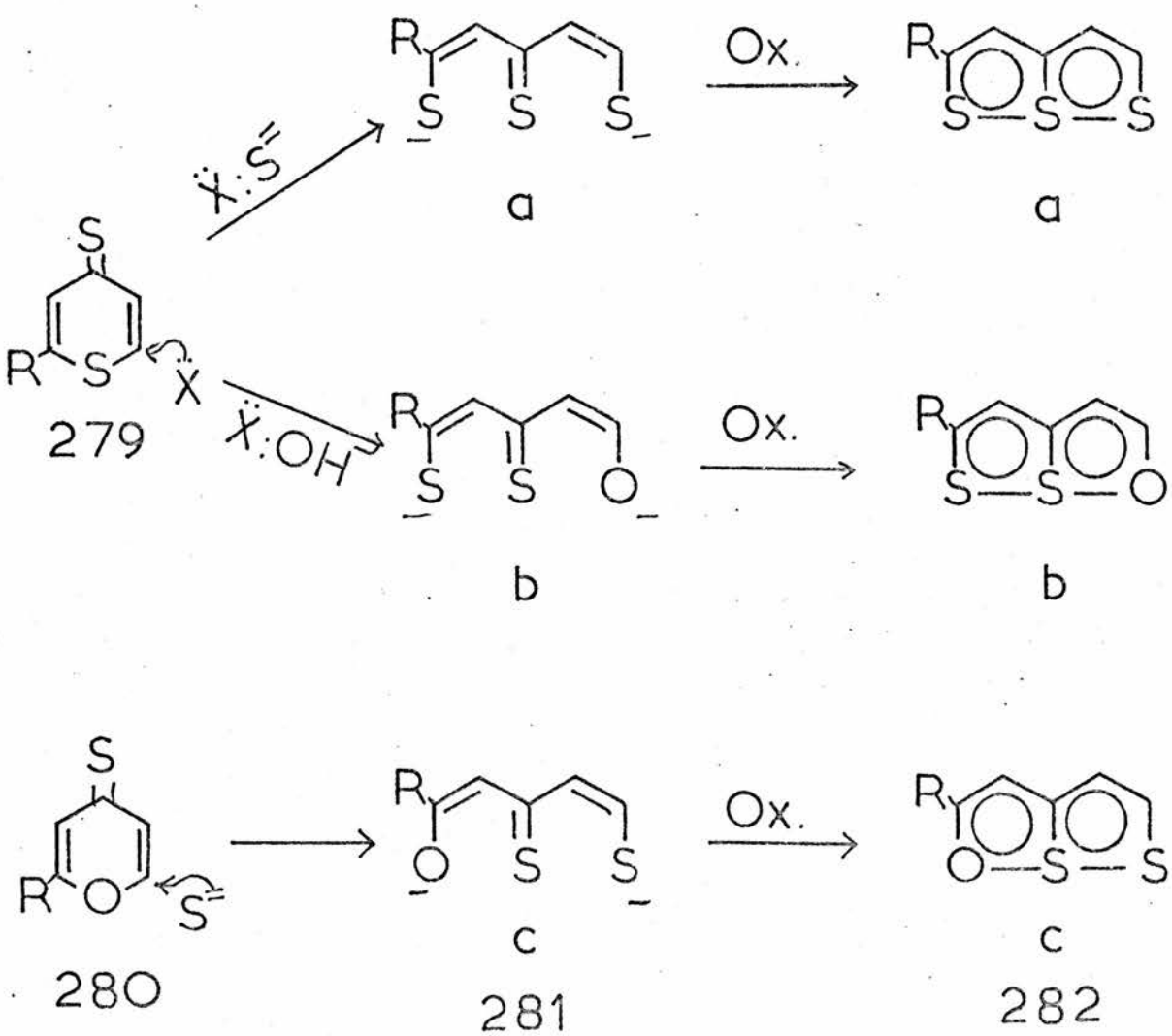
(iii) Rearrangements Reactions

The interconvertability of systems related to trithiapentalenes (271) and the thiones (270) have been of interest for some time. For interconversion between these systems an oxidation or reduction is required, the trithiapentalenes being at a higher oxidation level than the thiones. Early work by Traverso showed[131,132,199,200] that 4H-pyran-4-thiones (272) could be converted to 1-oxa-6,6a-dithiapentalenes (273), the intermediate (274) presumably undergoing aerial oxidation to the product. He has also shown in these same papers that the 1-oxa-6,6a-dithiapentalenes (273) could be converted to 4H-thiopyran-4-thiones (275). Dingwall and Reid have shown[197] that trithiapentalenes (276,a-g)



276 277 278

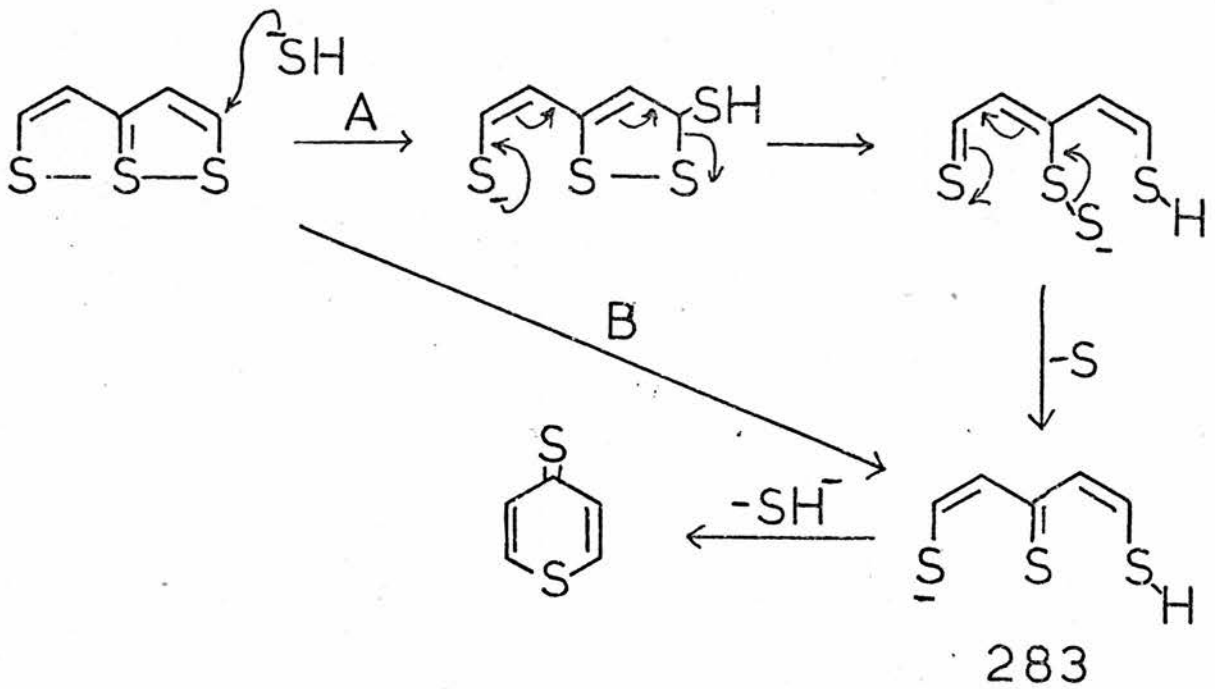
	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	Ø	H	Ø	H
d	Ø	H	Me	H
e	H	Ø	Ø	H
f	Ø	H	H	H
g	Bu^t	H	H	H
h	H	Me	Me	H



are readily reduced to 4H-thiopyran-4-thiones (277,a-g). The reverse reaction has also been investigated fully[10,198] for the 4H-thiopyran-4-thiones (277a,c,d,f,g,h) using sulphide and ferricyanide oxidation. It has also been shown that the thiones (277c,d,f,g,h) gave the corresponding oxadithiapentalenes using hydroxide then ferricyanide oxidation.

The mechanism of the oxidative reaction seems fairly certain. Nucleophilic attack on the 2(6) position of 4H-thiopyran-4-thione (279) or 4H-pyran-4-thione (280) by sulphide or hydroxide leads to dianions (281) which can be oxidised by potassium ferricyanide, air or iodine to give the products (282). Dipolar aprotic solvents such as dimethylformamide and dimethylsulphoxide enhance the nucleophilicity of the reagent (sulphide or hydroxide) making attack on the ring more facile. Where the substrate carries 2 and 5 alkyl or aryl substituents, ring opening is hindered and low yields of products are obtained. It should also be noted that ring-opening of corresponding 2-substituted 4H-pyran-4-thiones and 4H-thiopyran-4-thiones with sulphide or hydroxide respectively leads to isomeric products (282 b,c)[10].

The mechanism for the reductive rearrangement is not settled. Two mechanisms for this rearrangement have been considered (Scheme IX). The first involved simple reductive cleavage of the sulphur-sulphur bonds (B) which give the anion (283). This then loses SH^- and cyclises to the thione [197]. The second mechanism (A) involves nucleophilic attack by sulphide at position 2 in the trithiapentalene and leads to the same anion (283). This latter mechanism has been favoured by Dingwall and Reid[197] due to the significance of the rearrangement of 2-phenyl and 2,4-diphenyl-1,6,6a-trithiapentalenes, with aqueous hydroxide in dimethylformamide,



Scheme IX

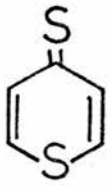
to 4H-thiopyran-4-thiones. Since the hydroxide ion has little reducing power compared to the sulphide ion a nucleophilic mechanism must be favoured in these cases. This does not imply that the rearrangement with sulphide follows the same route. Electronic effects also favour a nucleophilic rearrangement since 2,5-disubstituted-1,6,6a-trithiapentalenes are almost inert to rearrangement whereas the 3,4-disubstituted compounds rearrange quantitatively extremely rapidly.

The investigations described here are concerned with the physical and chemical properties of oxygen analogues of 1,6,6a-trithiapentalenes. A convenient route to 1-oxa-6,6a-dithiapentalene and hence to 1,6,6a-trithiapentalene has been developed. Investigations on oxidative coupling has furnished a synthetically useful route to 1,6-dioxa-6a-thiapentalenes and, in poorer yields, to 1,6-dioxa-6a-selenapentalenes. The reactivity of 1,6-dioxa-6a-thiapentalene has been investigated. Some chemistry of 1-oxa-6,6a-dithia-2-azapentalenes and 3-nitromethylene-3H-1,2-dithioles has also been studied.

Methylation and protonation of numerous 1,6,6a-trithiapentalene derivatives were investigated.

In this section the nmr spectra referred to are 1H nmr spectra. Chemical shift data are given in terms of δ values in ppm downfield from the tetramethylsilane signal.

1



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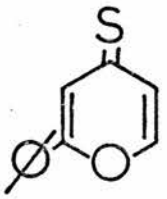

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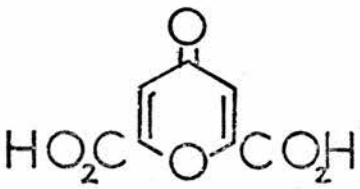

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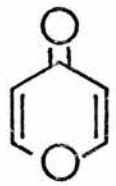

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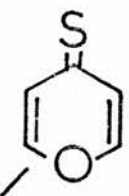

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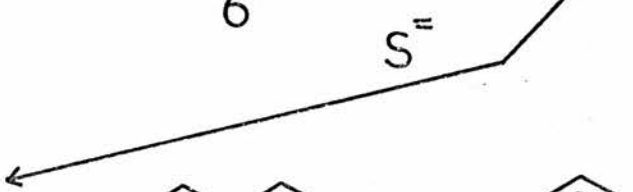
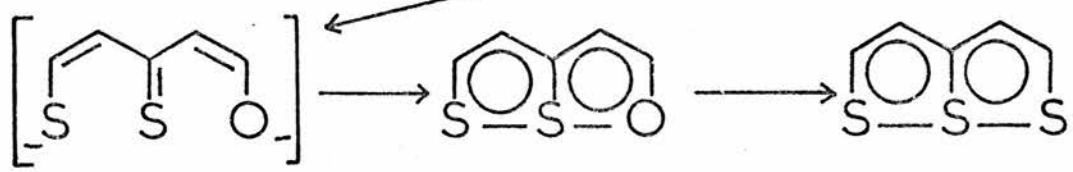


$S^{=}$



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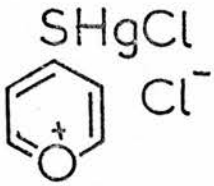


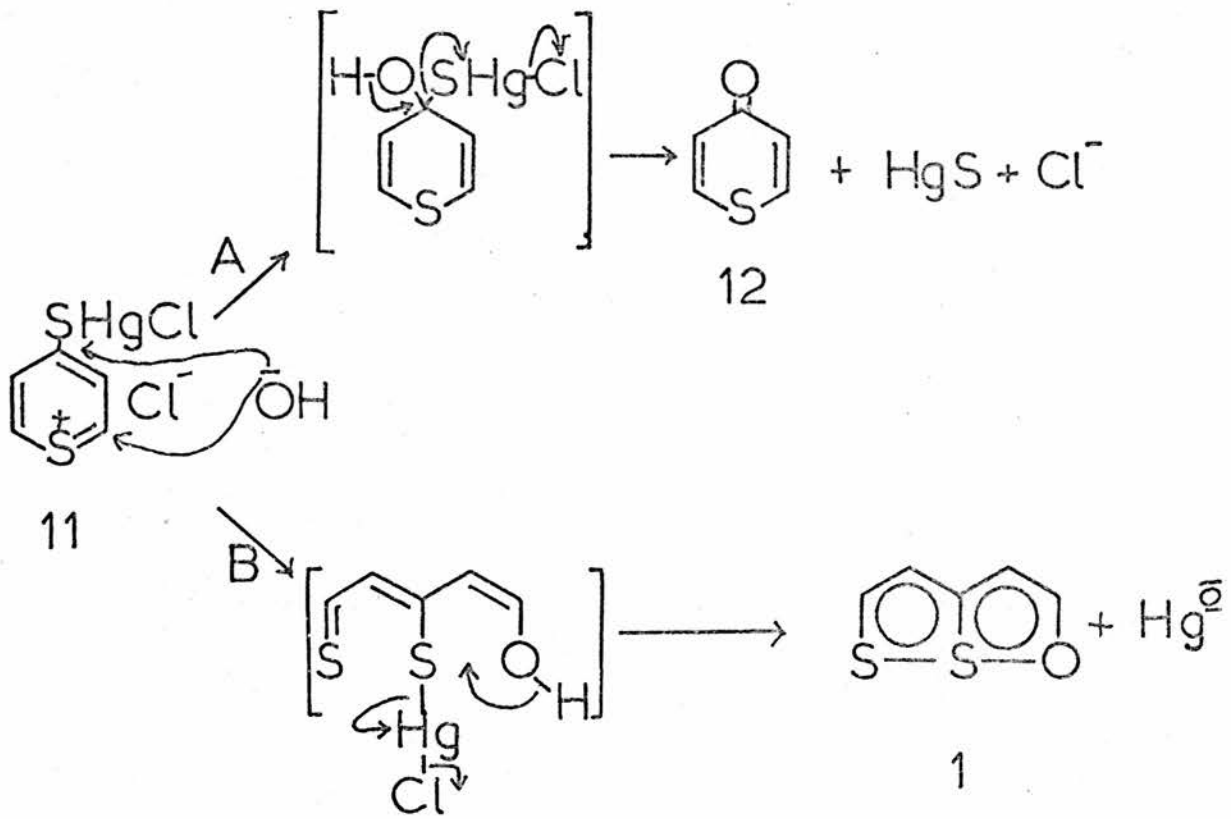
10

A 1-Oxa-6,6a-dithiapentalene and 1,6,6a-Trithiapentalene

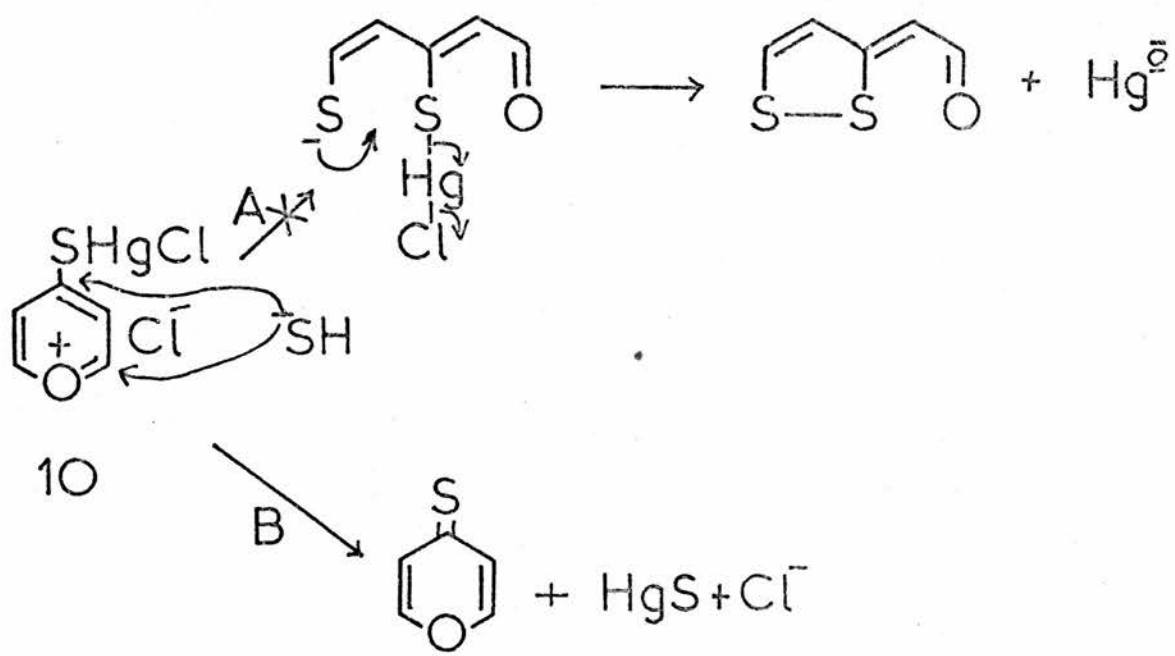
Nitrogen[134] and selenium[73] analogues of trithiapentalenes have received considerable attention in these laboratories recently. Since oxygen analogues had received little attention it was decided to investigate oxygen analogues of 1,6,6a-trithiapentalenes.

1-Oxa-6,6a-dithiapentalene (1) has been obtained from the difficultly accessible 4H-thiopyran-4-thione (2) in low yield[9]. Since ring-opening and oxidative coupling of 2-phenyl-4H-pyran-4-thione (3) had produced the oxadithiapentalene (4)[10], it was thought that this procedure, suitably modified, might serve as a useful route to this compound. The starting material, γ-pyrone (6), is readily available in large quantities from the copper catalysed decarboxylation[202] of technical grade chelidonic acid (5)[201]. γ-Pyrone had been thionated previously[23,204] but experimental details were lacking. Thionation of γ-pyrone not only gave the expected 4H-pyran-4-thione (7) but also a small quantity of 1,6,6a-trithiapentalene (0.4%). The origin of this latter compound was not established. A possible precursor is 1,3-diformylacetone or a derivative thereof produced under the reaction conditions. Oxidative thionation of 1,3,5-tricarbonyl compounds, leading to 1,6,6a-trithiapentalenes, is a well-established reaction.

Ring-opening of 4H-pyran-4-thione (7) in dimethylsulphoxide-water (4:1, v/v) gave a deep red solution of the anion (9). Intramolecular oxidative coupling by aqueous potassium ferricyanide gave 1-oxa-6,6a-dithiapentalene. The nmr spectrum of the oxidation product showed the presence of a small amount of starting material. Treatment of the crude oxadithiapentalene with mercuric chloride in ether precipitated the unreacted thione (7) as the mercuric chloride complex (10). Subsequent chromatographic



Scheme I



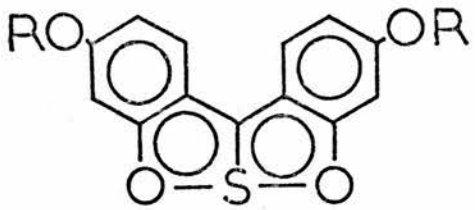
Scheme II

purification gave the bright yellow 1-oxa-6,6a-dithiapentalene (1) in 23% yield. The nmr spectrum of 1-oxa-6,6a-dithiapentalene shows two pairs of doublets of differing coupling constants. The protons in the dithiole ring resonate at δ7.23 (4-H) and δ7.48 (5-H) (J = 5.9 Hz), those in the oxathiole ring at δ6.86 (3-H) and δ9.38 (2-H) (J = 1.6 Hz).

Thionation of 1-oxa-6,6a-dithiapentalene with phosphorus pentasulphide in refluxing benzene gave 1,6,6a-trithiapentalene in 58% yield. The steps (7)⟶(1)⟶(8) can be expediently combined into a single operation for the purpose of preparing 1,6,6a-trithiapentalene (8). Thionation of the crude oxidation product gave 1,6,6a-trithiapentalene (8) in 25% yield from 4H-pyran-4-thione. 1,6,6a-Trithiapentalene (8) is thus readily available from γ-pyrone in 12% overall yield by a three step synthesis, comprising two operations. This constitutes the simplest synthesis of 1,6,6a-trithiapentalene from readily available starting materials (D.H. Reid and R.G. Webster, JCS Perkin I, 1972, 1447).

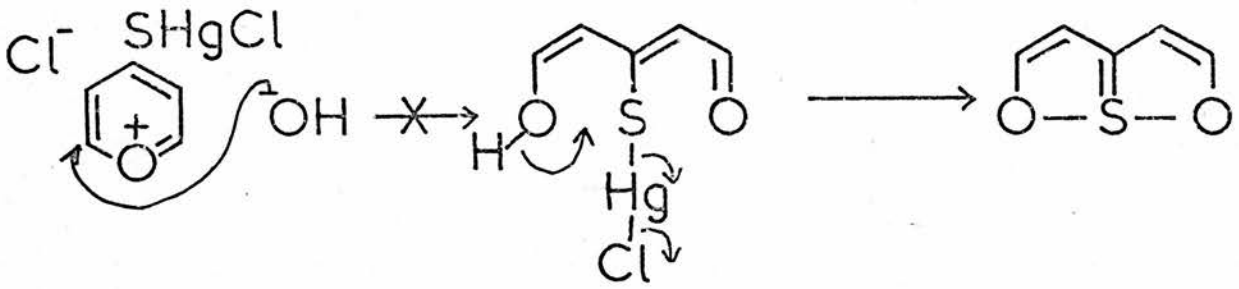
An extension of this work was suggested by Traverso's work[9] in which an internal oxidising agent (Hg^{2+}) was used, perhaps inadvertently, to oxidise the ring opened species. Traverso found that treatment of the mercuric chloride complex of 4H-thiopyran-4-thione (11) with base gave two products. The first, 4H-thiopyran-4-one (12) arose from attack at the 4-position of the thiopyrylium salt (11) (Scheme IA). The major product, 1-oxa-6,6a-dithiapentalene (1), resulted from attack on the thiopyrylium ring at position 2 (Scheme IB). It was hoped that ring opening of 4-chloromercuri-thiopyrylium chloride (10) with hydrosulphide might lead to a one-step synthesis of 1-oxa-6,6a-dithiapentalene (Scheme IIA). The hope however was tempered with the knowledge that a similar attempted

reaction[10] of 4-chloromercurithio-1-thiopyrylium chloride with hydrosulphide yielded only the thione. In the event the reaction followed the same route and 4H-pyran-4-thione was obtained in high yield together with mercuric sulphide. The presence of 1-oxa-6,6a-dithiapentalene was not detected. It was not determined in either case whether the hydrosulphide ion attacked at the 4-position in the ring (as hydroxide did in Scheme IA) or at the mercury atom.



R : H, Me, Ac

13



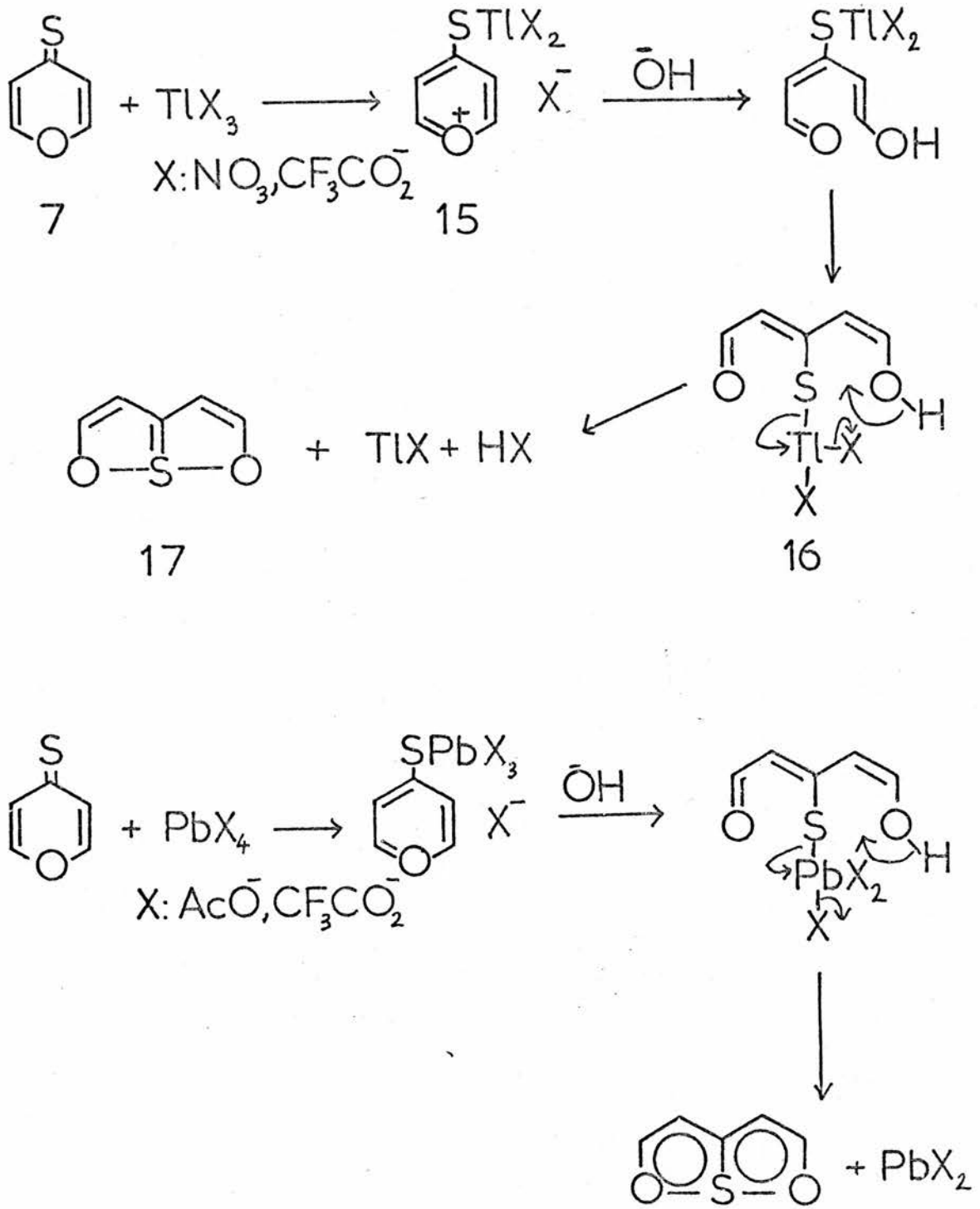
14

Scheme III

B 1,6-Dioxa-6a-thiapentalenes

A general interest in syntheses involving oxidative coupling reactions led to an attempt to prepare 1,6-dioxa-6a-thiapentalenes. Previously, the dibenzo-derivatives (13) were the only known members of this system. It was hoped that treatment of the pyrylium salt (10) with base would produce the compound in a fashion similar to Traverso's synthesis of 1-oxa-6,6a-dithiapentalene[9] (Scheme IB). Hydroxide destroyed the substrate; no dioxathiapentalene was produced (Scheme III) and no starting material was recovered (as thione). Since no product of any type was isolated it seemed unlikely that attack at the 4-position of the ring by hydroxide had occurred since this would have produced γ-pyrone (6). The further possibility that attack at the mercury atom had occurred seemed unlikely since no thione (7) was produced. The remaining possibility was that attack in the ring at the 2-position had occurred (Scheme III), producing the intermediate (14). The reaction could then have failed if the $Hg^{2+} \longrightarrow Hg^{0}$ process did not have a sufficient oxidation potential to oxidatively couple the sulphur and oxygen atoms. This seemed to be unjustifiable at the time since the same process had successfully produced 1-oxa-6,6a-dithiapentalene by oxidative coupling, albeit in lower yield.

The principle behind the method still seemed to be attractive but the method did not work in practice possibly due to the use of the wrong oxidising system. The redox potential for the $Hg^{II} \rightarrow Hg^{0}$ couple (E^{o} = -0.85 V)[204] was found to be considerably less than the redox potentials for two other processes, that of $Tl^{III} \longrightarrow Tl^{I}$ (E^{o} = -1.25 V)[204] and $Pb^{IV} \longrightarrow Pb^{II}$ (E^{o} = -1.46 V)[204]. McKillop and Taylor have made considerable use of the energetically favourable process, $Tl^{III} \longrightarrow Tl^{I}$, in a wide variety of reactions on organic

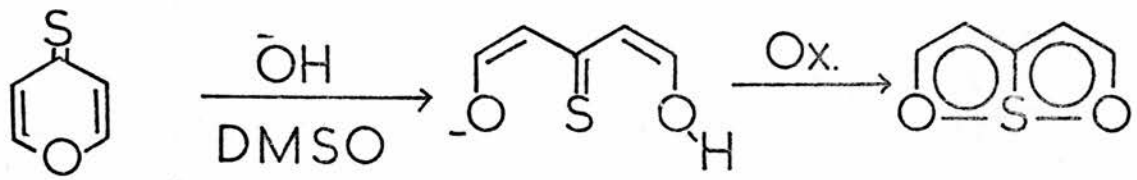


Scheme IV

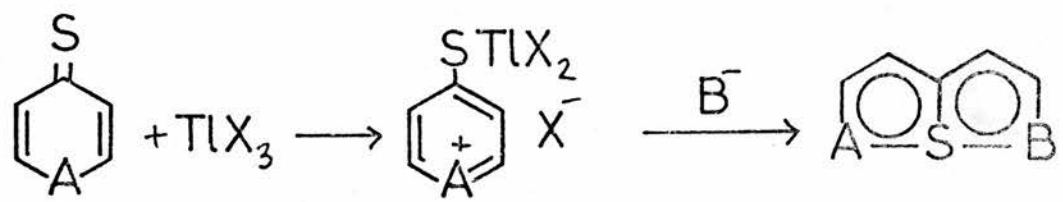
compounds. The thallium system was thus given preference. Reaction of 4H-pyran-4-thione (7) with thallium(III) nitrate in acetonitrile gave a pale brown solution which was assumed to contain the pyrylium salt (15). Addition of hydroxide after one minute and conventional workup afforded 1,6-dioxa-6a-thiapentalene (17) (35%). Changing the oxidising system evidently had a considerable effect on the course of the reaction. Use of thallium (III) trifluoroacetate in place of the nitrate gave a substantially better yield (56%).

Isolation of the pyrylium salt intermediate (15) was found to be impracticable. Addition of dry ether to the pyrylium salt solution failed to precipitate the intermediate. Furthermore the nmr spectrum of the residue from the evaporated solution (this was soluble in deuteriochloroform) showed only the presence of 1,6-dioxa-6a-thiapentalene. Evidently the pyrylium salt was very labile and was ring-opened even by traces of water. This was confirmed by substituting water for hydroxide in the synthesis, whereupon a very similar yield (61%) of 1,6-dioxa-6a-thiapentalene was obtained.

Since increasing the redox potential of the internal oxidant had produced such a useful change in the course of the reaction it was of interest to see whether increasing the redox potential of the oxidant still further had any effect on the reaction. The reaction of lead(IV) acetate and lead(IV) trifluoroacetate with 4H-pyran-4-thione was therefore studied (Scheme IV). Both reactions were successful but gave poor yields, the trifluoroacetate being marginally better (7.6%) than the acetate (1.3%). This difference in yields is readily explained on the basis of trifluoroacetate ion being a better leaving group than acetate ion.

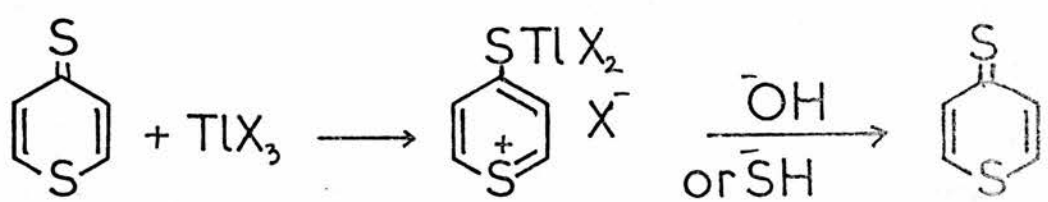


7 18 17



A : O,S ; B: O,S,NMe 19

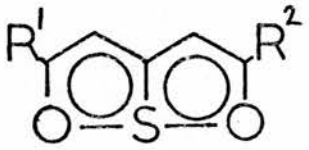
Scheme V



2 20

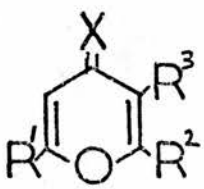
A further method for synthesising 1,6-dioxa-6a-thiapentalene by oxidative coupling, which with hindsight was perhaps the most obvious method, involved a modification of the previously described synthesis of 1-oxa-6,6a-dithiapentalene. Ring-opening 4H-pyran-4-thione (7) with hydroxide in aqueous dimethylsulphoxide produced a deep purple-brown colouration, due to the anion (18). Oxidation after ten minutes with aqueous potassium ferricyanide yielded 1,6-dioxa-6a-thiapentalene but in low yield (2.3%). These oxidative coupling reactions forming sulphur-oxygen bonds are of considerable interest since few methods for sulphur-oxygen bond formation are known[206].

Since the reaction with thallium(III) trifluoroacetate produced a good yield of 1,6-dioxa-6a-thiapentalene it was of interest to extend the synthesis to the preparation of other systems. The possibilities are shown in Scheme V. Treatment of 4H-thiopyran-4-thione (2) with thallium(III) trifluoroacetate gave the intermediate (20) which on solvolysis with hydroxide or hydrosulphide returned the starting material (2) in 4.9% and 27% yields respectively. Attack at the thallium atom in the complex (20) seems to be the most likely initial step of this reaction. This also appears to have been the case when the thallium complex of 4H-pyran-4-thione was treated with hydrosulphide; starting material was recovered (49%). Treatment of 4H-pyran-4-thione with thallium(III) trifluoroacetate and then aqueous methylamine produced 1,6-dioxa-6a-thiapentalene in 44% yield. Repetition of the reaction with rigorous exclusion of moisture until the methylamine was added merely reduced the yield of 1,6-dioxa-6a-thiapentalene to 3.4%. Evidently treatment of 4H-pyran- and 4H-thiopyran-4-thiones with thallium(III) trifluoroacetate does not constitute a general synthesis of the pentalene derivatives (19). Only 1,6-dioxa-6a-



17

	R^1	R^2
a	H	H
b	Me	Me
c	Ø	H
d	CO_2Et	H
e	CO_2Et	CO_2Et



21, X:O

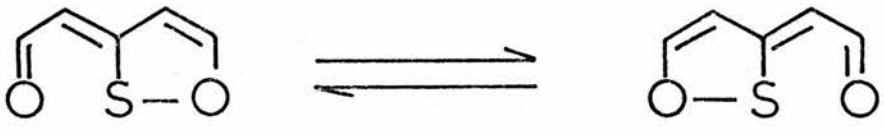
22, X:S

	R^1	R^2	R^3
a	H	H	H
b	Me	Me	H
c	Ø	H	H
d	CO_2Et	H	H
e	CO_2Et	CO_2Et	H
f	H	Me	OH
g	H	Me	OAc

thiapentalenes can be obtained by this route.

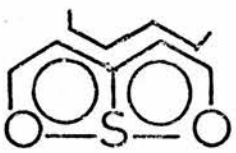
A series of 1,6-dioxa-6a-thiapentalenes (17a-e) has been prepared by the method described. The only limitation of the synthesis is the availability of γ-pyrones and the effect of the substitution pattern of the pyrones. 2-Substituted γ-pyrones and the corresponding thiones produced no difficulties since ring-opening of the thallium complex occurred readily at the 6-position giving good yields of the 1,6-dioxa-6a-thiapentalenes (17a,c,d). 2,6-Dimethyl-4H-pyran-4-thione (22b) gave a poor yield of the corresponding 1,6-dioxa-6a-thiapentalene (17b) due to hindrance to ring-opening by water or hydroxide caused by the methyl groups. 2,6-Diaryl-4H-pyran-4-thiones were not employed in this study. The diester (22e) ring-opened readily due to the presence of the electron withdrawing groups which facilitated nucleophilic attack at the 2(6)-position in the ring. Other available pyrones are naturally occurring compounds of which the only one available in quantity is maltol (21f). This compound undergoes thionation in low yield (27 %) to give compound (22f) which, however, does not give a 1,6-dioxa-6a-thiapentalene; indeed no product was isolated from this reaction.[229] The course of reaction is thus affected adversely by the presence of the hydroxyl group and further investigations were temporarily abandoned when the acetoxy compound (22g) failed to give a product.[229]

Use of water in place of hydroxide for the ring-opening step did not alter the yields significantly in the case of the simple compounds (17a,b). The fact that replacement of hydroxide by water did not give a significantly different result in the synthesis of 2,5-dimethyl-1,6-dioxa-6a-thiapentalene (17b) suggests that the low yield is not due to an electronic effect but is due to steric hindrance at the 2(6)-positions. Use of



a b

23



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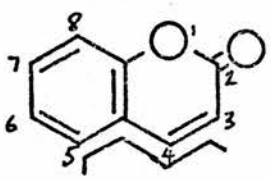

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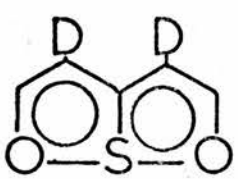
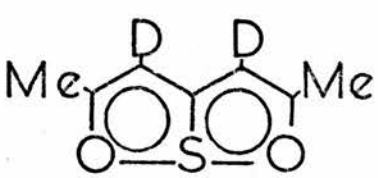
26

a) X: S

b) X: Se



27



28

water for ring-opening was obligatory in the cases of the esters (17d,e) since the ester functions were hydrolysed by hydroxide. The yield of product (17e) from the diester (22e) dropped considerably on going from water (61%) to hydroxide (21%).

1,6-Dioxa-6a-thiapentalenes are colourless, crystalline, low melting solids, extremely soluble in a wide range of solvents, especially so in cold hydrocarbon solvents. The parent compound (17a) is very volatile. These compounds darken on prolonged exposure to light but can be stored indefinitely in the dark, below room temperature. Dioxathiapentalenes have a characteristic musky smell.

The nmr spectra of the 1,6-dioxa-6a-thiapentalenes (17) have been determined in deuteriochloroform (Table I). Close examination of these is necessary since nmr spectroscopy forms the basis for structure assignments of reaction products (Section IIC). The nmr spectra are consistent with formulation of the 1,6-dioxa-6a-thiapentalenes as bicyclic heterocycles. The spectrum of the unsubstituted compound shows two doublets at δ6.90 (3,4-H) and δ8.64 (2,5-H). The possibility of valence tautomerism (23a $\rightleftharpoons$ 23b) appears to be precluded since the spectra of this compound in deuteriochloroform and carbon disulphide are unchanged in pattern down to -50°. The lower field signal is assigned to 2(5)-H since this proton is attached to a carbon atom also bonded to the oxygen heteroatom(s). The coupling constant (2.5 Hz) between 2-H and 3-H is smaller than that which appears in 1,6,6a-trithiapentalenes (ca 6.3 Hz) but is larger than that occurring in the oxygen ring in 1-oxa-6,6a-dithiapentalenes (ca 1.6 Hz). The ring protons in 1,6-dioxa-6a-thiapentalenes are more shielded than their counterparts in the corresponding 1,6,6a-trithiapentalenes, the

3,4-protons (ca 1 ppm) by more than 2,5-protons (ca 0.5 ppm) (Table II).

An interesting feature of the spectrum of the parent system (17a) is the appearance of a 2-4 coupling (24). This type of coupling has not hitherto been observed in trithiapentalene chemistry. The magnitude of the coupling is small (0.4 Hz). Long range coupling of this type has been reported to occur in coumarins (25)[207], the 3-5 coupling being of the order of 0.4 Hz. This coupling does not occur in the monosubstituted dioxathiapentalenes, nor does it occur in monosubstitued reaction products. Examination of the nmr spectra of 1,6,6a-trithiapentalene (26a) and 1,6-dithia-6a-selenapentalene (26b) failed to reveal a similar coupling.

The electronic spectra of 1,6-dioxa-6a-thiapentalenes (Table III) are characterised by three bands at around 220, 260 and 350 nm. 2-Phenyl-1,6-dioxa-6a-thiapentalene differs from the other derivatives in having a multiplicity of bands in the region 213-365 nm. This may be accounted for by assuming that the phenyl group is conjugated with the bicyclic ring system. Similarities between 1,6-dioxa-6a-thiapentalenes and 1,6,6a-trithiapentalenes may be seen from a comparison of the electronic spectra of corresponding derivatives. Transitions in dioxathiapentalenes (17a,b,d,e) occurring around 230 and 260 nm occur in similar positions for the corresponding trithiapentalenes. The long wavelength transition (ca 470 nm) in trithiapentalenes undergoes a hypsochromic shift, so that in dioxathiapentalenes the transition occurs at around 350 nm.

The infrared spectra of the 1,6-dioxa-6a-thiapentalenes (17) have been determined in carbon tetrachloride (Table IV). No

Fig. I

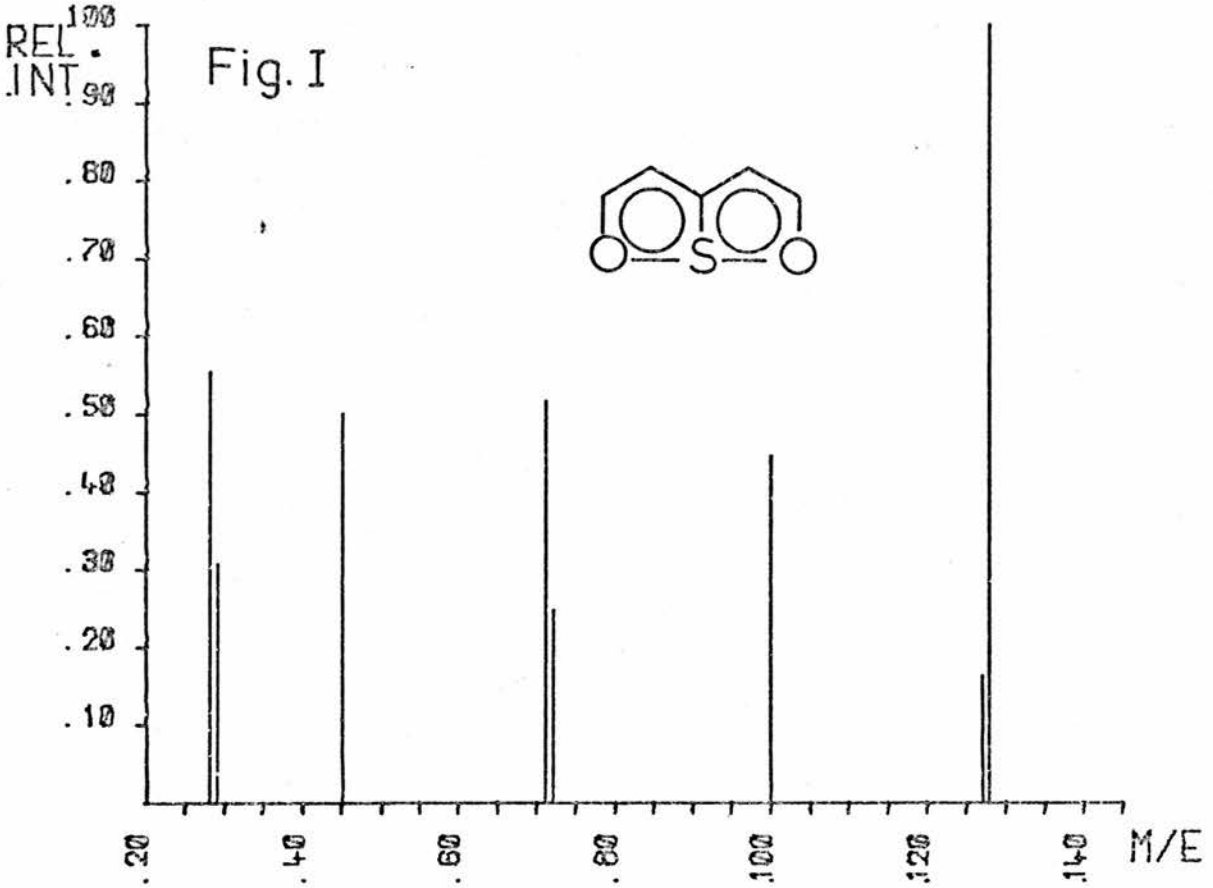
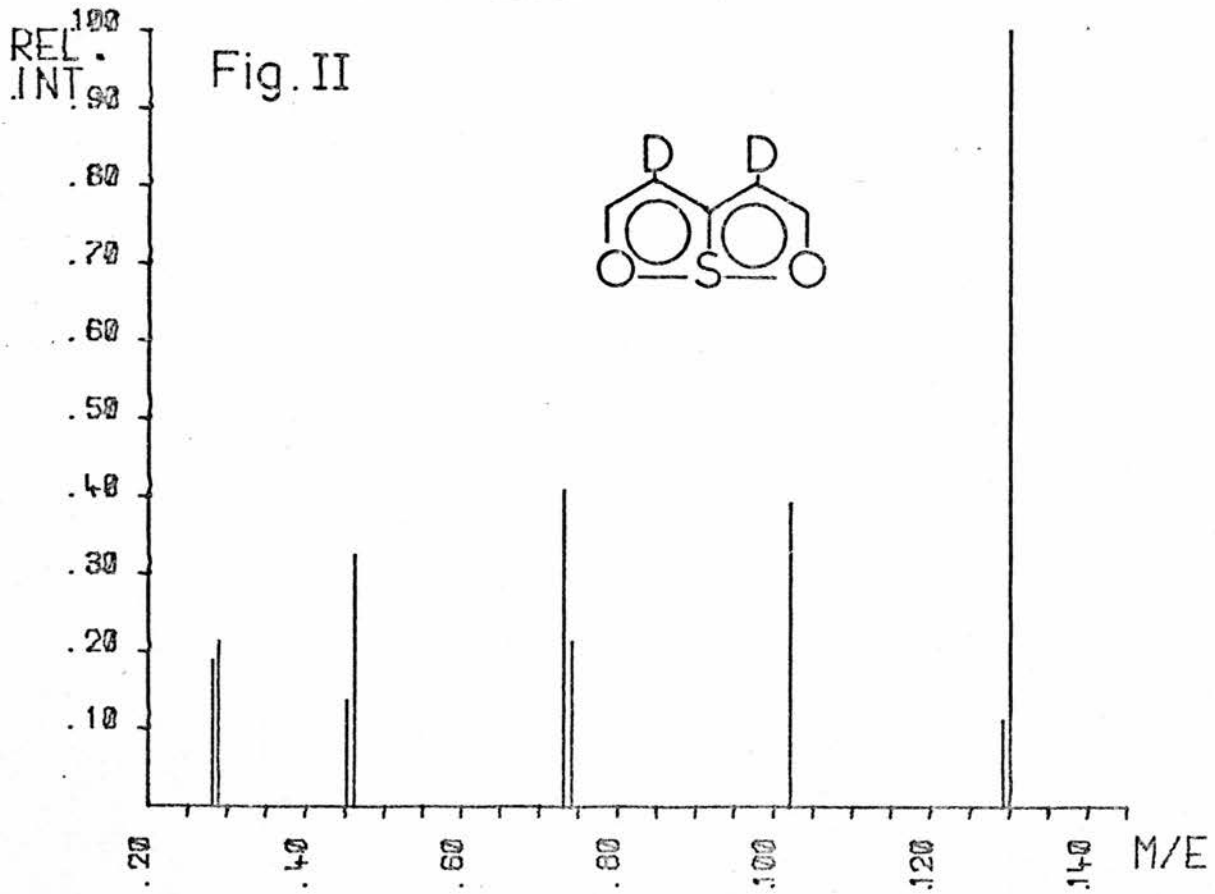

REL. INT.
100
90
80
70
60
50
40
30
20
10
S
20
40
60
80
100
120
140
M/E

Fig. II


REL. INT.
100
90
80
70
60
50
40
30
20
10
D
D
S
20
40
60
80
100
120
140
M/E

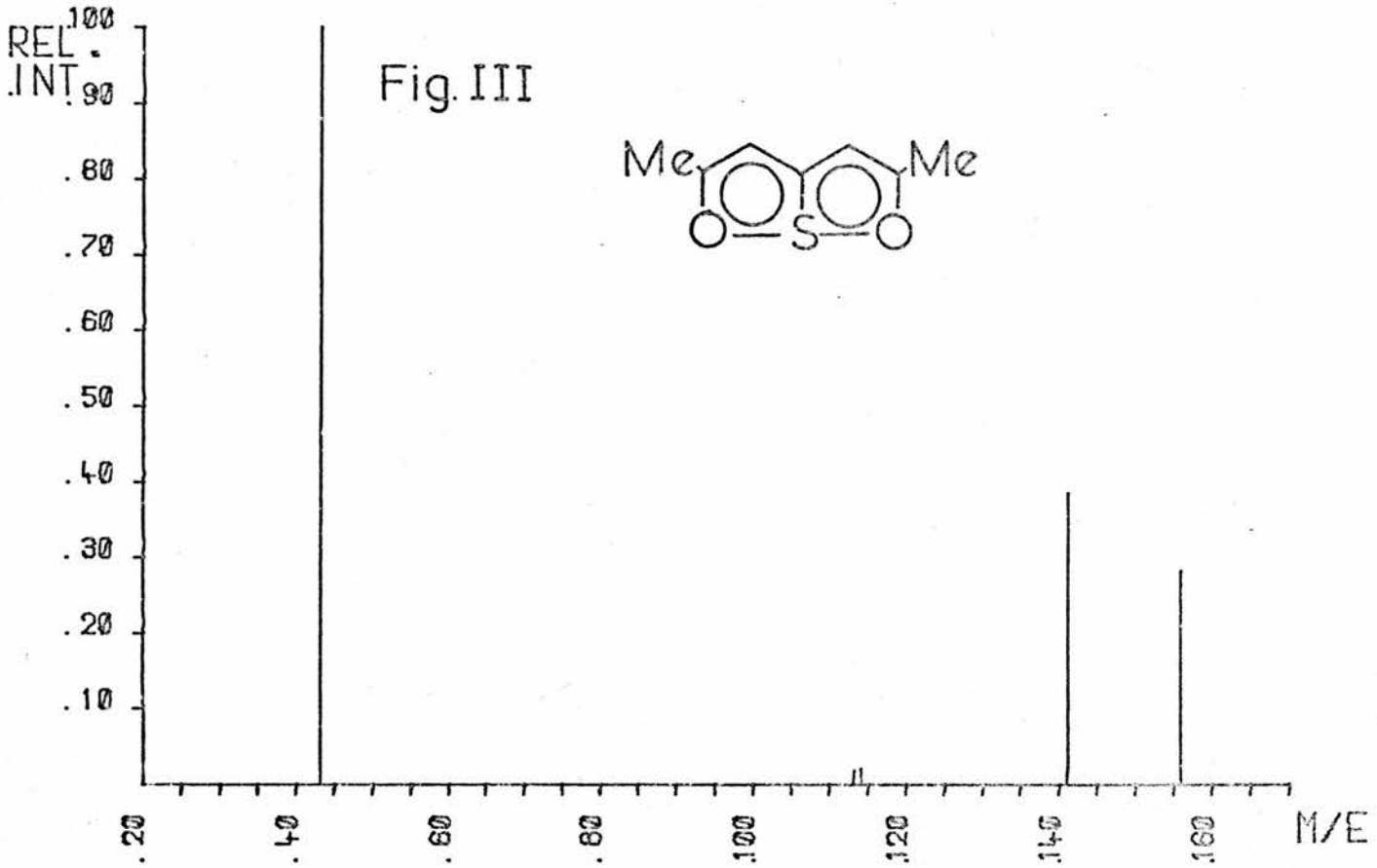


Fig. III

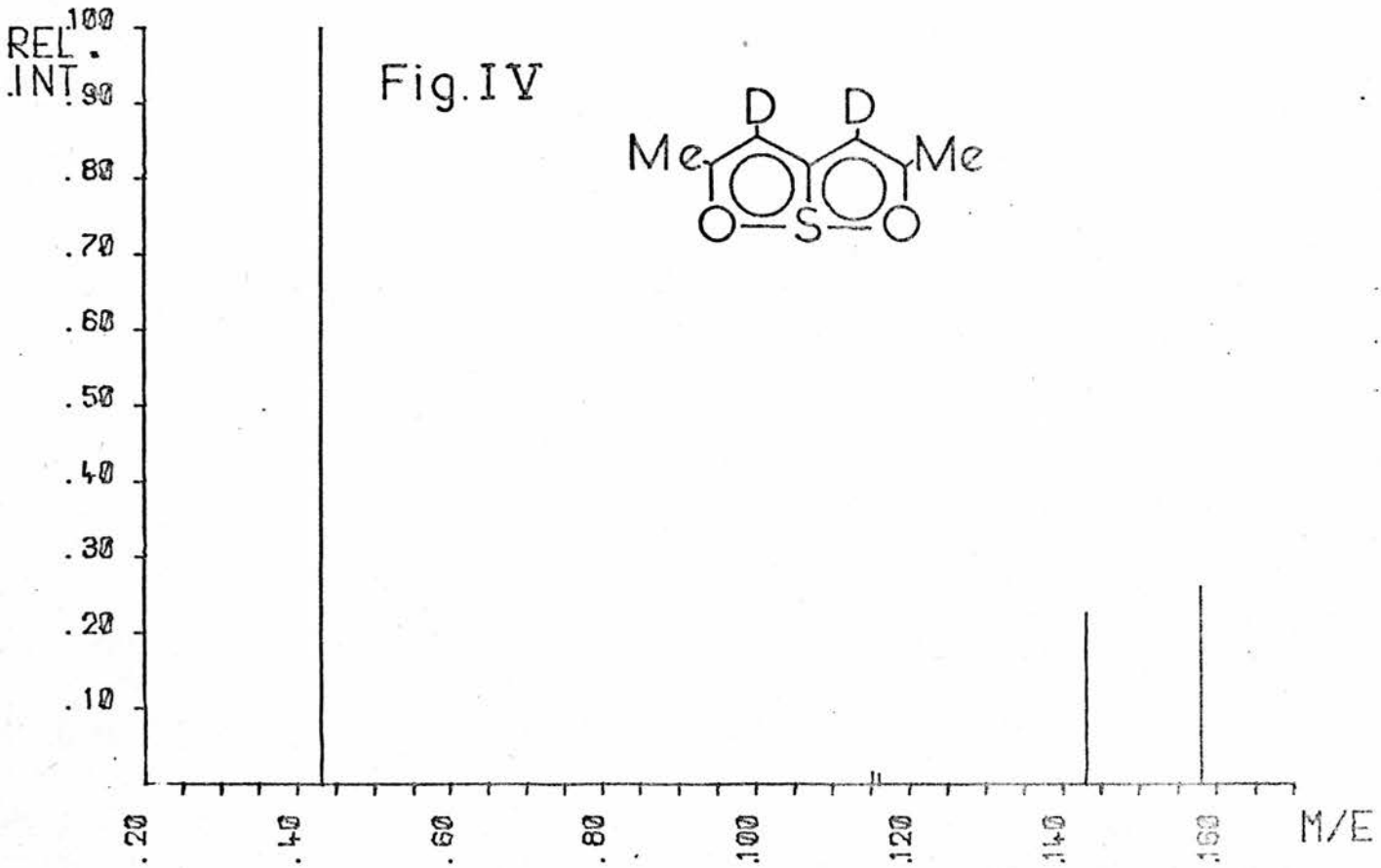
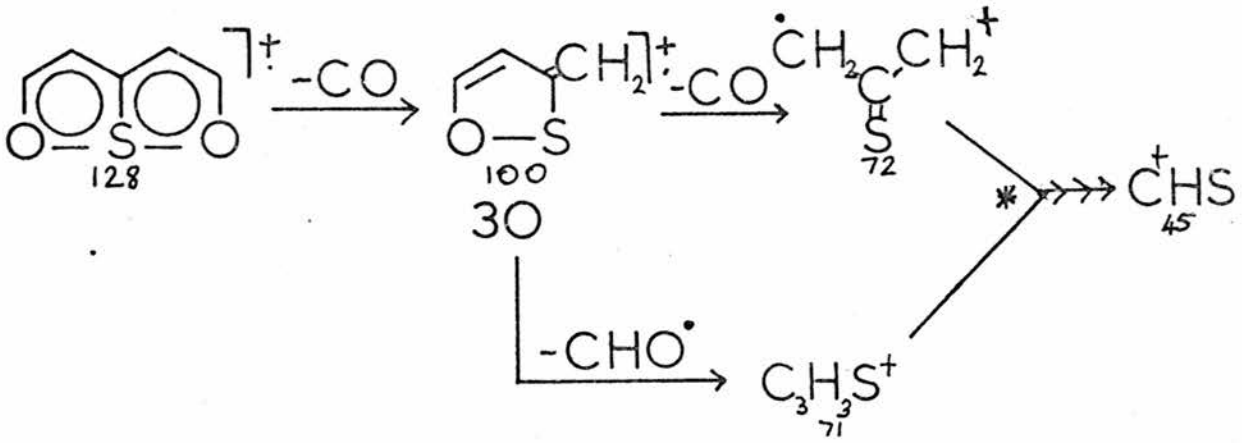
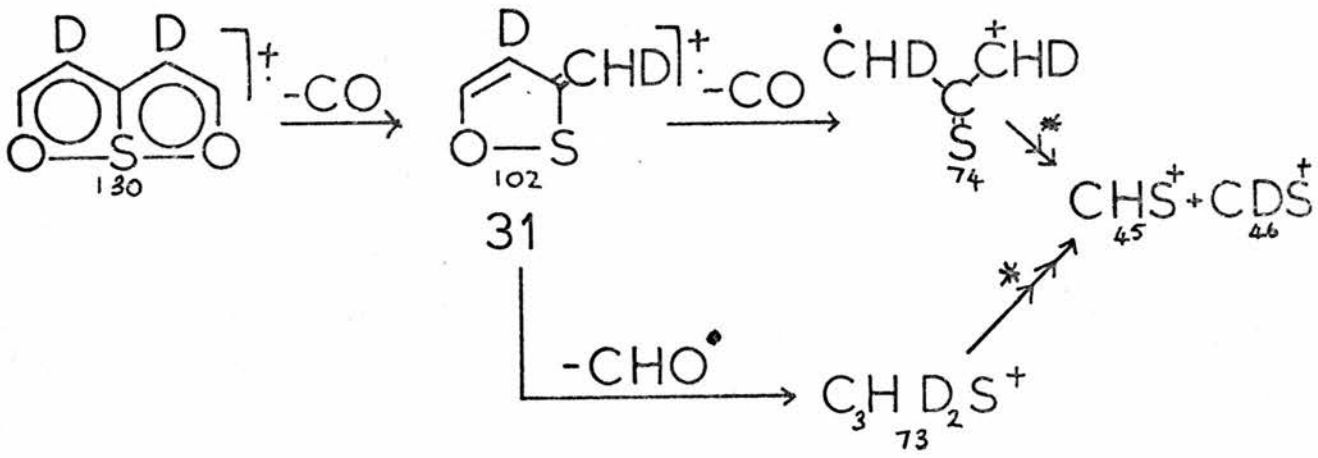


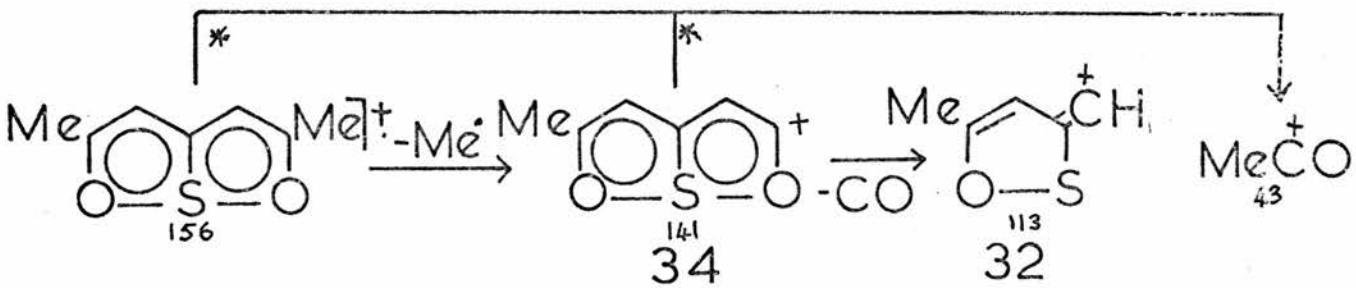
Fig. IV



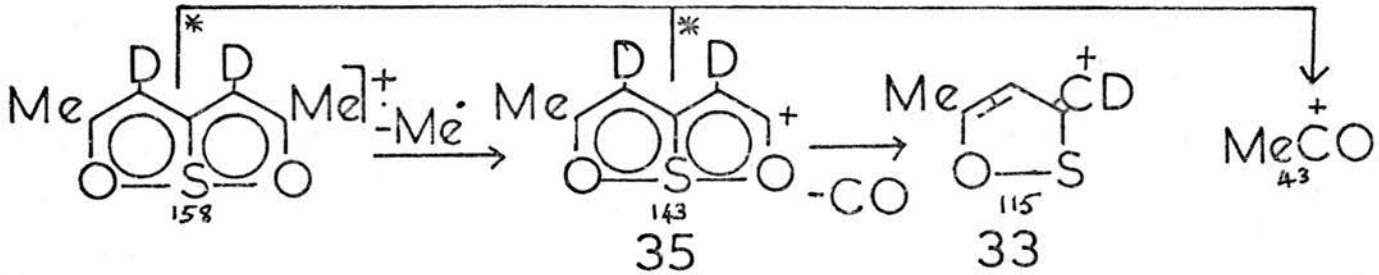
Scheme VI



Scheme VII



Scheme VIII



Scheme IX

* Scheme or ion structure tentative

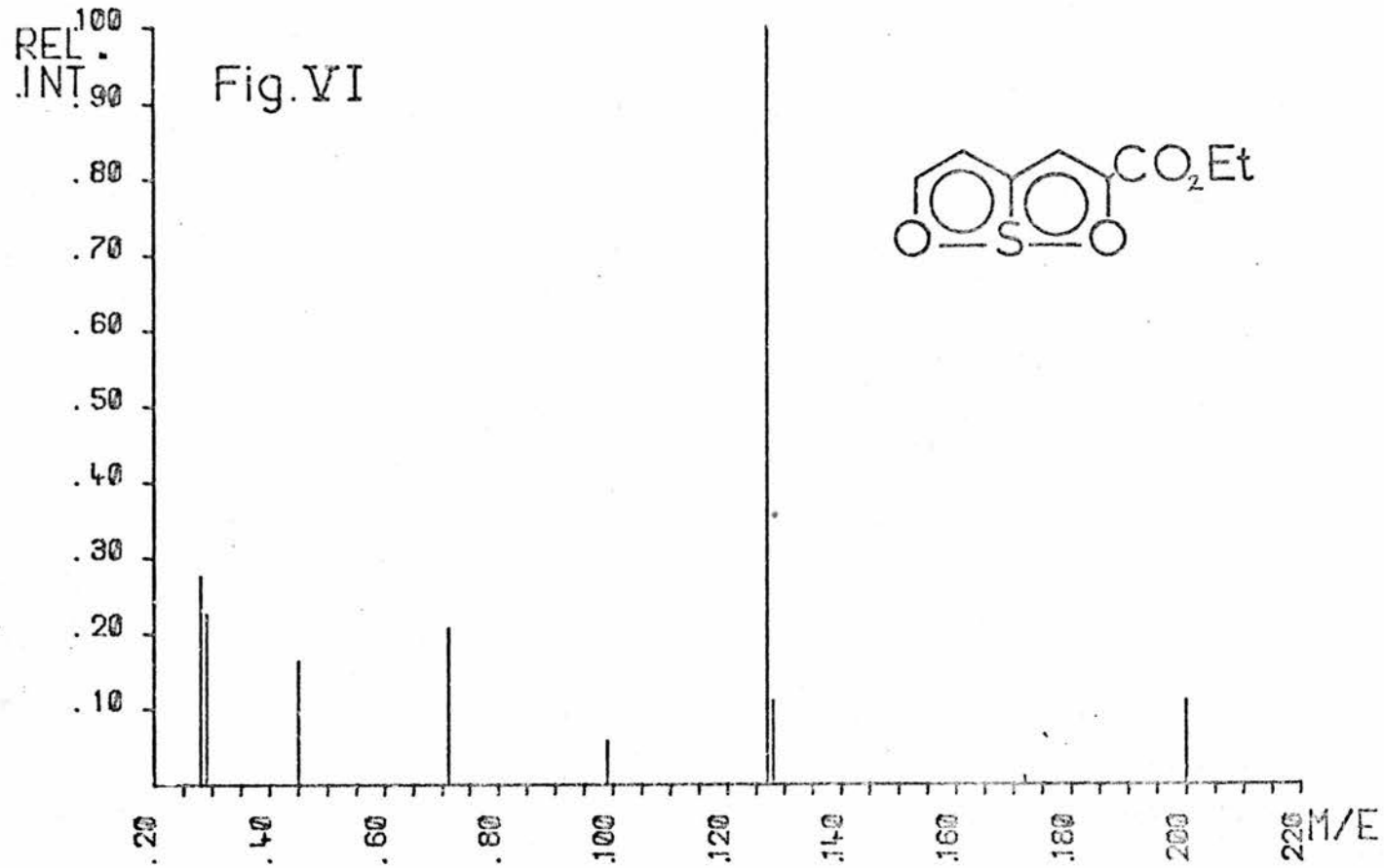
absorption due to a carbonyl group is apparent in the spectra of the parent, dimethyl and phenyl compounds (17a-c) above 1510 cm^{-1}. From the low number of bands appearing in the spectra of the symmetrically substituted compounds, a high degree of symmetry in these molecules may be inferred.

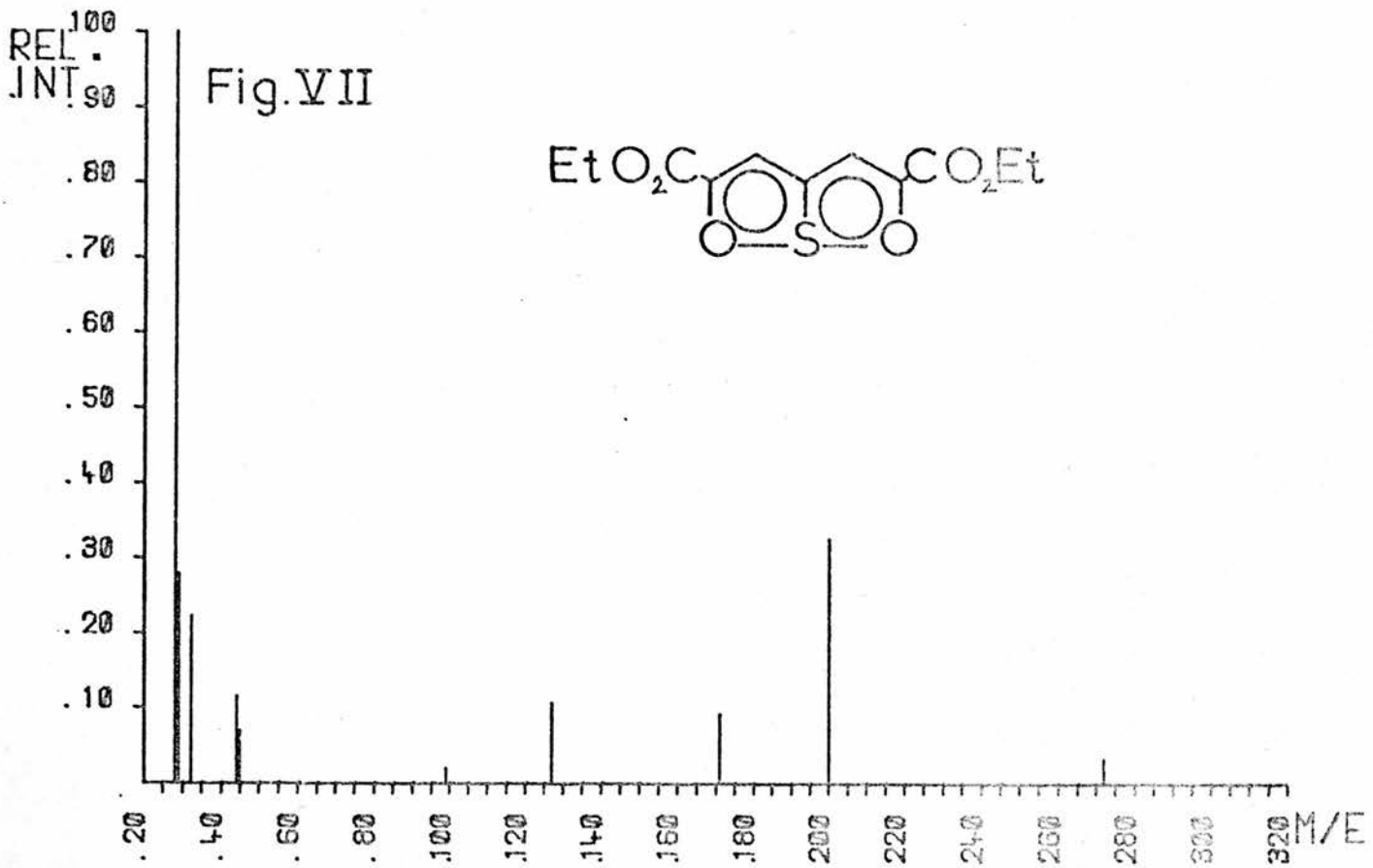
The mass spectra of the 1,6-dioxa-6a-thiapentalenes have been determined (Table V, Figures I-VII). The mass spectra of the deuterated derivatives (27,28) will also be discussed here but their syntheses will be described in a later section. The breakdown patterns of the parent compound and its dideuterio-derivative (27) are identical in pattern (Schemes VI and VII). Loss of carbon monoxide from the molecular ion leads to the unknown 1,2-oxathiole system. The origins of the peaks due to the 1,2-oxathiole cations (30 and 31) are confirmed by the presence of metastable peaks at m/e 78 (calculated m/e = 78.2) and m/e 80 (calculated m/e = 80.0) respectively. Further loss of CO and $CHO^{\bullet}$ from this ion leads to the thione peaks at m/e 71-74 and thence to the ions CHS^{+} and CDS^{+}. The molecular ion formed the base peak for these compounds. The base peak for the dimethyl derivatives (17b and 28; Figures III and IV respectively) was that due to the ion CH_3CO^{+} (m/e 43). This might seem to imply that the molecular ion decomposes by loss of acetyl to give the oxathiole structures (32,33). This does not occur however, since the oxathiole structures can be shown, by the presence of metastable peaks to arise by loss of CO from the demethylated dioxathiapentalenes (34, 35). The acetyl peak most probably arises from degradation of the oxathiole structures. Loss of one methyl group only from the parent ion tends to confirm this possibility.

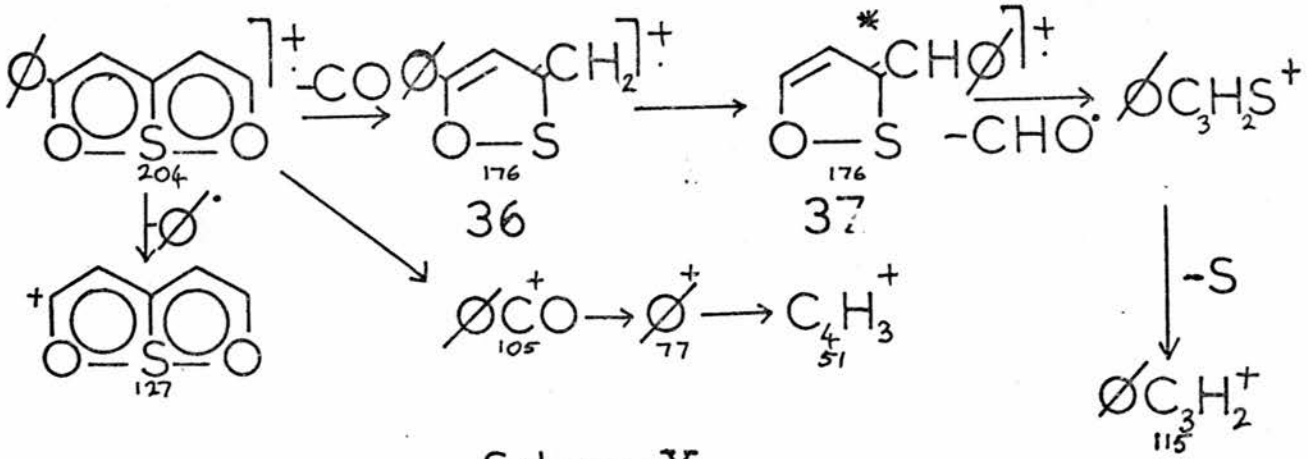
2-Phenyl-1,6-dioxa-6a-thiapentalene (17c) loses carbon monoxide in a similar manner to the parent compound, yielding the

Fig. V

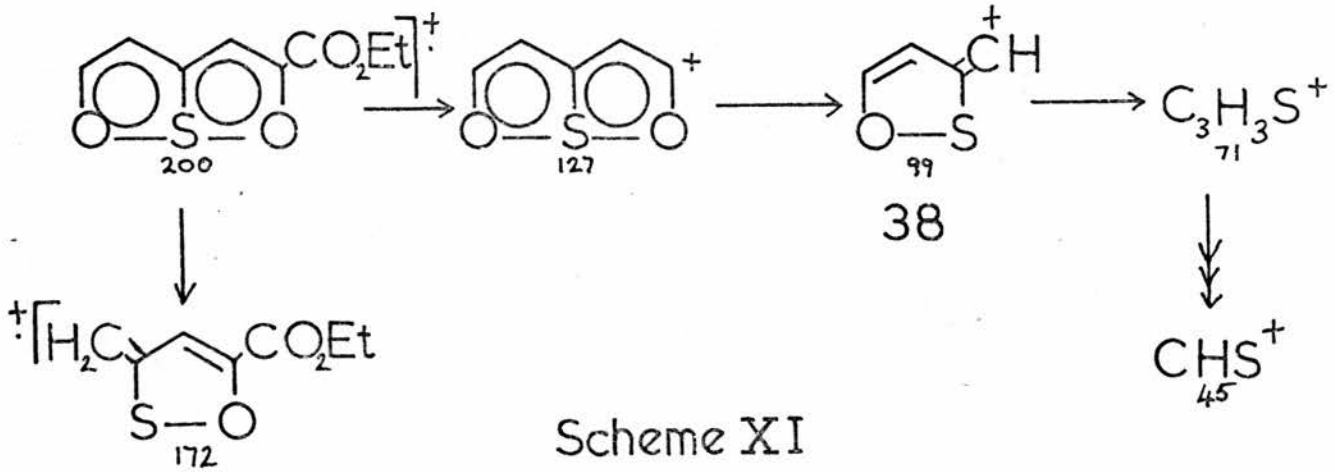
REL. INT.
100
90
80
70
60
50
40
30
20
10
20
40
60
80
100
120
140
160
180
200
220
M/E


REL. INT.
100
90
80
70
60
50
40
30
20
10
Fig.VI
CO2Et
S
20
40
60
80
100
120
140
160
180
200
220
M/E

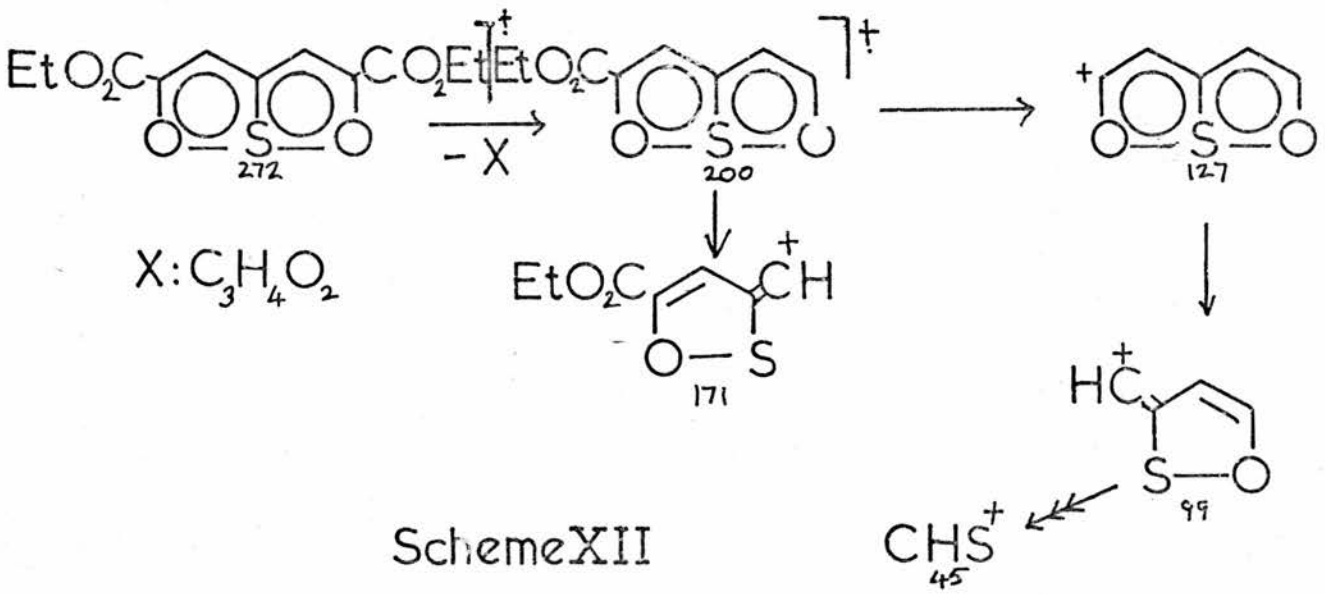

REL. INT.
100
90
80
70
60
50
40
30
20
10
Fig.VII
EtO2C
CO2Et
S
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
M/E



Scheme X



Scheme XI



Scheme XII

* Ion structure tentative

oxathiolium ion (36) (Scheme X, Figure V). This is confirmed by the presence of the metastable ion at m/e 152 (calculated m/e = 151.8). This oxathiole ion then undergoes a rearrangement to another oxathiolium ion (37). It is necessary to postulate such a rearrangement to account for the subsequent loss of CHO$^{\bullet}$ (m/e 29) from this ion, since it would appear unlikely that the primary ion (36) could possibly lose CHO$^{\bullet}$. This decomposition has a confirmatory metastable peak at m/e 123 (calculated m/e = 122.8). The original oxathiole ion (36) not only rearranges but loses a benzoyl ion (m/e 105) which appears strongly in the mass spectrum. The benzoyl ion decomposes in two stages by loss of carbon monoxide, then acetylene, with confirmatory production of the requisite metastable peaks. Loss of a phenyl group from the molecular ion is also observed, but only to a small extent.

The molecular ion for the ester (17d) (Figure VI) is particularly weak, the base peak being due to the ion of m/e 127, signifying loss of the ester group. The metastable peak at m/e 80.5 (calculated m/e = 80.6) confirms this transition. The resulting ion (m/e 127) then decomposes (Scheme XI) in a fashion similar to the parent dioxathiapentalene by losing carbon monoxide to give an oxathiole ion, with the corresponding metastable peak at m/e 77 (calculated m/e = 77.1). The molecular ion also loses carbon monoxide to give an oxathiole ion (39) but, as in the case of the phenyl compound (17c), only to a small extent. The diester (17e) (Scheme XII, Figure VII) after loss of a first ester group breaks down in the same manner as the monoester.

From this limited study of the mass spectra of the dioxathiapentalenes certain decomposition features become apparent. Loss of carbon monoxide from the molecular ion is common and the

peak due to carbon monoxide (m/e 28) is present in every spectrum. The oxathiole ion residue then loses carbon monoxide or a "CHO$^{\bullet}$" group (m/e 29), the latter ion being observed in most spectra. Peaks in the region of m/e 70 are due to the C_3H_nS ion (n = 0-4), and are due to the last-mentioned transition. Peaks due to CHS^+ (m/e 45) and CS^+ (m/e 44) are also apparent in most spectra. The molecular ion peak is normally fairly intense and indicates that the system is relatively stable.

1,6-Dioxa-6a-thiapentalenes constitute the simplest possible system of the trithiapentalene type. From the spectroscopic evidence presented there is no reason to suppose that these compounds cannot be represented by the bicyclic formula (40). A bicyclic formulation has been proposed[157] for the dibenzo derivative (41) on the basis of an Xray crystallographic determination. On this basis, in the absence of Xray crystallographic data, a bicyclic formulation is in order.

40

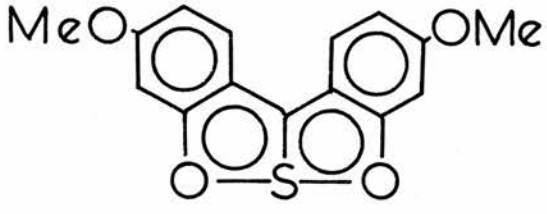


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Table I

Chemical shift data (δ values in ppm downfield from the tetramethylsilane signal) in the nmr spectra of 1,6-dioxa-6a-thiapentalenes (in deuteriochloroform unless otherwise stated)

J values in Hz

	Proton Signals (δ)			
Compound	R^2	R^3	R^4	R^5
17a[a]	H, 8.64 dd $J_{(2,3)}$=2.5 $J_{(2,4)}$=0.4	H,6.90 dd $J_{(3,2)}$=2.5 $J_{(4,2)}$=0.4	H, 6.90	H, 8.64
17b	Me, 2.32 d $J_{(2,3)}$=0.4	H, 6.49 b	H, 6.49	Me, 2.32
17c	Ø, 7.44 m[b] 7.91 m[c]	H, 7.23	H, 6.85 d $J_{(4,5)}$=2.6	H, 8.57 d $J_{(5,4)}$=2.6
17d	CO_2Et,1.40 t 4.41 q J_{Et} = 7.2	H, 7.51	H, 7.10 d $J_{(4,5)}$=2.5	H, 8.75 d $J_{(5,4)}$=2.5
17e	CO_2Et,1.42 t 4.43 q J_{Et} = 7.0	H, 7.65	H, 7.65	CO_2Et, 1.42 t 4.43 q

a = Spectrum unchanged down to -50° in deuteriochloroform and carbon disulphide

b = Meta + para protons

c = Ortho protons

Values refer to singlet absorptions unless otherwise stated.

For multiplets, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet, b = broad

Table II

The change in chemical shift ($\Delta\delta$) of the ring protons of 1,6-dioxa-6a-thiapentalenes compared with the chemical shifts of the equivalent protons in the corresponding 1,6,6a-trithia-pentalenes[14] in deuteriochloroform

	$\Delta\delta$			
Compound	R^2	R^3	R^4	R^5
17a	0.54	1.06	1.06	0.54
b	0.32*	1.07	1.07	0.32
c		1.03	1.09	0.61
d		1.04	0.97	0.51
e		1.07	1.07	

* Methyl group

Table III

UV Spectra of 1,6-dioxa-6a-thiapentalenes (in cyclohexane)

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
17a	198	3.78	17b	220	3.35
	222	3.38		260	3.32
	257	3.35		338	4.24
	339	4.06			
17c	213	4.05			
	229	4.12			
	233	4.15			
	286	3.71			
	291	3.69			
	365	4.36			
17d	206	3.89	17e	220	3.96
	245	3.40		263	3.50
	271	3.44		373	4.16
	359	4.11			

Table IV

Infrared spectra of 1,6-dioxa-6a-thiapentalenes in carbon tetrachloride (0.02M) in the range 4000-850 cm^{-1}

w = weak m = medium s = strong br = broad

Compound	17a	17b	17c	17d	17e
	3020w	2980w	3200w	2980w	2980m
	1510m	2930w	1511s	1756s*	1757s*
	1454s	1509m	1502m	1734s*	1736s*
	1442s	1481s	1461s	1508m	1511w
	1248s	1413s	1449s	1471m	1482w
	1214s	1373m	1376s	1399s	1472w
	1082m	1301s	1323m	1376m	1453w
	860m	1146m	1309m	1324s	1420m
		986m	1222s	1288sbr	1400m
		960m	1181m	1118m	1375s
			1090w	1083w	1314s
			1077w	1030m	1279m
			1033w	958w	1221s
			897s	948w	1140w
					1111s
					1029s
					962w
					948w

* $\nu_{C=O}$ for ester group

Table V

Mass spectral data for 1,6-dioxa-6a-thiapentalenes

Compound	m/e	R.I.(%)
17a	128	100
	127	16
	100	45
	78[a](78.2[b])(128-100[c])	
	72	25
	71	52
	45	50
	29	31
	28	56
17b	156	28
	141	39
	127.5[a](127.3[b])(156-141[c])	
	114	2.1
	113	1.8
	90.5[a](90.5[b])(141-113[c])	
	43	100
17c	205	11
	204	60
	203	12
	176	40
	152[a](151.8[b])(204-176[c])	
	147	25
	127	11
	123[a](122.8[b])(176-147[c])	
	115	20
	105	59
	77	100
	56.5[a](56.5[b])(105-77[c])	
	51	50
	50	17
	45	19
27	130	100
	129	11
	102	39
	80[a](80.0[b])(130-102[c])	
	74	21
	73	41
	46	32
	45	14
	29	21
	28	19
28	158	26
	143	23
	129.5[a](129.3[b])(158-163[c])	
	116	1.4
	115	1.6
	92.5[a](92.5[b])(143-115[c])	
	43	100
17d	200	11
	172	1.0
	128	11
	127	100
	99	5.8
	80.5[a](80.6[b])(200-127[c])	
	77[a](77.1[b])(127-99[c])	
	71	21
	45	16
	29	23
	28	28

Table V contd.

Compound	m/e	R.I.(%)
17c	39	21
	33.8[a] (33.8[b]) (77-51[c])	
	28	25
17e	272	3.3
	200	33
	171	9.2
	147[a] (147.0[b]) (272-200[c])	
	127	11
	99	2.0
	45	7.0
	44	12
	32	22
	29	28
	28	100

a = Metastable peak

b = Calculated value for metastable peak

c = Transition A $\longrightarrow$ B giving rise to metastable peak

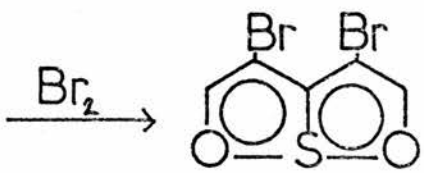
42

a. R:H

b. R:Bu^t

c. R:Ø

43



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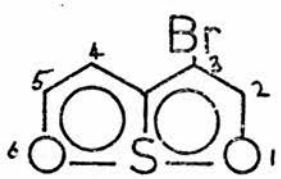

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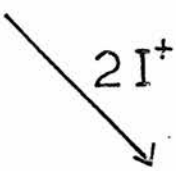
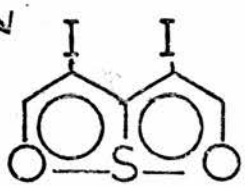
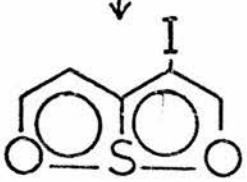


$2I^+$



46

I^+



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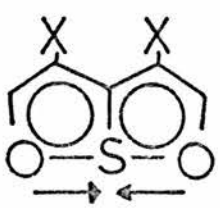

X: Br, I

48

C Reactions of 1,6-dioxa-6a-thiapentalenes

Since 1,6-dioxa-6a-thiapentalenes had become readily available by the synthetic route described, it was of interest to investigate the reactivity of these compounds. Almost no work has been done on the reactivity of other analogues of trithiapentalenes and little on trithiapentalenes themselves. The reactions which have been studied have employed highly substituted derivatives. Exceptionally formylation has been carried out in these laboratories on the parent system (42a) and other simple members of the series (42b,c). It was therefore decided to limit this investigation of dioxathiapentalenes to the parent compound (43). The reactions carried out and the products obtained will be discussed individually, and the general features of the reactions will be discussed afterwards. Secondary reactions will be discussed separately.

(i) Halogenation

1,6-Dioxa-6a-thiapentalene (43) reacted immediately at room temperature with bromine in carbon tetrachloride. The ratio of bromine:substrate had no effect on the product other than its yield; regardless of the ratio of reactants the product was always the dibromo derivative (44). The intermediacy of the mono-bromo compound (45) can be assumed. The effect of a bromine atom on the charge densities at C-4,5 (45) in the other ring is likely to be small and, since the size of a bromine atom is not large enough to cause steric effects (Van der Waals radius = 1.95 Å [42]), substitution occurs readily in the other ring. Steric hindrance may play a part in the iodination of dioxathiapentalene. The iodinating agent, iodine-silver acetate, is effectively iodonium acetate:

$$AgOAc + I_2 \longrightarrow AgI + I^{+}OAc^{-}$$

Use of an excess of iodinating agent gave the di-iodo derivative (46). Use of equimolecular amounts of substrate and iodine, with only a limited excess of silver acetate and a shorter reaction time, yielded a mixture of starting material, 3-iodo-1,6-dioxa-6a-thiapentalene and 3,4-di-iodo-1,6-dioxa-6a-thiapentalene. Starting material and the di-iodo compound were present in a small amount and recrystallisation gave the pure mono-iodo compound (47). The halo compounds (44,46, 47) were all isolated in high yields.

Use of the pseudo-halogens cyanogen [$(CN)_2$] and thiocyanogen [$(SCN)_2$] failed to give substituted materials under reaction conditions similar to those employed in the halogenations. Cyanogen bromide (CNBr) also failed to react with dioxathiapentalene. Starting material was recovered in high yield.

The position of substitution in the dioxathiapentalene may be inferred from an examination of the nmr spectra of the halo compounds (Table VI). Introduction of a halogen atom (Br,I) into benzene causes the ortho protons to be deshielded by no more than 0.2-0.3 ppm[208]. Since there is a considerable difference between the chemical shifts of 2(5)-H and 3(4)-H, the residual proton signals should be indicative of the position of substitution. All the spectra of the halo-compounds show residual proton signals at ca δ8.7. The absence of a signal at ca δ6.9 in the symmetrical compounds (44,46) further indicates that substitution occurs at the 3 and 4 positions. The mono-iodo compound (47) displays a signal at δ6.98 (1H) and an overlapping singlet and doublet at ca δ8.7 (2H), adding further evidence for substitution having occurred at the 3-position.

Substitution of one iodine atom into the dioxathiapentalene

system causes little difference to the UV spectrum. Two bands appear at 213 and 231 nm in place of the single band at 222 nm in the parent compound and the long wavelength band, which occurs at 339 nm in the unsubstituted compound now appears at 355 nm. Substitution by two halogen atoms has a considerable effect upon the long wavelength transition, especially in the di-iodo compound. Two bromine atoms move the band by 35 nm and two iodine atoms move the band by 142 nm, both to longer wavelength. This can only be caused by the proximity of the halogen atoms to each other; electronic effects would not be likely to cause such changes in the UV spectra since bromine and iodine have similar electronegativities (Br, 2.8; I, 2.5[42]). The effect is more noticeable in the di-iodo-dioxathiapentalene and may be due to the size of the halogen atoms. Using the bond lengths and angles found for the dibenzodioxathiapentalene the separation between C-3 and C-4 can be calculated to be about 2.6 Å (Appendix A). Furthermore using known data on C-Br and C-I bond lengths it is possible to calculate the separations of the halogens in the symmetrical compounds by assuming that the geometry will be similar (Appendix A). Bromine and iodine atoms in the *peri* (3,4) positions will be separated by about 3.6 and 3.7 Å, respectively. Since the Van der Waals contact distances for these atoms are 3.9 and 4.3 Å respectively it is apparent that steric clash between the halogen atoms in the *peri* positions can occur, more especially in the case of the di-iodo compound (46). This steric clash can be relieved in two ways, by the molecule losing its planarity or by compression of the sulphur-oxygen bonds accompanied by adjustment of bond angles (48). Loss of planarity would appear to be unlikely since this would disturb the O-S-O array of atoms, which might have an adverse effect on the sulphur-oxygen overlap. Sulphur-oxygen bond compression and adjustment

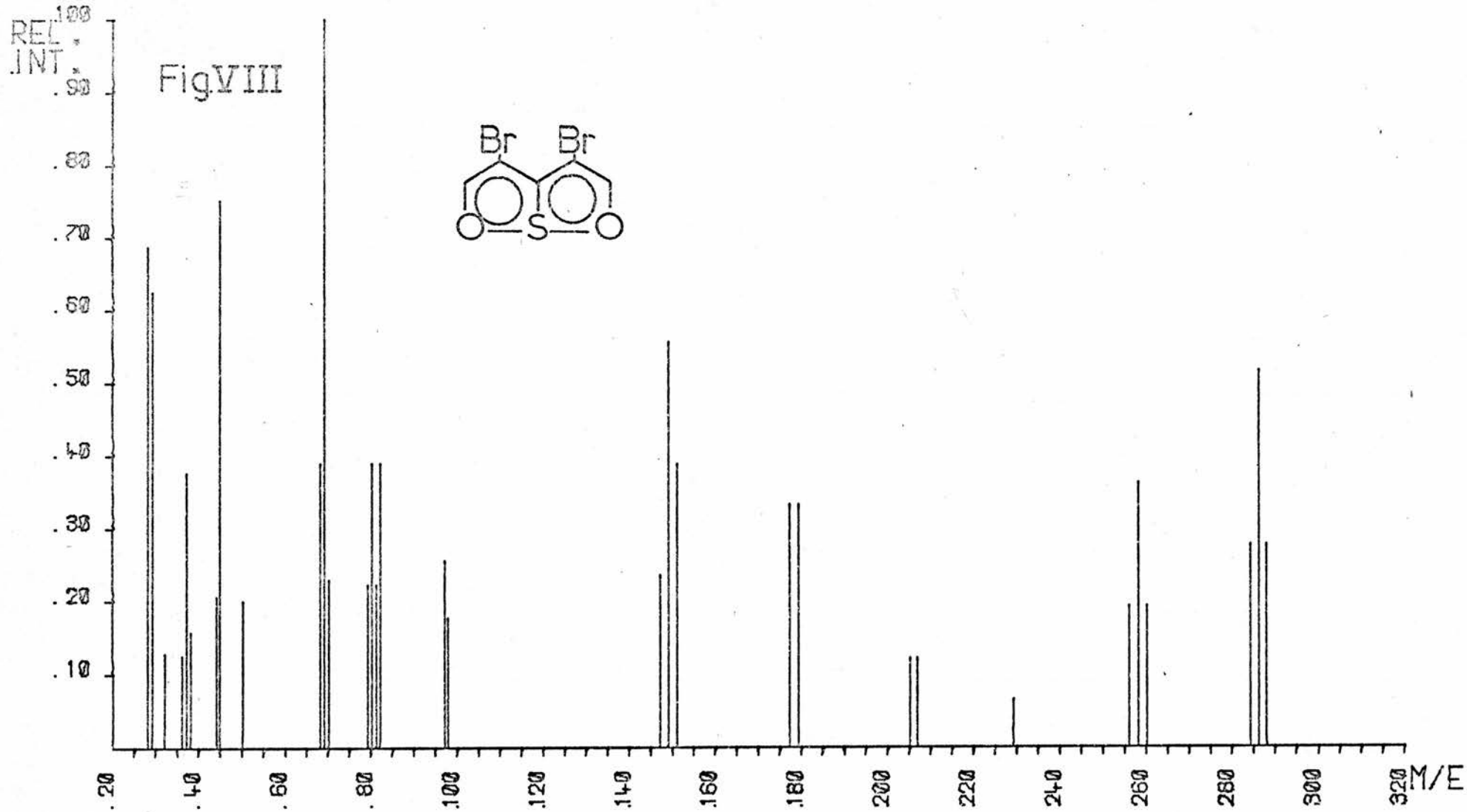
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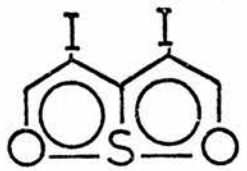
Fig.VIII

Fig.IX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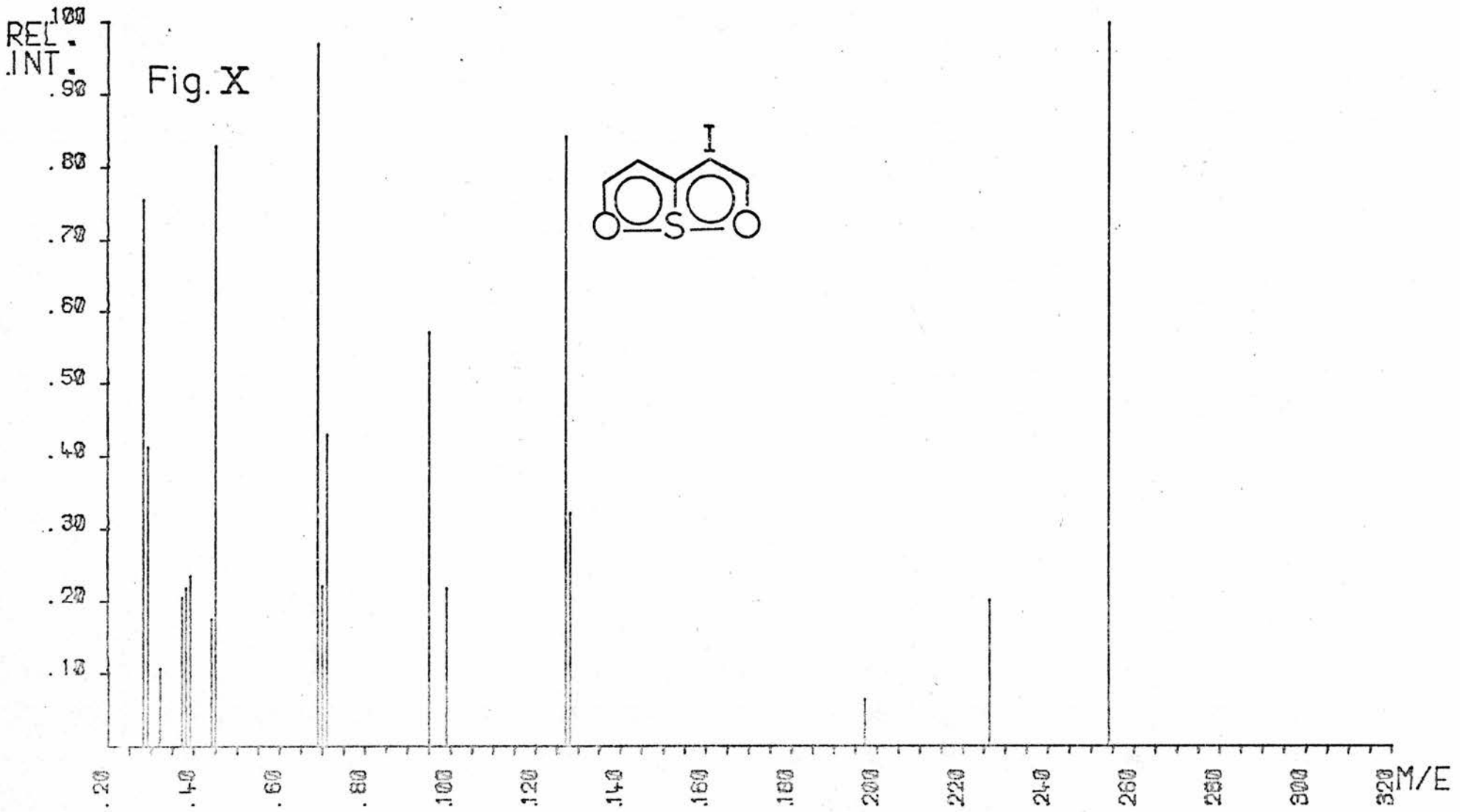
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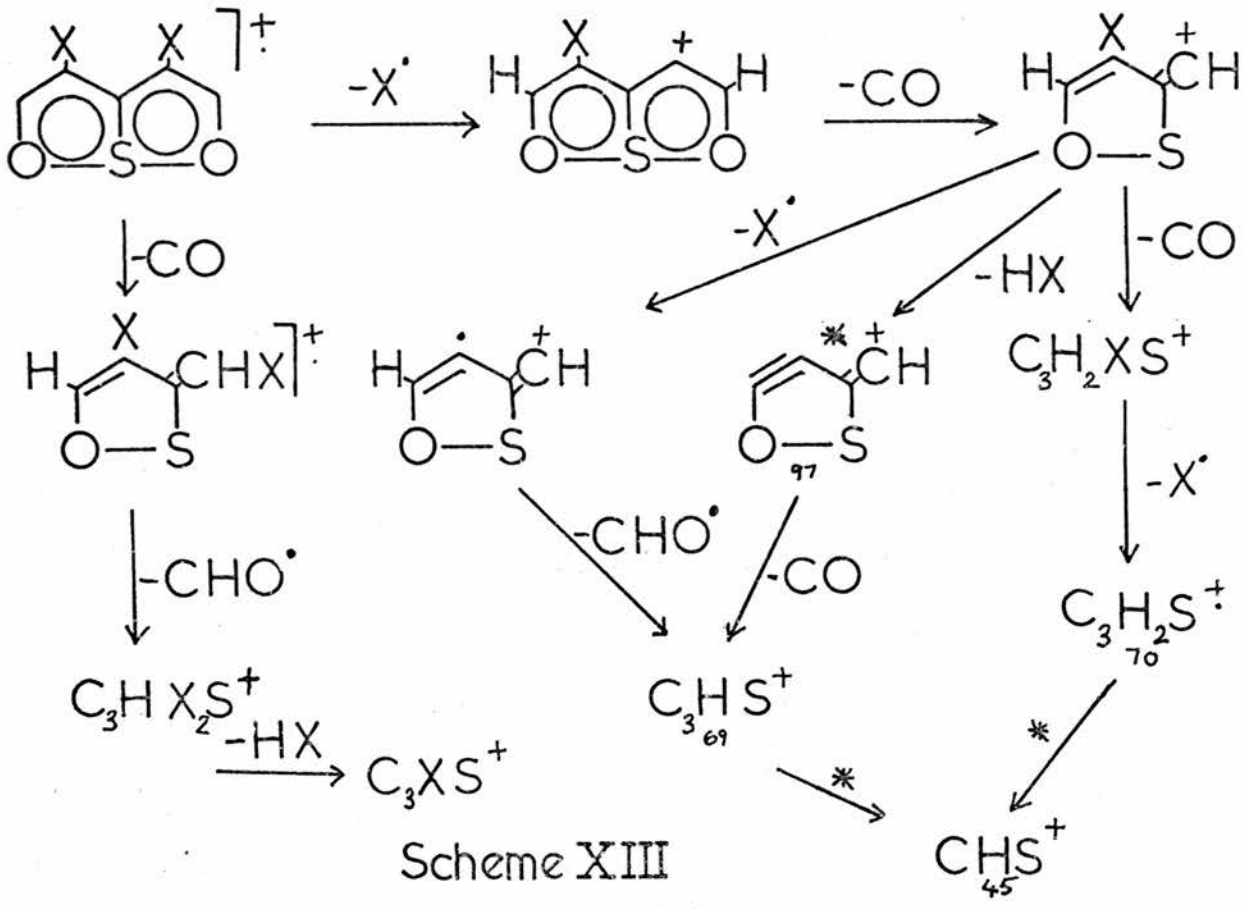
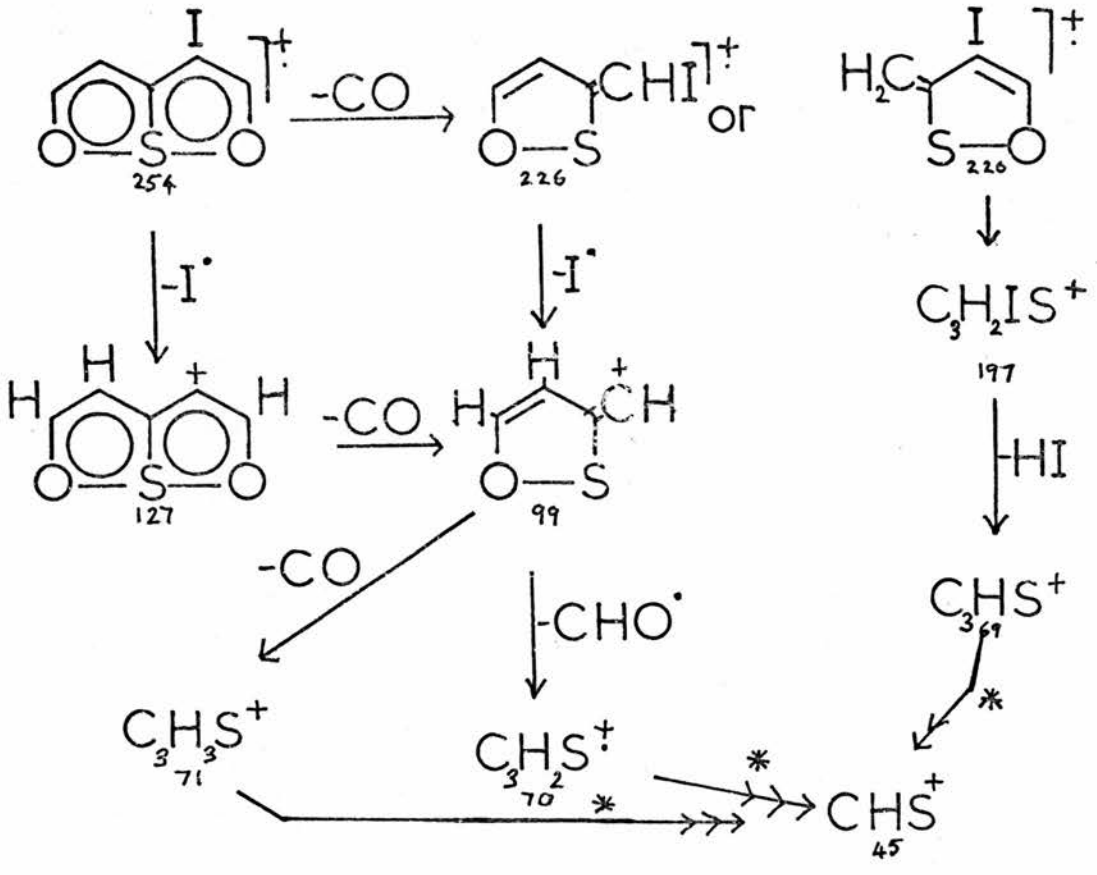
Fig. X



Scheme XIII



Scheme XIV

* Scheme or ion structure tentative

of the internal bond angles seems to be the likely course to alleviate the strain; this had been observed previously in the chemistry of the trithiapentalenes and was discussed in an earlier section of the thesis.

The mass spectra of the di-halodioxathiapentalenes (Scheme XIII, Figures VIII, IX) are identical in pattern. Two decomposition pathways are possible and both are observed. No metastable peaks were observed in the spectrum of the dibromo compound. However this is no drawback to assignment of particular peaks since naturally occurring bromine has two isotopes, Br^{79} and Br^{81}, which have similar abundances. Thus ions with one or two bromine atoms have distinctive patterns and this feature enabled interpretation of the mass spectrum to be made with reasonable certainty. The initial degradations present in the mass spectrum of the di-iododioxathiapentalene were accompanied by metastable peaks chracteristic of loss of carbon monoxide (m/e 326, calculated m/e = 326.0) or iodine (m/e 168.5, calculated m/e = 168.5) from the molecular ion. Loss of iodine from the molecular ion is followed by loss of carbon monoxide and this transition is also accompanied by a metastable peak (m/e 200, calculated m/e = 200.0). The base peak for both compounds is the ion at m/e 69, due to C_3HS^+. The mono-iododioxathiapentalene (47) decomposes in a very similar manner, the only confirmed transition being the loss of carbon monoxide from the molecular ion which is accompanied by a metastable peak at m/e 201 (calculated m/e = 201.0). The spectra are similar in pattern to those of the unsubstituted compounds in that successive loss of CO or $CHO^{\bullet}$ occurs. Peaks due to the halogen atoms bromine (m/e 79, 81; 1:1) and iodine (m/e 127) and also to hydrogen bromide (m/e 80,82; 1:1) and hydrogen iodide were also observed. The mass spectral data are reproduced in Table VIII.

(ii) Acylation

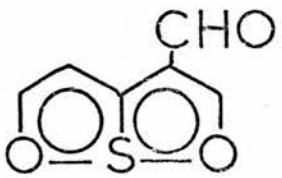
Acylations were attempted on 1,6-dioxa-6a-thiapentalenes under various conditions. No product was obtained from Vilsmeier formylation of dioxathiapentalene and no starting material was recovered. Dioxathiapentalene was stable to acetylation by sodium acetate in refluxing acetic anhydride (76% recovery) but was almost totally destroyed when acetyl chloride-stannic chloride was employed (7.7% recovery). Trifluoroacetylation by use of trifluoroacetic anhydride-triethylamine in refluxing methylene chloride was also unsuccessful (62% recovery). No explanation can be offered for the lack of reactivity of dioxathiapentalene towards acylation. 3-Formyl-1,6-dioxa-6a-thiapentalene (49) was isolated by another route and is a stable compound, therefore lack of stability of the products would not seem to be the problem.

(iii) Nitration

The classical nitrating agent (HNO_3-H_2SO_4) finds limited use in sulphur heterocyclic chemistry. No attempt was made to use it in this study since dioxathiapentalene is sensitive to acid. Copper nitrate in acetic anhydride and nitric acid in acetic anhydride both failed to produce nitrodioxathiapentalenes and mostly destroyed the substrate. Dioxathiapentalene was stable to tetranitromethane in ethanol, even in the presence of pyridine. Nitronium fluoroborate ($NO_2^+BF_4^-$) also failed to produce a nitro compound but did not completely destroy the substrate. No further nitrations were attempted.

(iv) Nitrosation

Although nitrosation of dioxathiapentalene with nitrous acid failed, use of nitrosonium hexafluorophosphate ($NO^+PF_6^-$) was



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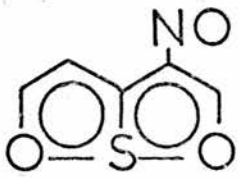

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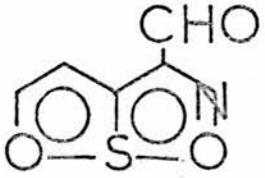

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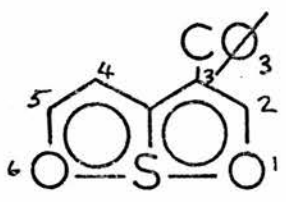

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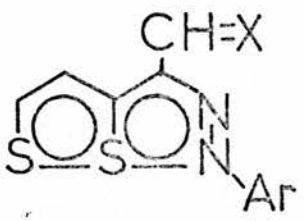

X: O, S, NMe

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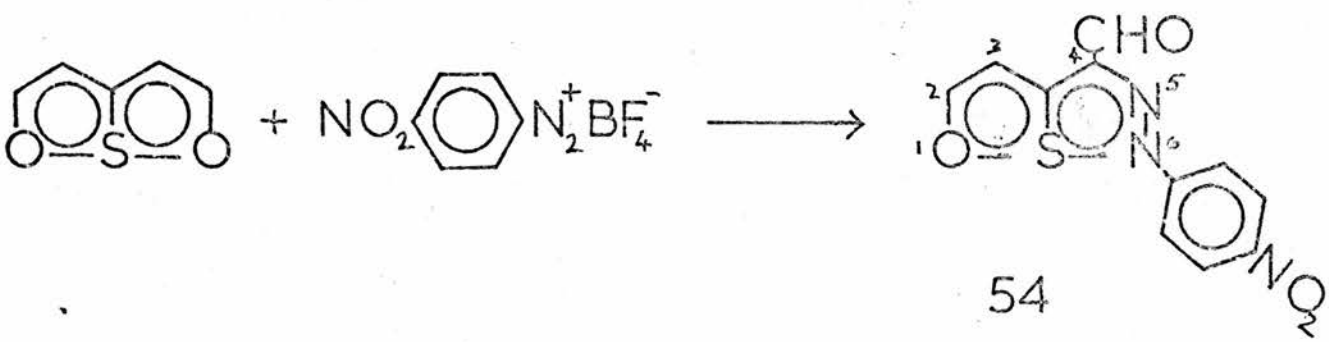

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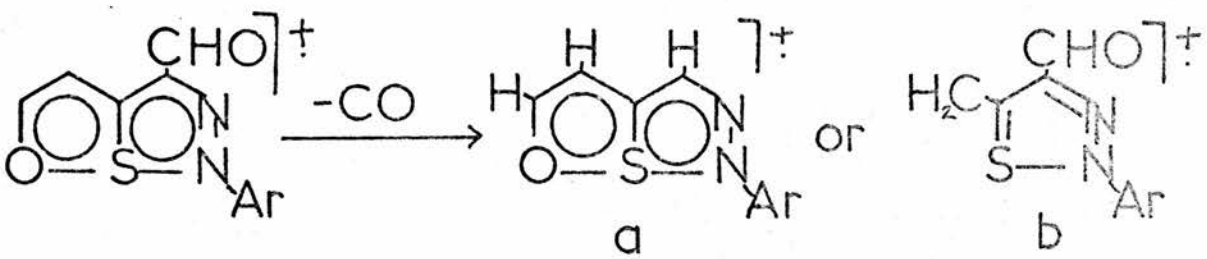


Scheme XV

successful. The product was a colourless solid which analysed correctly for $C_5H_3O_3SN$, but which evidently did not have a simple nitroso structure (50) since a nitroso compound would be expected to be blue-green. The nmr spectrum of the compound showed the presence of a pair of AB doublets (δ8.02, δ9.26; J = 2.2 Hz) and a singlet (δ10.4) which, taken together, confirmed that substitution had occurred. Significantly the chemical shift of the singlet (δ10.40) falls outwith the normal range for dioxathiapentalenes (δ8.5-8.8) but is nearer the normally accepted values for formyl compounds (δ9.9-10.5[208]).

A rearrangement had thus occured to give 3-formyl-1,6-dioxa-6a-thia-2-azapentalene (51). The mechanism for the formation of this compound will be discussed in a later section (Section Cviii). This compound is the first known member of its series and since other derivatives will be described in a later section (Section E) a description of the properties of this compound will be deferred to that section.

(v) Tritylation

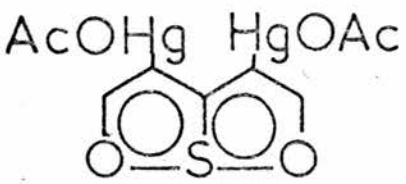
Since nitrosation had been effected by use of a preformed nitrosonium ion it was of interest to attempt to carry out substitution reactions by other cationic species. The triphenylmethyl (trityl) carbonium ion has been shown[209,210] to react in two ways, as a hydride abstractor and as an electrophile. Its use as the latter was of interest in this study. Dioxathiapentalene and trityl perchlorate ($Ph_3C^+ClO_4^-$) in methylene chloride reacted slowly to form 3-triphenylmethyl-1,6-dioxa-6a-thiapentalene (52) in high yield (76%). Only monosubstitution occurs owing to the bulk of the trityl group. The nmr spectrum (Table VI) of the trityl dioxathiapentalene is consistent with substitution having

occurred at the 3-position since two signals appear at ca δ8.3, namely a singlet and a doublet. These are assigned to 2-H and 5-H respectively. The remaining ring proton signal, a doublet, occurs at δ5.97 and is assigned to 4-H. The shielding of this proton relative to that of the 3-proton of the unsubstituted compound (0.93 ppm) is attributed to through-space ring-current shielding of the trityl group.

(vi) Coupling with Arene Diazonium Fluoroborates

Trithiapentalenes and their oxygen and nitrogen analogues couple readily with arene diazonium fluoroborates to give rearranged products (53)[168]. It was of interest therefore to determine whether 1,6-dioxa-6a-thiapentalene would undergo a similar type of reaction. The reaction was successful in so far as the expected product (54) was isolated. The yield was extremely poor (7.1%) but the substrate underwent 24% conversion to the product since the bulk of the starting material (74%) was recovered. The mechanism for the rearrangement will be discussed in Section C(viii). 4-Formyl-6-p-nitrophenyl-1-oxa-6a-thia-3,6-diazapentalene (54) is the first known member of its series and is an orange, crystalline, high melting, insoluble solid. Its nmr spectrum shows a pair of doublets at δ8.05 and 8.42 arising from the aryl group. Proton signals due to 4-H (δ7.91) and 5-H (δ9.45) were not fully resolved. The signal due to the formyl proton (δ10.25) lies in the usual range for aromatic aldehydes. The carbonyl stretching frequency for this aldehyde (1682 cm^{-1}, KBr) is normal, indicating that there is little electron-release at the 4-position, perhaps implying that a low reactivity may be found for the unsubstituted system.

The mass spectrum of compound (54) does not show a simple decomposition pattern. Loss of carbon monoxide from the molecular



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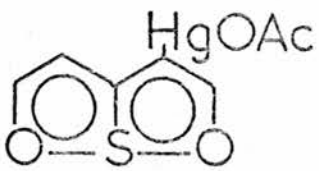

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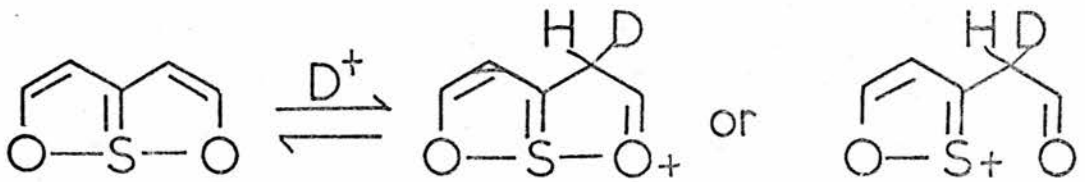

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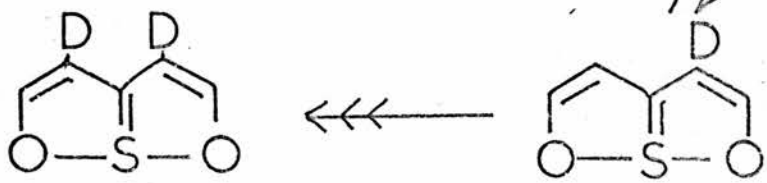

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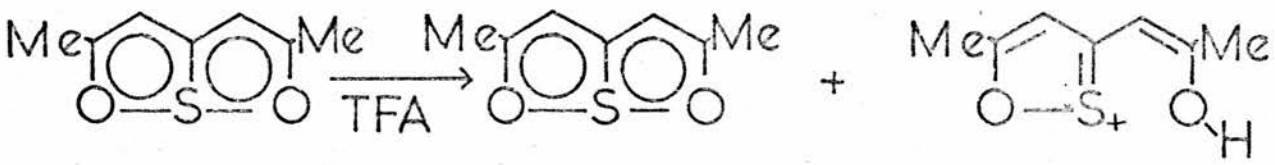

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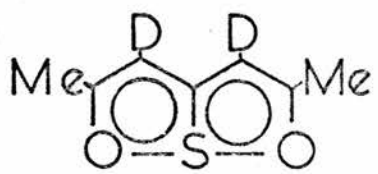

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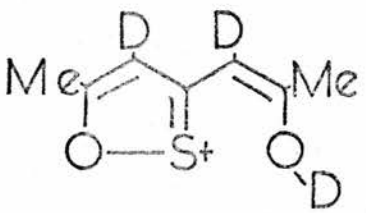

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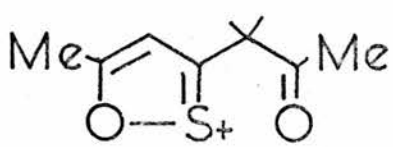

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ion is the only transition which may be recorded with certainty due to the presence of a metastable peak at m/e 224 (calculated m/e = 224.0). As can be seen immediately from Scheme XV, two structures are possible for this ion and it is not possible to state which ion is the more likely. A peak due to the aryl group (m/e 122 for $C_6H_4NO_2$) is present. The base peak (m/e = 112) does not correspond to the loss of any simple fraction and may be due to a rearrangement. No information on this is available. The data are reproduced in Table VIII.

(vii) Oxymercuration

Addition of an acetic acid solution of mercury(II) acetate (2 mol) to a solution of dioxathiapentalene (1 mol) in acetic acid instantaneously produced a white precipitate of the disubstituted derivative (55). Reaction could not be controlled to give the monosubstitution product (56). The dimercurated compound (55) was highly insoluble and investigation of its properties was not attempted. The reaction is interesting in that once again dioxathiapentalene shows a high reactivity, substitution occurring in both rings.

(viii) Protonation and the Mechanism of Substitution of Dioxathiapentalenes

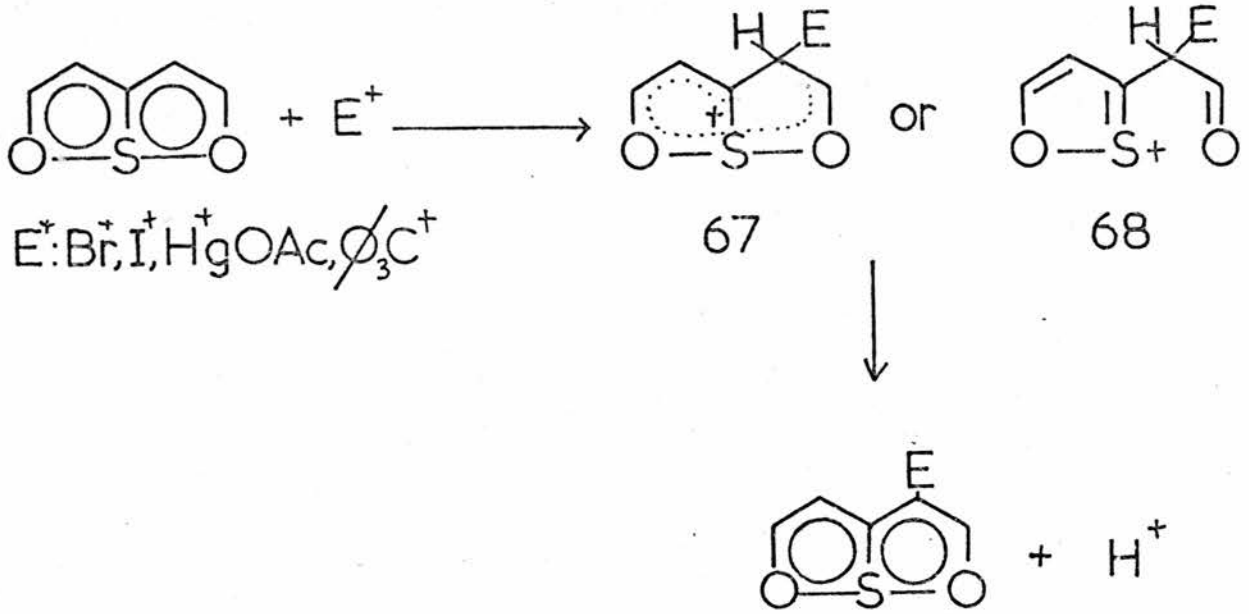
Protonation is of interest since it is the simplest possible electrophilic process and a knowledge of how dioxathiapentalenes protonate may give an insight into the mechanism of electrophilic substitution in this system. The simplest method of following protonation is by nmr spectroscopy.

In trifluoroacetic acid solution, the spectrum of 1,6-dioxa-6a-thiapentalene (57) shows only slight chemical shift differences from its spectrum in deuteriochloroform. Addition of perchloric

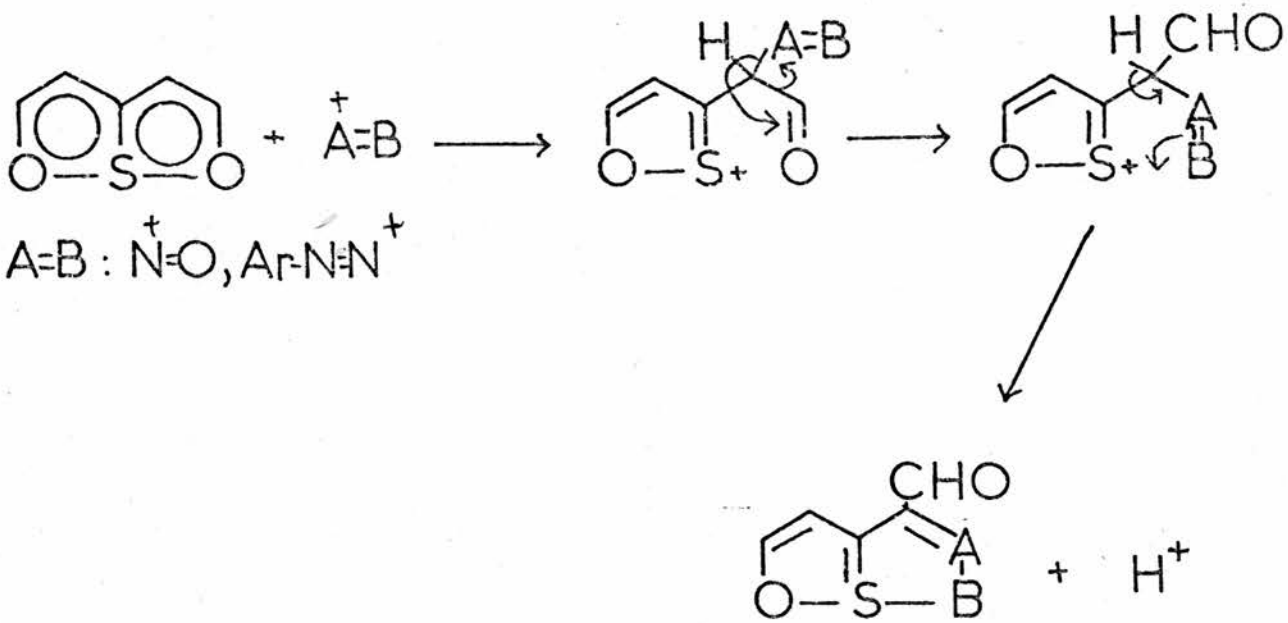
acid (up to 10% v/v) to the solution did not change its nmr spectrum. The sample coloured rapidly in the presence of perchloric acid, perhaps indicating that protonation and hence decomposition was occurring. When the spectrum was obtained in deuteriotrifluoroacetic acid definite evidence for protonation was found since only one signal was apparent, that due to 2(5)-H (δ8.65). A trace of residual doublet at δ6.99 [3(4)-H] was also observed (<<5%). This indicates that protonation has occurred, below the limits of detection by nmr spectroscopy. Two structures are possible for the intermediate, (58) or (59). Evidence for the more likely structure (59) is obtained by examination of the protonation of 2,5-dimethyl-1,6-dioxa-6a-thiapentalene (62). In trifluoroacetic acid solution the dimethyl compound (62) shows the presence of two species. The first species is due to unprotonated material, the chemical shifts of the protons being similar to those found in deuteriochloroform solution.

The other species is evidently unsymmetrical having two distinct methyl groups and two ring signals, and is most probably due to the O-protonated species (63). In deuteriotrifluoroacetic acid solution signals due to the methyl groups alone, in the deuterated species (64) and (65), are observed. Direct evidence for C-protonation comes from the nmr spectrum of this compound (62) in trifluoroacetic acid - 5% perchloric acid solution. This spectrum is consistent with the 3-acetonyl-1,2-oxathiolium cation (66) a derivative of the hitherto unknown 1,2-oxathiolium system. This derivative is evidently none too stable since its solutions turn black within an hour of preparation. The relevant nmr spectral data are reproduced in Table VI.

Quenching a deuteriotrifluoroacetic acid solution of either



Scheme XVI



Scheme XVII

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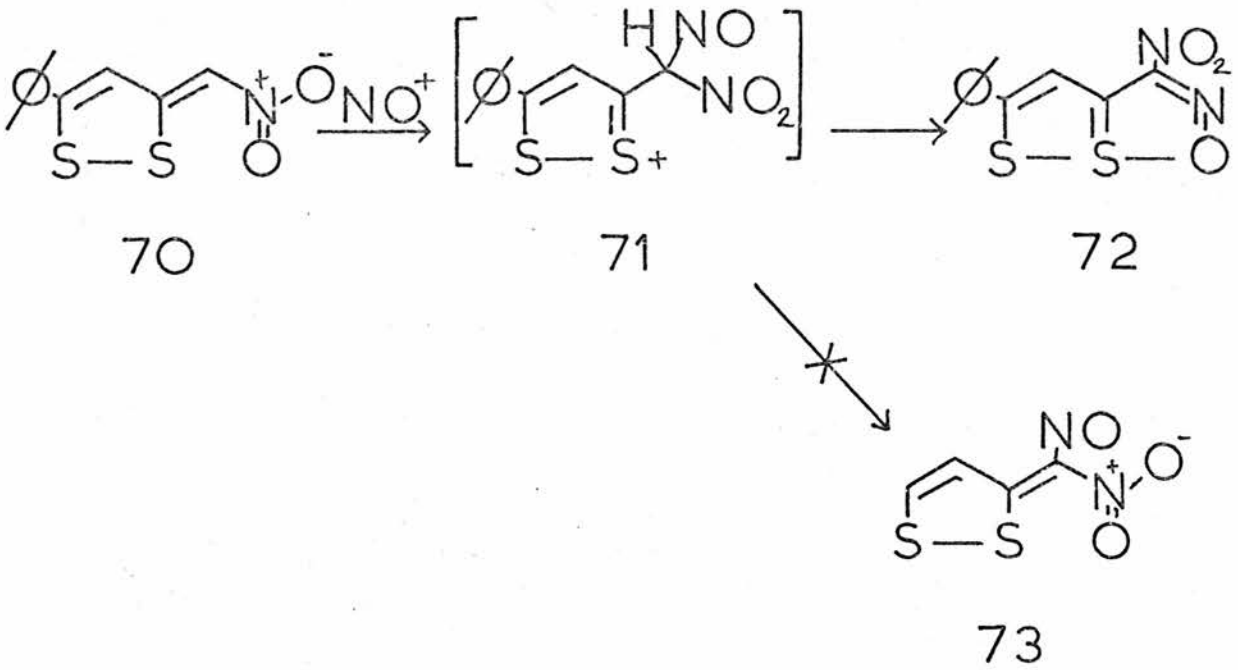
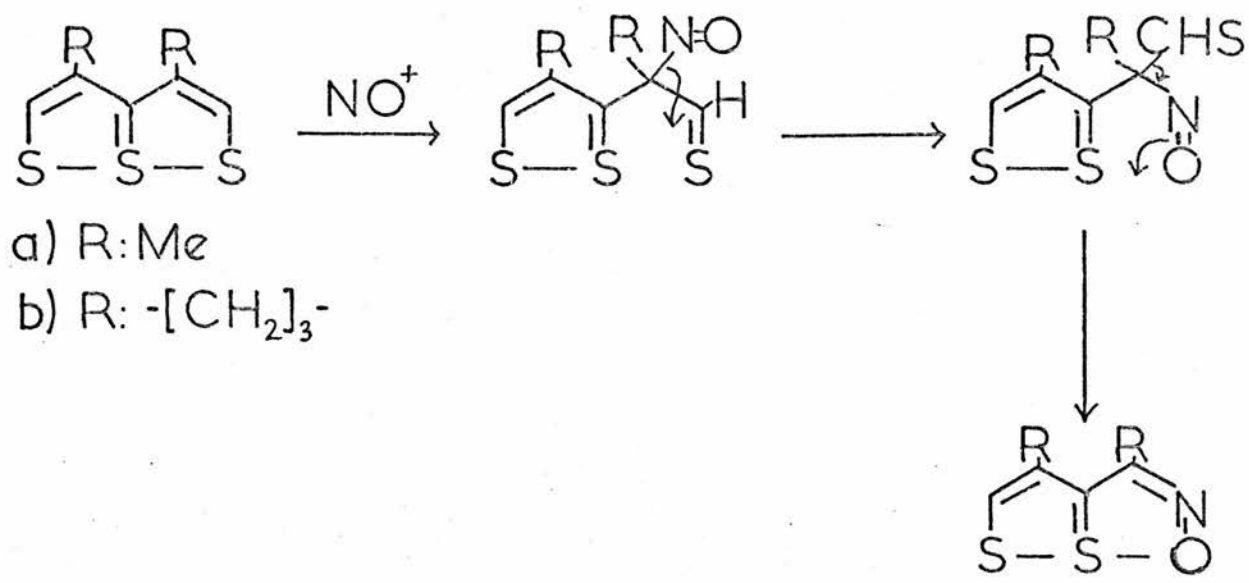
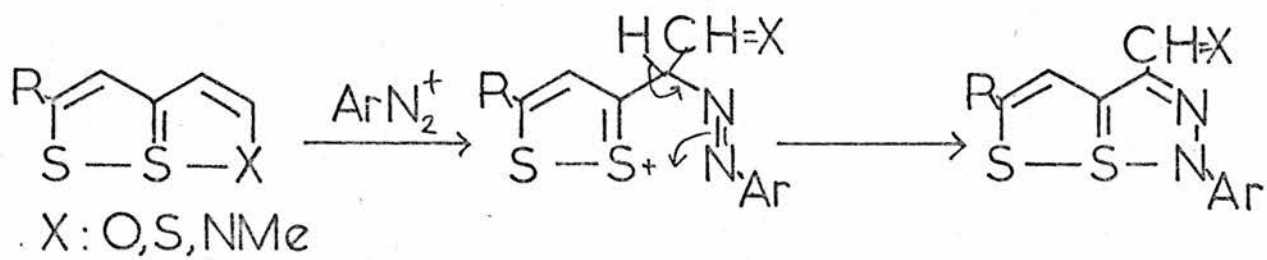
dioxathiapentalene (57,62) with sodium carbonate in deuterium oxide permitted the isolation of the dideuteriated dioxathiapentalenes (6D) and (64). The extent of deuterium incorporation was extremely good; integration of the nmr spectrum showed it to be better than 95%. The mass spectra of these compounds have been discussed previously.

The formation of an oxathiolium intermediate in the protonation of dioxathiapentalenes serves as a pointer towards the mechanism of electrophilic substitution in dioxathiapentalenes. With simple electrophiles (Scheme XVI) a conventional Wheland type of intermediate (67) cannot be excluded but, from what follows about more complex electrophiles, the monocyclic intermediate would appear to be more likely. With more complex electrophiles such as NO^+ and $ArN{=}N^+$ the possibility of rearrangements occurs (Scheme XVII). Rearrangement will occur if the "A-B" group, when in position, forms a stronger three centre O-S-B bond than that in the substrate. These electrophiles have already been seen to react readily with dioxathiapentalene to give the rearranged products (51) and (54). Thus the O-S-O and O-S-N bonds appear to have greater stability than the O-S-O bond. This mechanism involving a monocyclic intermediate is not limited to this system but may be extended to other analogues of trithiapentalenes.

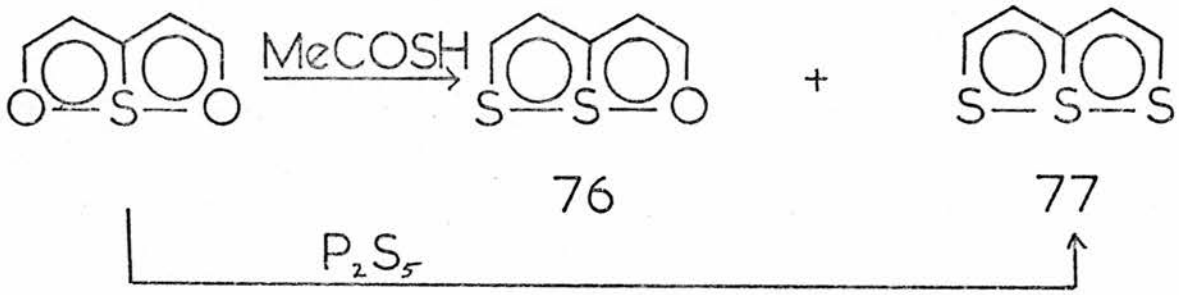
Consideration of the rearrangement of trithiapentalenes and analogues on reaction with arenediazonium fluoroborates led to the mechanism (Scheme XVIII, R.M. Christie and D.H. Reid, unpublished data). Nitrosation of the nitromethylene dithiole(70)[162] may give rise to a monocyclic intermediate (71). Cyclisation then gives the oxadithia-azapentalene (72) and not the nitromethylene dithiole(73). The results of nitrosation reactions which occurred

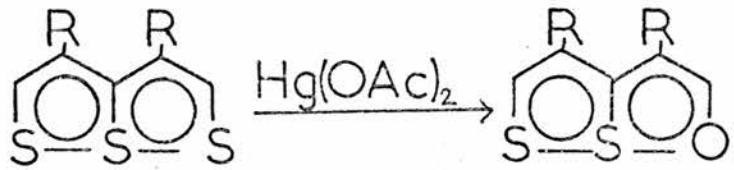




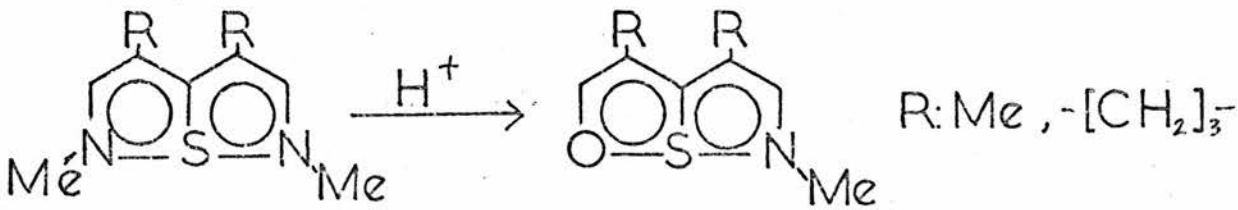


Scheme XVIII

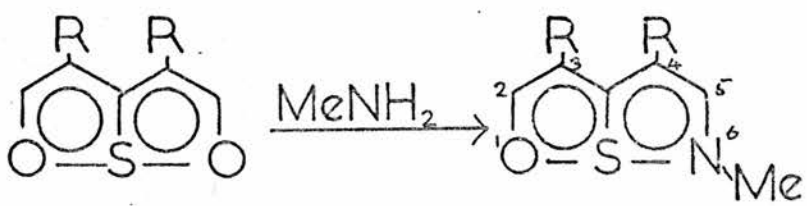




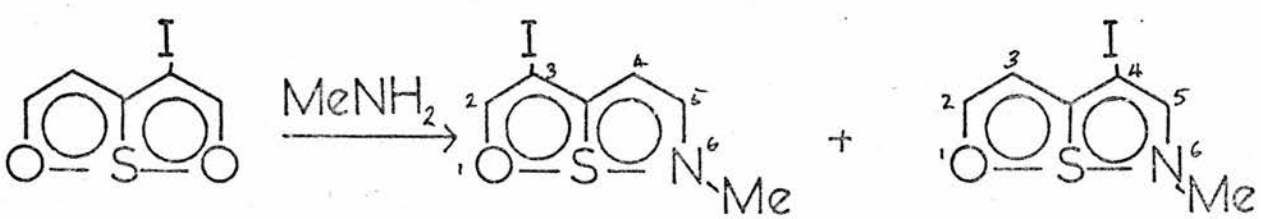
78 79



80 81



82 83



84 85 86

during attempted nitrations of 3,4-disubstituted trithiapentalenes may also be explained by this mechanism. The thioformyl group is readily lost since the nitroso group interacts more strongly with the dithiole nucleus than does the thioformyl group.

(ix) Thionation of Dioxathiapentalene

The results of the thionation of 1,6-dioxa-6a-thiapentalene points to a close structural relationship between the three analogues 1,6,6a-trithiapentalene, 1-oxa-6,6a-dithiapentalene and 1,6-dioxa-6a-thiapentalene. Thionation of dioxathiapentalene by boiling thiolacetic acid, a little used method, yielded mainly the oxadithiapentalene (76) (38%) and a small amount (12%) of trithiapentalene (77). Phosphorus pentasulphide in boiling benzene gave only the trithiapentalene (77) in poor yield (20%). The reverse reaction, desulphurisation, is not so straightforward. Desulphurisation of trithiapentalenes(77) with mercuric acetate occurs rapidly but oxadithiapentalene is not isolated nor indeed is any other product isolated[211]. 3,4-Disubstituted trithiapentalene (78) may be desulphurised to the corresponding oxadithiapentalenes (79) in high yield by use of mercury(II) acetate in chloroform[211]. The other sulphur atom is resistant to removal by mercuric acetate, even in boiling acetic acid. Other methods for desulphurisation have not been reported.

(x) Secondary Reactions

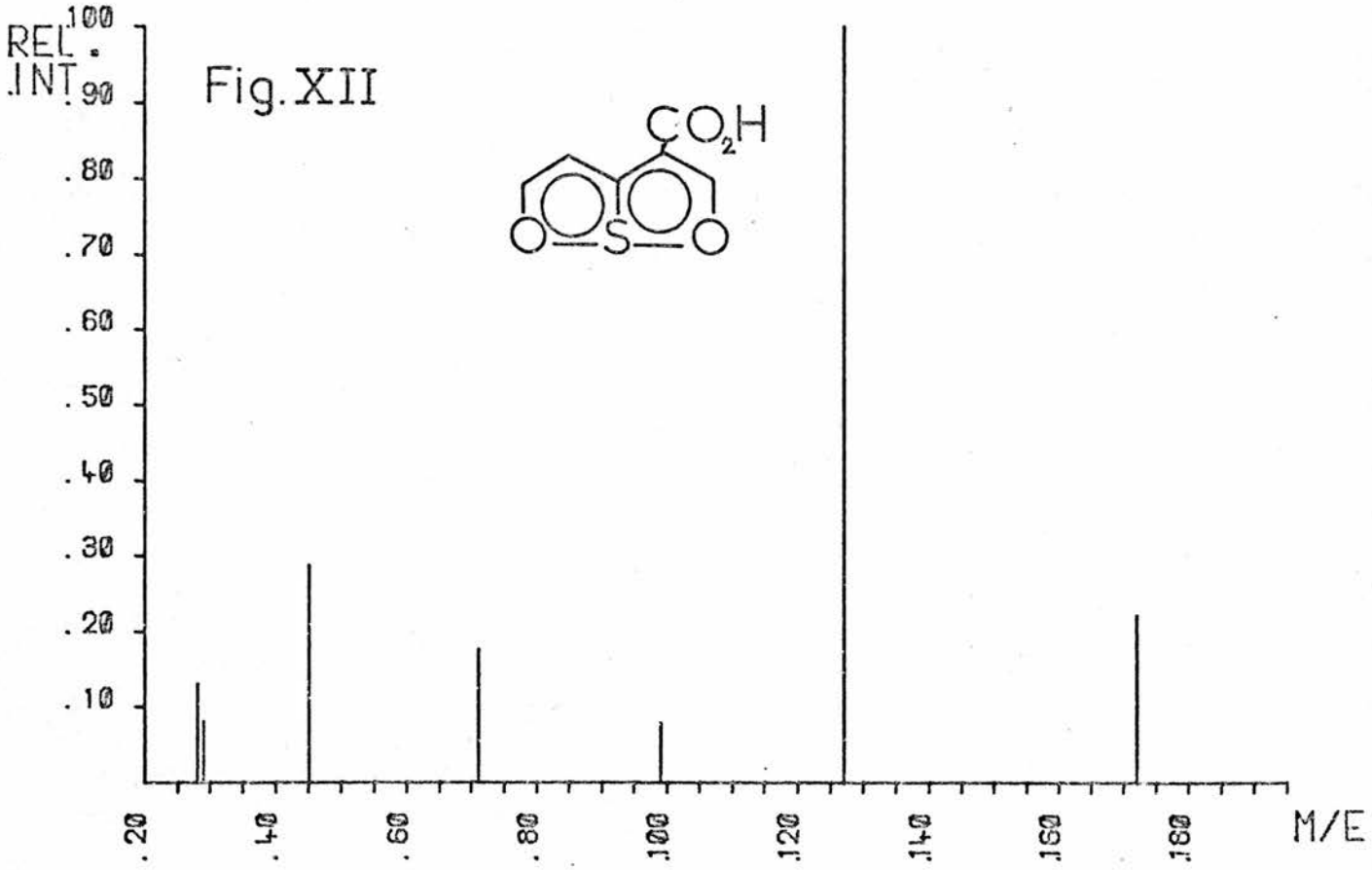
a) 1-Oxa-6a-thia-6-azapentalenes

1,6,6a-Trithiapentalenes react readily with methylamine to give 1,6a-dithia-6-azapentalenes in good yield[17]. It was of interest to determine whether a similar reaction would occur for dioxathiapentalene. However 1,6-dioxa-6a-thiapentalene failed to

react with methylamine. Under more forcing conditions aniline gave a yellow colouration to an acetic acid solution of dioxathiapentalene, but the colouration was due to the presence of an insignificant amount of product, starting material being recovered in high yield. Increasing the severity of the conditions merely produced a black tar.

Halogenated dioxathiapentalenes reacted readily with methylamine to give 1-oxa-6a-thia-6-azapentalenes in good yield. Derivatives of this system (81) have been isolated previously[134] by acid catalysed hydrolysis of 6a-thia-1,6-diazapentalenes (80). Dibromo (82a) and di-iodo-dioxathiapentalene (82b) both reacted smoothly with aqueous methylamine to give 3,4-dibromo (83a) and 3,4-di-iodo-1-oxa-6a-thia-2-azapentalene(83b)in high yield (ca 80%). The nmr spectra of these compounds (Table VI) show a signal due to the N-methyl group (ca δ3.66) together with two ring signals one of which occurs to lower field of the other (ca 1 ppm). Assignment of the higher field signal is facilitated by the presence of a small coupling (0.4 Hz) present in the dibromo compound (83b) revealing an interaction between this proton and the N-methyl group. Hence the upper field signal is assigned to 5-H.

The mono-iododioxathiapentalene (84) also reacted with aqueous methylamine. The product, which was homogeneous to thin layer chromatography, was obtained in excellent yield (95%). However, the nmr spectrum of this compound showed two sets of signals due to the isomers (85) and (86). Only one signal due to the N-methyl groups was observed (δ3.64). The signal at δ7.70 is a quartet (J = 0.4 Hz) and can be assigned with certainty to 5-H in (86). Other ring signals in this isomer must be a pair of doublets, one component of which must occur around 1 ppm to lower field of the


REL. INT.
100
90
80
70
60
50
40
30
20
10
Fig. XII
CO2H
S
O
O
20
40
60
80
100
120
140
160
180
M/E

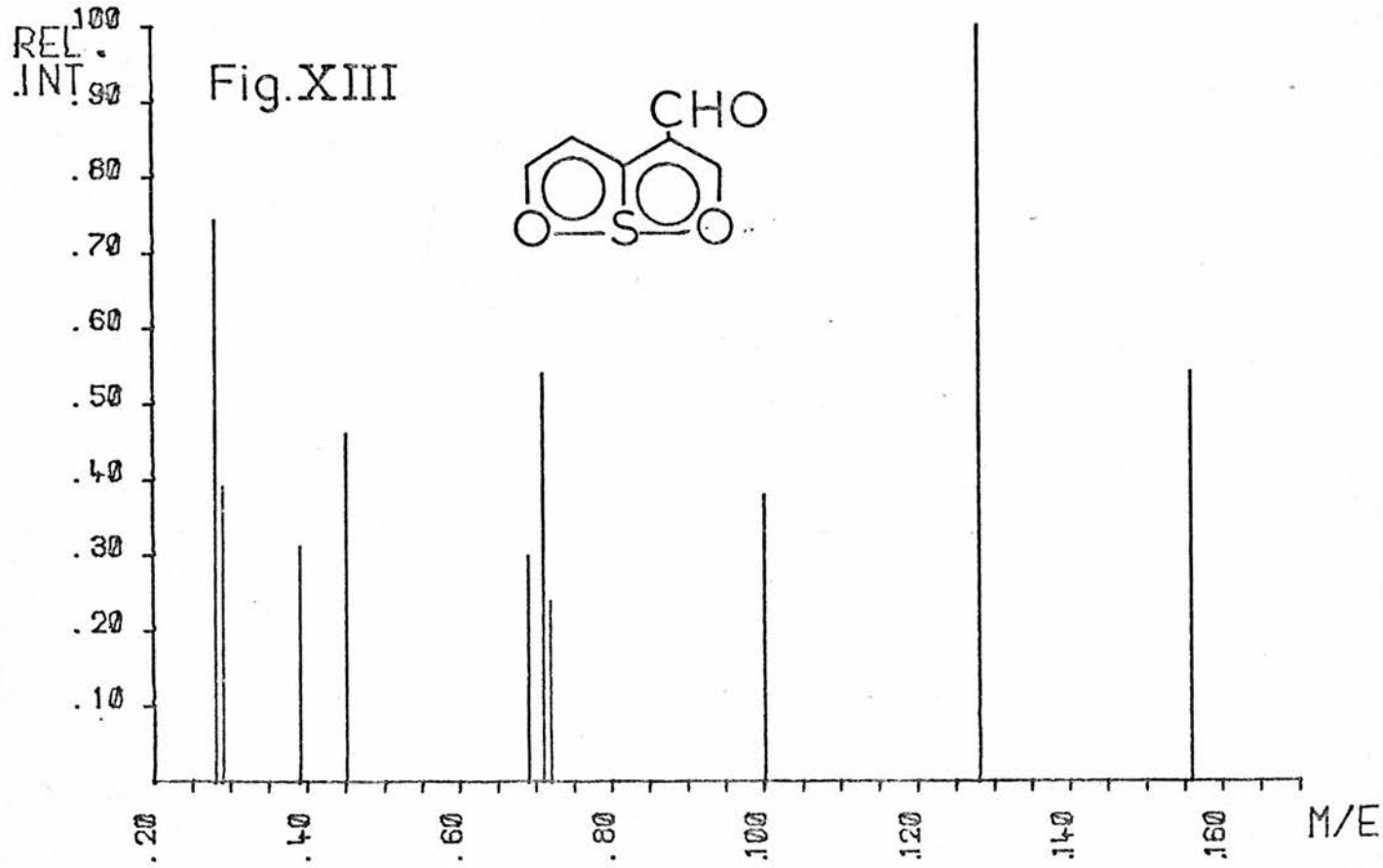

REL. INT.
100
90
80
70
60
50
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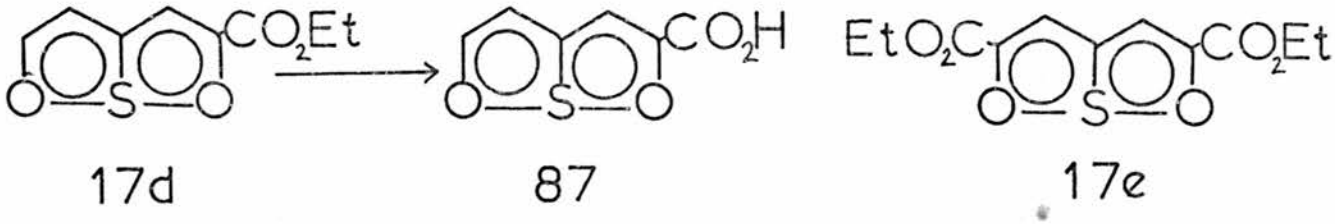
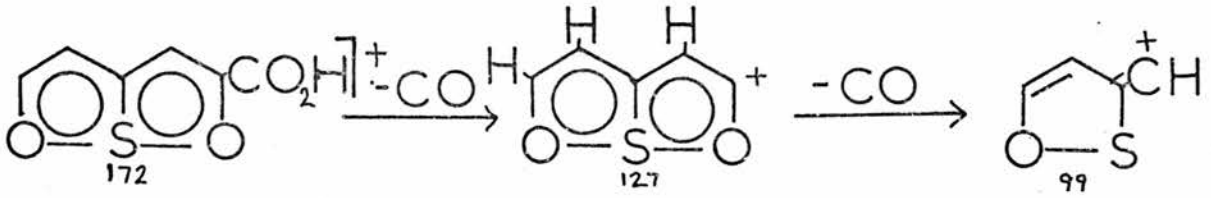
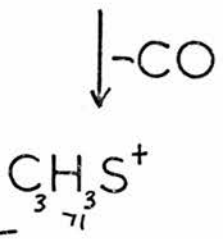
Fig. XIII
CHO
S
O
O
20
40
60
80
100
120
140
160
M/E

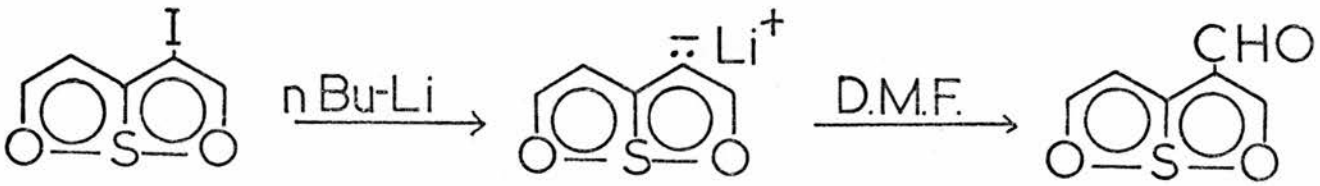


17d 87 17e

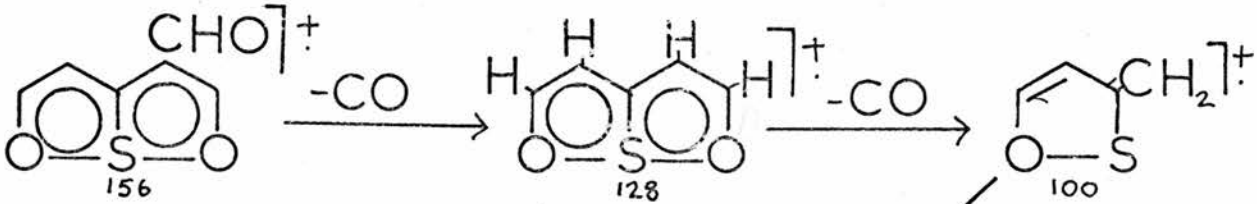


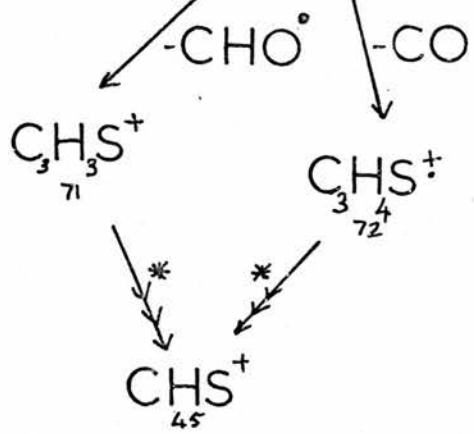


Scheme XIX



84 88 89





Scheme XX

* Scheme tentative

signal assigned to 5-H (δ7.70). The doublets at δ6.38 and δ8.85 meet these requirements and the coupling constant between these protons (2.5 Hz) lies in the range usually found for "oxathiole" ring protons in these hypervalent heterocycles. These signals can be assigned to 3-H and 2-H respectively. The remaining singlet (δ8.82) can be assigned to 2-H in the other isomer (85). The doublets at δ7.75 and δ6.74 can be assigned in the same way to 5-H and 4-H respectively. The coupling constant in this last pair of doublets (3.4 Hz) lies in the range usually found for "isothiazole" ring protons in these hypervalent heterocycles[17,134,188].

The ratio of isomers (85):(86) was found to be 2:1 by integration of the nmr spectrum of the mixture. It is surprising that the single iodine atom in the substrate (82b) has activated the potential carbonyl group in the other ring to a greater extent than the nearer carbonyl group. These reactions of halogenated dioxathiapentalenes with methylamine reveal the potential aldehyde character of these compounds.

b) Hydrolysis of 2-Carbethoxy-1,6-dioxa-6a-thiapentalene

Since the use of water rather than hydroxide had been necessary to prevent hydrolysis at the ring-opening stage of the syntheses of the esters (17d,e), it was of interest to deliberately hydrolyse one of these compounds. Hydrolysis of the ester (17d), using M-aqueous sodium hydroxide, was complete after only five minutes. The carboxylic acid (87) was obtained in excellent yield (78%). The only feature of note in the nmr spectrum of this compound (Table VI) is the presence of a small *peri* (3,4) coupling (J= 0.4 Hz). This type of coupling has been observed in naphthalene chemistry[212]. The mass spectrum of the acid shows the characteristic

breakdown pattern (Scheme XIX, Fig. XII) shown by most dioxathiapentalenes ie loss of functional group followed by successive elimination of carbon monoxide. The initial decompositions are characterised by metastable peaks at m/e 94 (calculated m/e = 93.8 for 172-127) and m/e 77 (calculated m/e = 77.2 for 127-99). The data are reproduced in Table VIII.

c) Metalation

Halogenated heterocycles such as thiophenes react with organometallic bases such as butyl lithium to produce the lithio derivative. These lithio compounds are highly reactive and can be used to introduce numerous functional groups. Since a monoiododioxathiapentalene was available it was of interest to determine whether a 3-lithio-dioxathiapentalene (88) could be used as an intermediate. Addition of n-butyl lithium to a solution of the dioxathiapentalene (84) in ether at -70° produced an intense green colouration. Addition of standard reagents in this reaction such as carbon dioxide, ethyl formate, acetaldehyde or benzaldehyde failed to produce the expected carboxylic acid, aldehyde or secondary alcohols respectively. Addition of N,N-dimethylformamide gave the aldehyde (89) in low yield. Addition of the Vilsmeier complex, $Me_2N^+=CHO-POCl_2Cl^-$, to the lithiated species also gave the aldehyde (89). The low yield of product obtained by addition of the charged, Vilsmeier electrophile compared to that obtained by addition of dimethylformamide tends to indicate a very low stability for the lithiated species.

As might be expected the nmr spectrum of 3-formyl-1,6-dioxa-6a-thiapentalene (89) (Table VI) shows a pair of doublets at δ8.02 and δ8.74, which are assigned to 4-H and 5-H, and two singlets at δ9.30 and δ9.90 which are assigned to 2-H and the formyl proton,

respectively. The large difference in chemical shift between these protons rules out the possibility of a monocyclic structure for dioxathiapentalene. Furthermore the nmr spectrum of this aldehyde in d_6-dimethylsulphoxide is unchanged up to 160° (at which point decomposition took place) showing that no rotation about the C-3 - C-3a bond had occurred. The first transition to occur in the mass spectrum of this aldehyde (Scheme XX, Fig. XIII) is the loss of carbon monoxide, with production of 1,6-dioxa-6a-thiapentalene, the base peak. Decomposition is then identical to that described for the parent system. The data are reproduced in Table VIII. The aldehyde has $\nu_{C=O}$ (CCl_4) at 1688 cm^{-1} which shows that the 1,6-dioxa-6a-thiapentalene system releases electrons at its 3-position as effectively as thiophene does at its 2-position. [2-formylthiophene $\nu_{C=O}$ (CCl_4) 1690 cm^{-1}, ref. 213].

Table VI

Chemical shift data (δ values in ppm downfield from the tetramethylsilane signal) in the nmr spectra of reaction products of 1,6-dioxa-6a-thiapentalenes (in deuteriochloroform unless otherwise stated) J values are in Hz

Compound	Proton Signals (δ) R^2	R^3	R^4	R^5
44	H, 8.67	Br	Br	H, 8.67
46	H, 8.78	I	I	H, 8.78
47	H, 8.67	I	H, 6.98 d $J_{(4,5)}=2.6$	H, 8.68 d[a]
51[b]	H, 9.26 d $J_{(5,4)}=2.2$	H, 8.02 d $J_{(4,5)}=2.2$	CHO, 10.40	NO
52	H, 8.23	Ph_3C, 7.20	H, 5.97 d $J_{(4,5)}=2.6$	H, 8.33 d $J_{(5,4)}=2.6$
54[b,c]	H, 9.45	H, 7.91	CHO, 10.25	d
83a[b]	H, 8.80	Br	Br	H, 7.78 d[e] $J_{(5,N\text{-}Me)}=0.4$
83b	H, 8.97	I	I	H, 7.90[f]
85[b]	H, 8.82	I	H, 6.74 d $J_{(4,5)}=3.4$	H, 7.75 d[g] $J_{(5,4)}=3.4$
86[b]	H, 8.85 d $J_{(2,3)}=2.5$	H, 6.38 d $J_{(3,2)}=2.5$	I	H, 7.70 q[g] $J_{(5,N\text{-}Me)}=0.4$
87[h]	H, 8.95 d $J_{(5,4)}=2.5$	H, 7.35 dd $J_{(4,5)}=2.6$ $J_{(4,3)}=0.4$	H, 7.65 d $J_{(3,4)}\doteq 0.2$	CO_2H, 7.14[j]
89	H, 8.74 d $J_{(5,4)}=2.5$	H, 8.02 d $J_{(4,5)}=2.5$	CHO, 9.90	H, 9.30
89[k,m]	H, 9.27 d	H, 7.98 d	CHO, 9.99	H, 9.73
89[k,n]	H, 9.15 d	H, 7.95 d	CHO, 10.00	H, 9.63
60	H, 8.62	D	D	H, 8.62
64	Me, 2.31	D	D	Me, 2.31

Table VI (cont)

Compound	Proton Signals (δ) R^2	R^3	R^4	R^5
57^p	H, 8.65 d $J_{(2,3)}=2.5$	H, 7.01 d $J_{(2,3)}=2.5$	H, 7.01 d	H, 8.65 d
57^q	H, 8.65 d	H, 7.01 d	H, 7.01 d	H, 8.65 d
57^r	H, 8.65	D	D	H, 8.65
62^p	Me, 2.43 b	H, 6.55 b	H, 6.55 b	Me, 2.43 b
$63^{p,s}$	Me, 2.69 b	H, 6.84 b	H, 4.43 b	Me, 1.71 b
64^q	Me, 2.43	D	D	Me, 2.43
$65^{q,s}$	Me, 2.69	D	D	Me, 1.71
$66^{r,s}$	Me, 2.90	H, 7.64	CH_2, 5.08	CH_2-Me, 2.68

a J value unobtainable due to overlap of signal with that of 2-H

b Rearranged product, see formula in text

c C.A.T. spectrum due to low solubility of compound

d p-Nitrophenyl protons, δ8.97 d; δ8.34 d

e N-Me at δ3.64 d, $J_{(N\text{-}Me\text{-}5)} = 0.4$

f N-Me at δ3.67

g N-Me at δ3.64

h In hexadeuterioacetone

j Undergoes H/D exchange on addition of D_2O

k In hexadeuteriodimethylsulphoxide

m At 34°

n At 160°

p In trifluoroacetic acid

q In trifluoroacetic acid - 5% perchloric acid

r In deuteriotrifluoroacetic acid

s Protonation product, see formula in text

Values refer to singlet absorptions unless otherwise stated. For multiplets, d = doublet, dd = double doublet, q = quartet, b = broad.

Table VII

UV spectral data for the reaction products of 1,6-dioxa-6a-thia-pentalene (In cyclohexane unless otherwise stated)

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
44	215	3.81	46	202	3.95
	242	3.56		229	3.85
	277	3.25		248	3.76
	374	4.02		289	3.36
				481	3.90
47	198	3.81	52	214	4.38
	213	3.81		252	3.42
	231	3.71		262	3.42
	263	3.29		267	3.35
	355	3.40		346	4.09
54	199	4.19	82a	216	3.91
	240	3.94		257	3.67
	305	3.84		275 infl	3.43
	334	3.93		404	4.05
	431	4.26			
82b*	266	1	87†	208	3.77
	407	2.16		242	3.35
				267	3.40
				355	4.11
89	204 infl	3.58			
	249	4.15			
	340	4.04			

* Saturated solution, intensities relative

† In methanol

infl = inflexion

Table VIII

Mass spectral data for the reaction products of 1,6-dioxa-6a-thia-pentalenes

Compound	m/e	R.I.(%)	Compound	m/e	R.I. (%)
44	288	28	46	380	50
	286	52		352	2.1
	284	28		326*	(326.0[a])(380-352[b])
	260	19		323	1.3
	258	36		254	27
	256	19.		253	48
	229	6.5		225	8.6
	207	12		221	22
	205	12		200*	(200.0[a])(253-225[b])
	179	33		197	20
	177	33		195	12
	151	39		168.5*	(168.5[a])(380-253[b])
	149	56		128	23
	147	24		127	55
	98	18		98	23
	97	26		97	13
	82	39		70	32
	81	22		69	100
	80	39		68	26
	79	22		50	23
	70	23		45	44
	69	100		38	14
	68	39		37	27
	50	20		29	36
	45	75		28	18
	44	21			
	38	16			
	37	38			
	36	12			
	32	13			
	29	62			
	28	69			

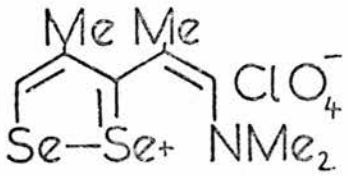
Table VIII (cont)

Compound	m/e	R.I. (%)	Compound	m/e	R.I. (%)
47	254	100	54	277	24
	226	20		249	17
	201* (201.0[a]) (254-226[b])			224* (224.0[a]) (277-249[b])	
	197	6.4		122	19
	128	32		112	100
	127	84		92	12
	99	22		90	8.0
	95	57		76	24
	71	43		75	22
	70	22		71	11
	69	97		70	6.6
	45	83		69	11
	44	17		64	14
	39	24		63	20
	38	22		50	22
	37	21		45	32
	32	11			
	29	41			
	28	76			
87	172	22	89	156	54
	127	100		128	100
	99	7.8		105* (105.0[a]) (156-128[b])	
	94* (93.8[a]) (172-127[b])			100	38
	77* (77.2[a]) (127-99[b])			72	24
	71	18		71	54
	45	29		69	30
	29	8.1		45	46
	28	13		39	31
				29	39
				28	74

* Metastable peak

a Calculated value for metastable peak

b Transition giving rise to metastable peak



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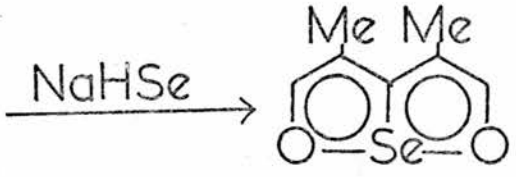

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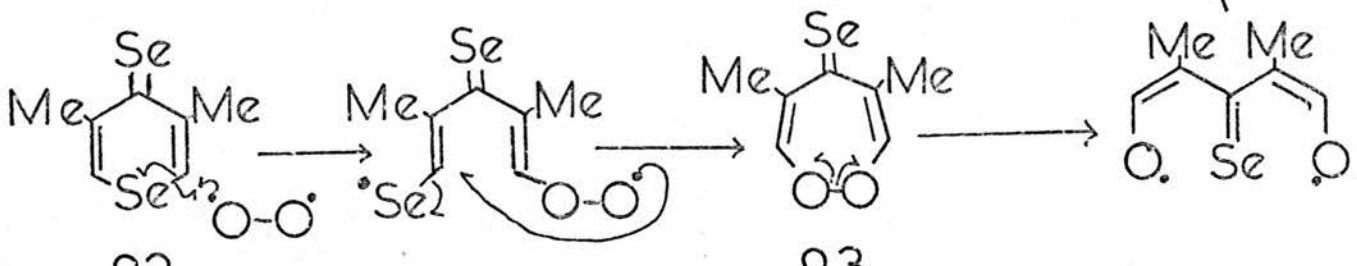
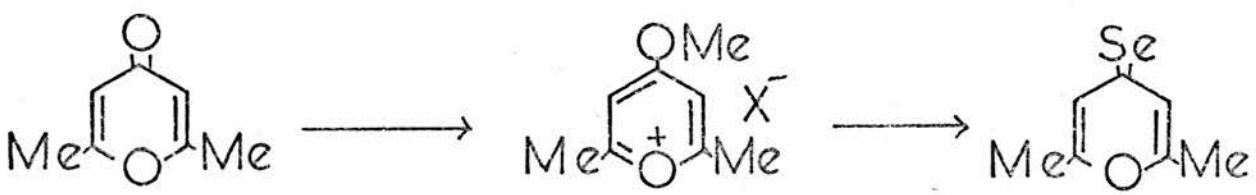
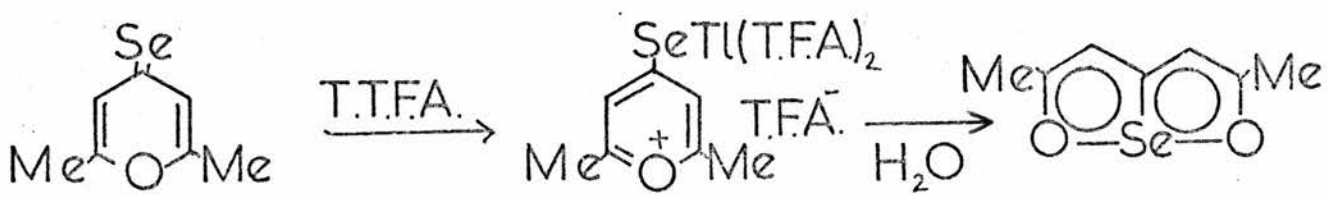


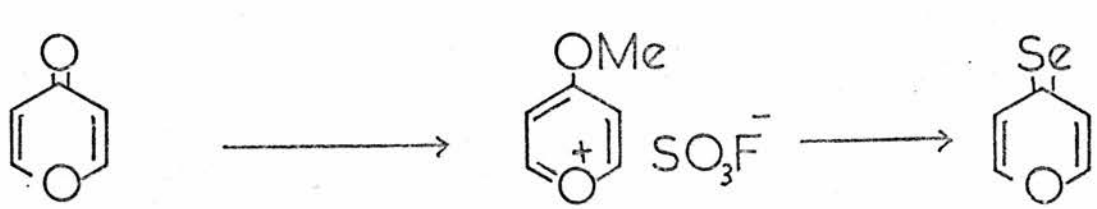
92 93



95 96 94



94 97 98



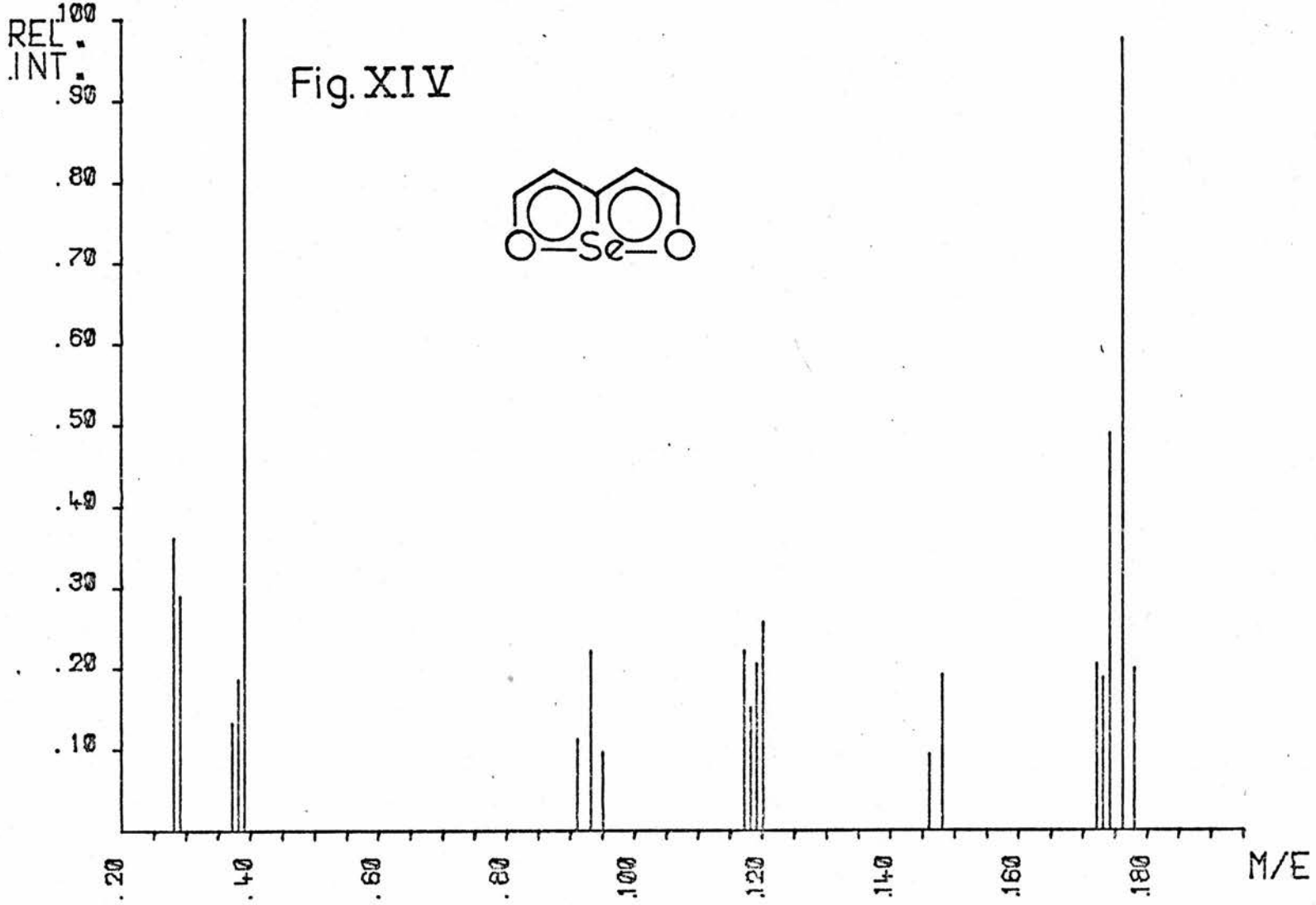
99 100 101

D 1,6-Dioxa-6a-selenapentalenes

The replacement of sulphur atoms in trithiapentalenes by selenium has been of interest in these laboratories for several years[72,73]. Jackson[73] has isolated a derivative (90) of the 1,6-dioxa-6a-selenapentalene series as a by-product in the reaction of a diselenolium salt (91) with sodium hydrogen selenide. The process leading to the product was believed to be a solid state reaction between 4H-selenopyran-4-selenoketone (92) and molecular oxygen in a radical process. The intermediacy of the seven-membered ring structure (93) was presumed. No confirmatory evidence for this mechanism was found. This reaction, although giving a low yield of the dioxaselenapentalene, reveals that the system is stable. Substitution of 4H-pyran-4-selenoketones for 4H-pyran-4-thiones in the synthetic route to dioxathiapentalenes described earlier was thus suggested. 2,6-Dimethyl-4H-pyran-4-selenoketone (94) was first prepared by Traverso[70]. Traverso methylated the pyrone (95) with dimethyl sulphate and converted the resulting pyrylium salt into its perchlorate (96, $X^- = ClO_4^-$). In this study methylation of the pyrone (95) with methyl fluorosulphonate gave a quantitative yield of the pyrylium salt as its fluorosulphonate (96, $X^- = SO_3F^-$). The pyrylium salt (96) was converted to the selenoketone (94) in good yield by reaction with sodium hydrogen selenide.

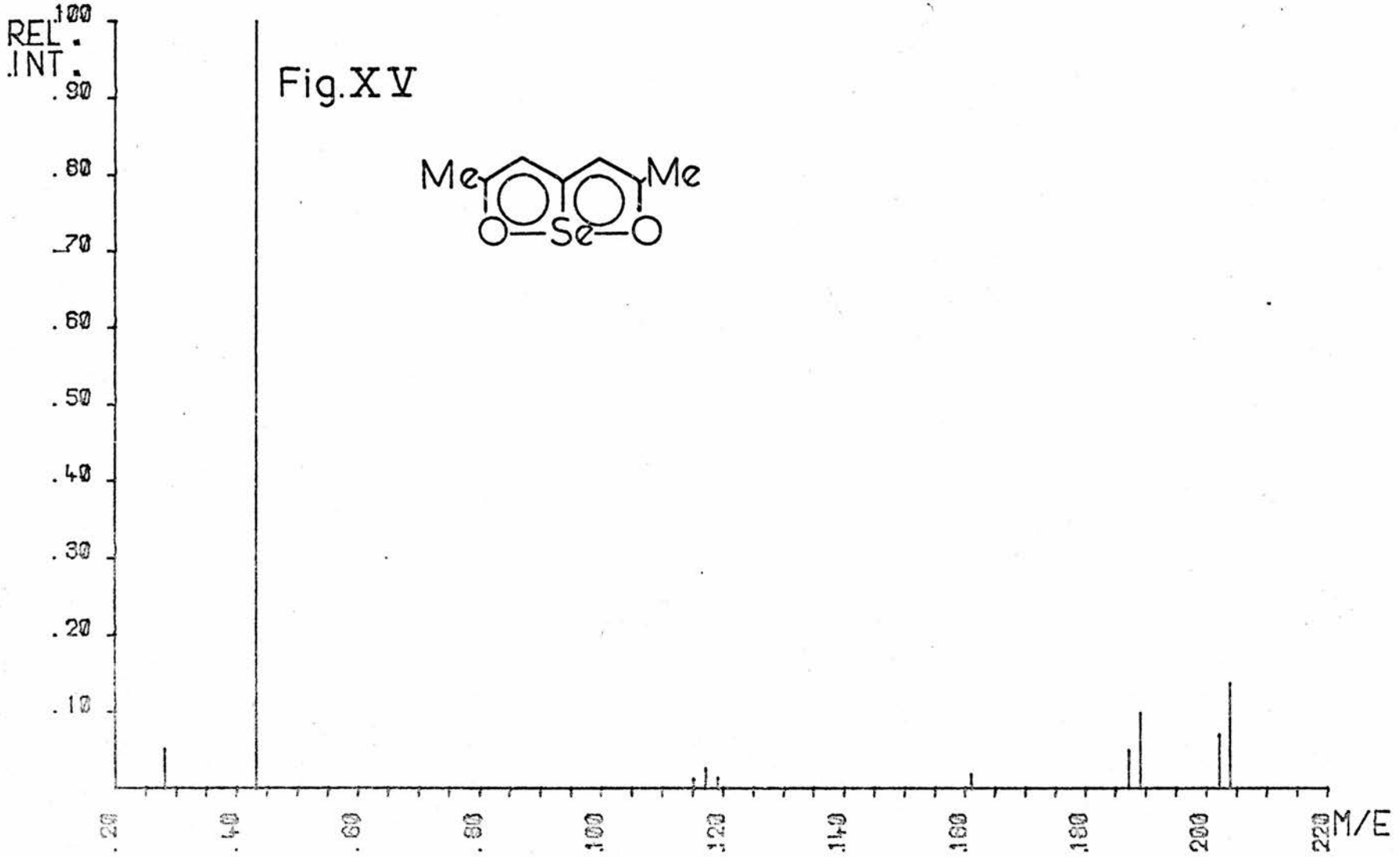
The selenoketone (94) reacted with thallium(III) trifluoroacetate in acetonitrile in a similar manner to the previously described thiones. The reactive intermediate (97) when treated with water gave the dioxaselenapentalene in low yield (1.9%). Attention was then turned to the unsubstituted compound (103). γ-Pyrone (99) was methylated and the pyrylium salt (100) was treated with sodium hydrogen selenide to give the selenoketone (101).

Fig. XIV

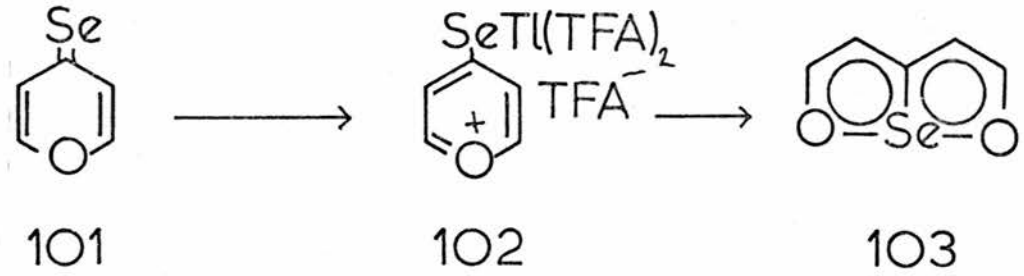

REL.
INT.
100
90
80
70
60
50
40
30
20
10
20
40
60
80
100
120
140
160
180
M/E
O—Se—O

Me2

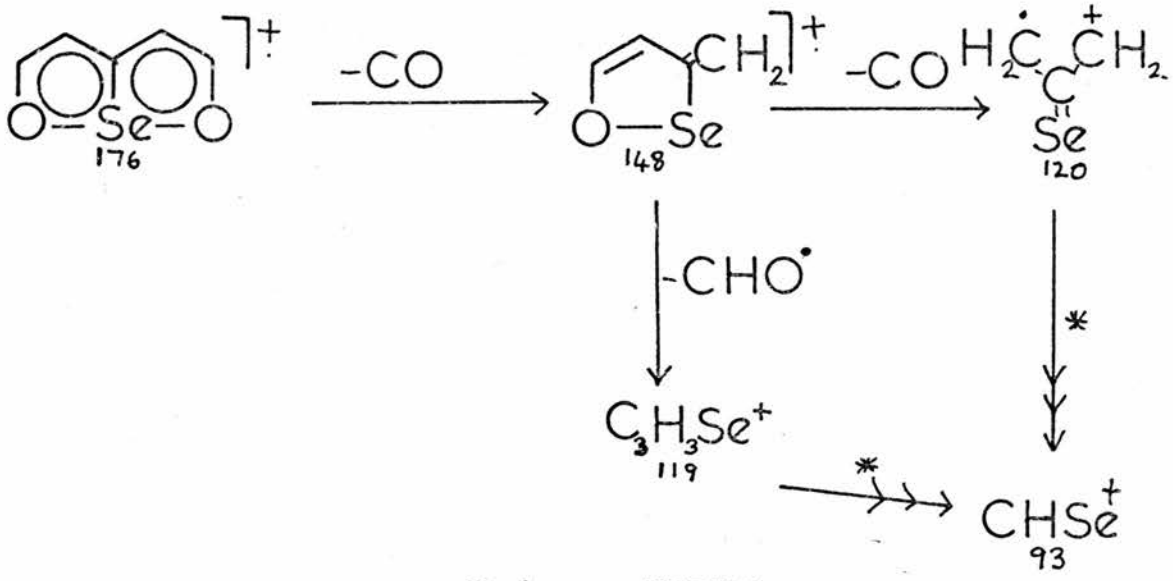
Fig.XV


REL.
INT.
100
90
80
70
60
50
40
30
20
10
20
40
60
80
100
120
140
160
180
200
220
M/E

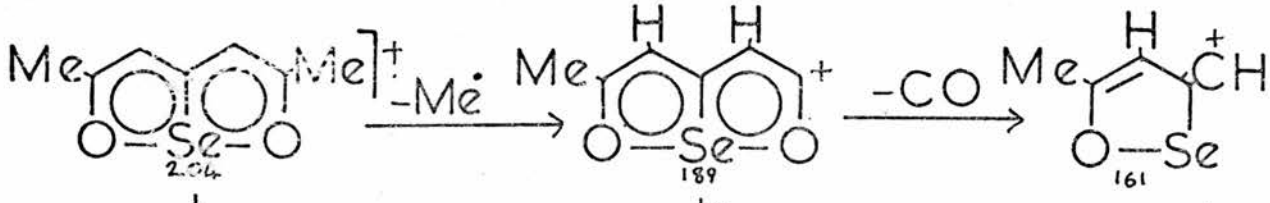
Me
Me
O
Se
O



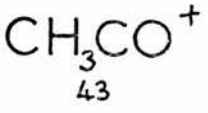
101 102 103

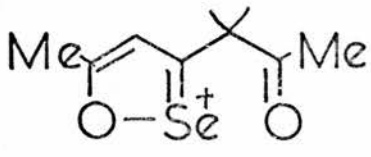


Scheme XXI



Scheme XXII





104

* Scheme tentative

Neither the pyrylium salt (100) nor the selenoketone (101) were characterised, due to the hygroscopic nature of the salt, the explosive nature of the perchlorate (100, ClO_4^- for SO_3F^-) and the instability of the selenoketone. The selenoketone (101) was allowed to react with thallium(III) trifluoroacetate, in acetonitrile, immediately after preparation. Hydrolysis of the intermediate (102) with water gave 1,6-dioxa-6a-selenapentalene (103) (15%).

Nmr spectral data are reproduced in Table IX. The ring protons of the dioxaselenapentalenes have undergone a downfield shift of 0.2-0.3 ppm relative to the corresponding protons in the dioxathiapentalenes. No coupling is observed in either of the two dimethyl derivatives (90, 98). The 2,4-inter-ring coupling observed in 1,6-dioxa-6a-thiapentalene is also present in 1,6-dioxa-6a-selenapentalenes (103), with a similar magnitude (J = 0.5 Hz). UV spectra (Table X) of the dioxaselenapentalenes are very similar to those of the corresponding dioxathiapentalenes. The bands which appeared at around 260 and 340 nm in the dioxathiapentalenes have undergone bathochromic shifts so that in the dioxaselenapentalenes these bands appear at 288 and 355 nm respectively. No comparative data are available for the compound (90) prepared by Jackson. However as observed in corresponding trithiapentalenes, the long wavelength band of compound (90) appears at longer wavelength than that in the spectrum of the parent (103) or dimethyl derivative (98). As suggested for the trithiapentalenes this may be due to close proximity of the methyl groups to each other. The mass spectra of the parent compound (103) (Fig. XIV) and the 2,5-dimethyl derivative (98) (Fig. XV) show identical breakdown patterns to the corresponding sulphur compounds (Schemes XXI and XXII respectively). The initial decompositions were confirmed by the presence of metastable peaks, as can be seen from the data in Table XI.

Due to the limited quantities of dioxaselenapentalenes available, a study of the reactivity of this system was not feasible. Sufficient quantities of material were obtained for an nmr spectroscopic investigation of the protonation of this system using the unsubstituted compound (103) and its dimethyl derivative (98). Neither compound appeared to be protonated in trifluoroacetic acid. The occurrence of protonation can be inferred, however, since the spectrum in deuteriotrifluoroacetic acid showed H/D exchange at position 3. The unsubstituted compound (103) was unstable to trifluoroacetic acid-5% perchloric acid and a spectrum could not be obtained. The dimethyl compound showed the presence of only one species in this solvent mixture, due to protonation at C-3 (104) producing a 1,2-oxaselenolium cation, a derivative of a hitherto unknown system.

Table IX

Chemical shift data (δ values in ppm downfield of the tetramethylsilane signal) in the nmr spectra of 1,6-dioxa-6a-selenapentalenes (in deuteriochloroform unless otherwise stated) J values are in Hz

Compound	Proton Signals (δ)			
	R^2	R^3	R^4	R^5
103	H, 8.91 dd $J_{(2,3)}=2.6$ $J_{(2,4)}=0.5$	H, 7.10 dd $J_{(3,2)}=2.7$ $J_{(4,2)}=0.5$	H, 7.10 dd	H, 8.91 dd
98	Me, 2.31	H, 6.83	H, 6.83	Me, 2.31
90[73]	H, 8.62	Me, 2.47	Me, 2.47	H, 8.62
98[a]	Me, 2.51 b	H, 6.4-7.4[b]	H, 6.4-7.4[b]	Me, 2.51 b
98[c,d]	Me, 2.80	H, 7.81 b	CH_2, 5.10 b	$CH_2\underline{Me}$, 2.77 b
103[a]	H, 8.91 db[e]	H, 7.22 db[e]	H, 7.22 db	H, 8.91 db
103[f]	H, 8.91	D	D	H, 8.91

a In trifluoroacetic acid

b Signal very broad

c In trifluoroacetic acid-5% perchloric acid

d Protonation product, see formula (104) in text

e $J \doteq 2.6$

f In deuteriotrifluoroacetic acid

Values refer to singlet absorptions unless otherwise stated. For multiplets d = doublet, dd = double doublet, b = broad

Table X

UV spectral data for the 1,6-dioxa-6a-selenapentalenes (in cyclohexane)

Compound	λ_{max} (nm)	log ε
103	204	3.64
	221 infl	3.26
	288	3.45
	363	4.11
98	202	3.80
	219 infl	3.45
	288	3.57
	352	4.32
90[73]	214	3.70
	240	3.35
	298	3.49
	381	4.17

infl = inflexion

Table XI

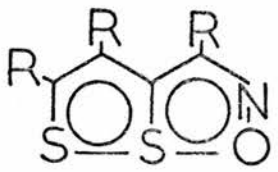
Mass spectral data for the 1,6-dioxa-6a-selenapentalenes

Compound	m/e	R.I. (%)	Compound	m/e	R.I. (%)
103	178	20	98	204	14
	176	98		202	7.0
	174	49		189	9.9
	173	19		187	4.9
	172	21		175*	(175.1[a])(204-189[b])
	148	19		161	1.9
	146	9.3		137*	(137.2[a])(189-161[b])
	124.5*	(124.5[a])(176-148[b])		119	1.5
	120	26		117	2.7
	119	21		115	1.3
	118	15		43	100
	117	22		28	5.1
	95	9.6			
	93	22			
	91	11			
	39	100			
	38	19			
	37	13			
	29	29			
	28	36			

* Metastable peak

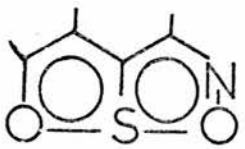
a Calculated value for metastable peak

b Transition giving rise to metastable peak



R:H, Alkyl or Aryl

105



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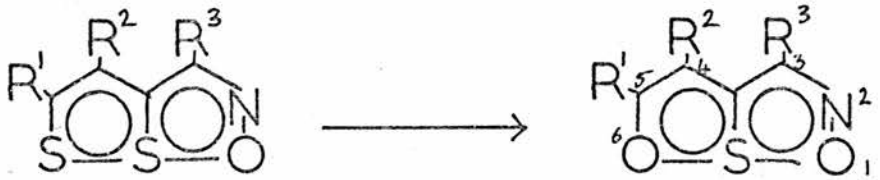
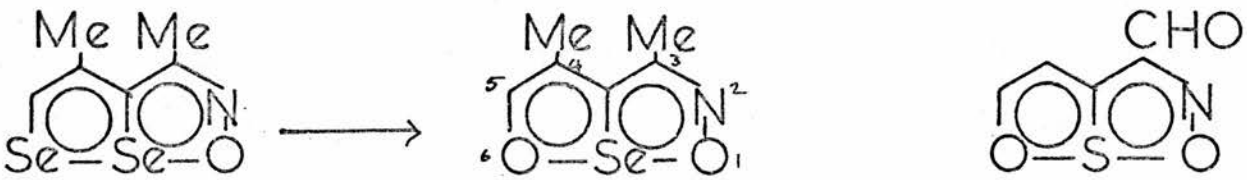
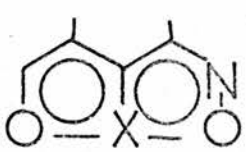


107 → 108

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

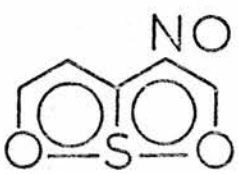


109 → 110 111

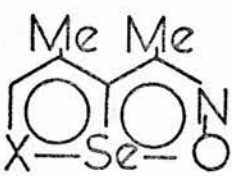


X:S, Se

112



113



X:O, S, Se

114

E Studies of 1,6-Dioxa-6a-thia-2-azapentalenes, 1-Oxa-6,6a-dithia-2-azapentalenes and Related Selenium Compounds

(i) Synthesis of 1,6-Dioxa-6a-thia-2-azapentalenes

A simple route to 1-oxa-6,6a-dithia-2-azapentalenes (105) has been developed in these laboratories. Desulphurisation of the 1-oxa-6,6a-dithia-2-azapentalenes (107a,b) with mercury(II)acetate in either boiling chloroform-acetic acid or boiling acetic acid yielded the 1,6-dioxa-6a-thia-2-azapentalenes (108a,b). Attempted desulphurisation of the parent compound (107c) resulted in 90% destruction of the substrate. This may be due to oxymercuration in the oxathiole ring of the product although no evidence on this point is available. The 2-t-butyl derivative (107d) was largely unaffected by desulphurisation. Treatment of the 1-oxa-6,6a-diselena-2-azapentalene (109) with mercuric acetate in boiling acetic acid produced the 1,6-dioxa-6a-selena-2-azapentalene (110) in high yield. Desulphurisation of 1-oxa-6,6a-dithia-2-azapentalenes and deselenisation of 1-oxa-6,6a-diselena-2-azapentalenes constitutes a simple synthesis of 3,4-disubstituted derivatives of compounds of type (112).

(ii) Spectral Properties and Structure of 1,6-Dioxa-6a-thia-2-azapentalenes and Selenium Analogues

The properties of compounds of these types will be discussed together with those of the previously isolated formyl derivative (111).

The nmr spectra of these compounds have been obtained (Table XII). No information from these spectra indicate that the compounds should not be formulated as bicyclic heterocycles. Assignment of the signals due to the methyl groups in compounds (108a) and (110) is facilitated by the presence of coupling between the ring proton and the higher field methyl group. This signal must be due to the 4-methyl group in these compounds. The formyl derivative (111) shows a pair of doublets and a singlet in its nmr spectrum.

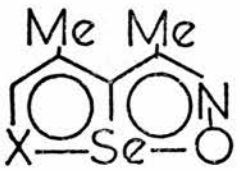
From the spectrum of this latter compound the 4-H - 5-H coupling constant (2.2 Hz) is seen to be similar to that in 1,6-dioxa-6a-thiapentalenes. Comparison of the UV data (Table XIII) for these compounds with the data of the corresponding dioxathiapentalenes is not easy since corresponding members of the two series are not available. The presence of the nitrogen atom at position 2 results in a bathochromic shift of most bands and the appearance of a new band at ca 200 nm. These systems thus have close structural similarities.

The mass spectra of these nitrogen systems show no definite breakdown pattern. Peaks due to loss of CO or NO are not observed. The peak due to the molecular ion from all these compounds is very intense. These systems evidently have a high stability. The 1,6-dioxa-6a-thia-2-azapentalene system does not appear to release electrons at its 3-position so effectively as does 1,6-dioxa-6a-thiapentalene. This may be inferred from the higher carbonyl stretching frequency of the aldehyde (111) (1715 cm^{-1}) when compared with that of 3-formyl-1,6-dioxa-6a-thiapentalene (89) (1688 cm^{-1}).

From this study, limited by the number and type of derivatives available, it is apparent that the system (112) has a high stability. The presence of the nitrogen atom at position 2 must confer extra stability on the system when compared with 1,6-dioxa-6a-thiapentalenes since 1,6-dioxa-6a-thiapentalene nitrosates readily and the product is the formyl dioxathia-azapentalene (111) and not the nitroso dioxathiapentalene (113).

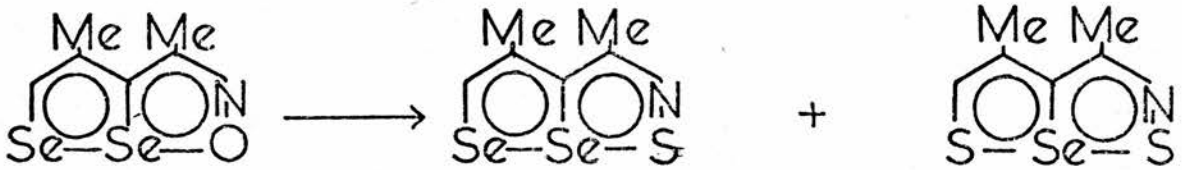
(iii) Reactivity of 1,6-Dioxa-6a-thia-2-azapentalenes

Little has been done regarding the reactivity of this system due to the limited types of derivatives available for study. Methylation of 1,6-dioxa-6a-thia-2-azapentalenes (Section F) occurs at O-1. The 1,6-dioxa-6a-thia-2-azapentalene (108a) does not undergo thionation to the 1-oxa-6,6a-dithia-2-azapentalene (107a)

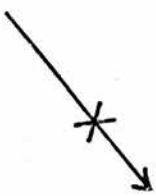


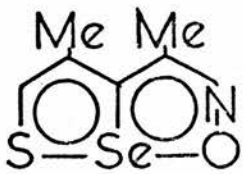
X:O,S,Se

114



115 116 117



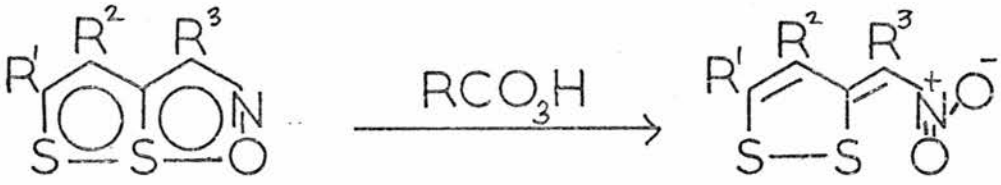


118

(phosphorus pentasulphide in boiling xylene) and does not undergo nitrosation.

(iv) Thionation of 3,4-Dimethyl-1-oxa-6,6a-diselena-2-azapentalene

An attempt was made to thionate the selenium compound (110) with a view to obtaining a compound of type (114) (X=S). This reaction was unsuccessful. However it was felt that it should be possible to exchange a selenium atom (Se-6) of compound (115) for sulphur by thionation. Selenium atoms at positions 1 or 6 in pentalene type derivatives have already been shown to be exchanged readily for sulphur by use of phosphorus pentasulphide in boiling benzene[73,214]. Exchange of an oxygen atom attached to a nitrogen atom for a sulphur atom by an inorganic thionating agent had not hitherto been recorded and this course of reaction seemed unlikely. Chromatography of the reaction mixture gave a fast moving red compound as the only product. A compound of type (118) would be expected to exhibit more polar properties on chromatography. The nmr spectrum of this product showed the presence of two species identified as compounds (116) and (117). Thionation had occurred at nitrogen to give compound (116) and this probably gave rise to the second product (117) by Se/S exchange. Reducing the reaction time did not affect the constitution of the product but considerably reduced the yield. Compound (116) was present in far greater amount than compound (117). In the nmr spectrum of the mixture the assignment of the signals due to the methyl groups in each component was facilitated by the presence of coupling between 5-H and one of the methyl groups in each component (Table XII). The mass spectrum of the mixture showed the presence of ions at m/e 237 and 284 which can only be due to the species (117) and (116) respectively. Compounds (116) and (117) were inseparable by chromatographic or crystallisation techniques. Elemental analysis was therefore not



107 119

	R^1	R^2	R^3
a	H	Me	Me
b	H	H	H
d	Bu^t	H	H

useful but accurate molecular weights were obtained by mass spectrometry.

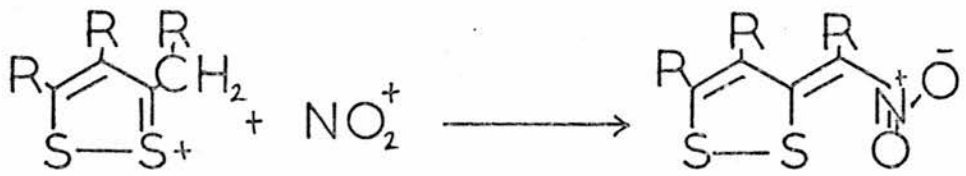
(v) Reactivity of 1-Oxa-6,6a-dithia-2-azapentalenes

Since 3,4-dimethyl-1-oxa-6,6a-diselena-2-azapentalene had undergone thionation at nitrogen it was of interest to determine whether or not the corresponding sulphur compound, 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (107a) would also undergo thionation by the same method. No thionation was observed and the substrate decomposed under the reaction conditions used.

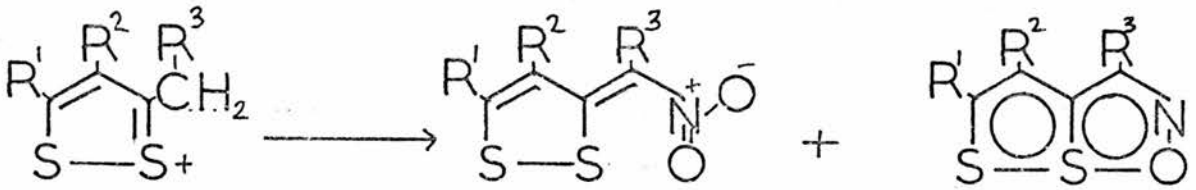
Several other reactions were also investigated for this system. 5-t-Butyl-1-oxa-6,6a-dithia-2-azapentalene (107d) failed to undergo nitration using tetranitromethane in dimethylformamide. Desulphurisation has already been seen to occur for 3,4-disubstituted derivatives of the series (Section Ei). Methylation (Section F) and protonation (Section G) will be shown to occur at O-1. The only other reaction to be investigated was oxidation. Since desulphurisation of compound (107c) with mercury(II)acetate had failed an attempt was made to desulphurise this compound with m-chloroperbenzoic acid. Desulphurisation did not occur but oxidation at nitrogen did occur. A series of 3-nitromethylene-3H-1,2-dithioles (119) was isolated. The yields of nitromethylene dithioles were poor and this method could not be used to produce the quantities of material necessary for other studies in these laboratories.[227]

(vi) Synthesis of 3-Nitromethylene-3H-1,2-dithioles

The poor yields of nitromethylene dithioles obtained by oxidation of 1-oxa-6,6a-dithia-2-azapentalenes or by nitration of 1,6,6a-trithiapentalenes[16] indicated that a new synthesis was

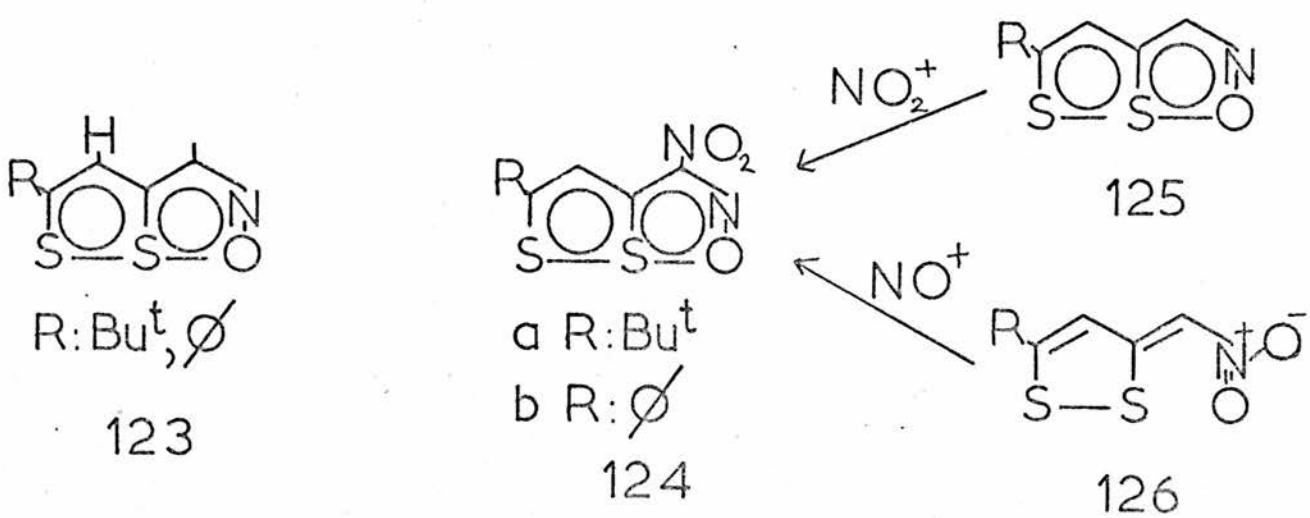


Scheme XXIII



120 121 122

	R^1	R^2	R^3
a	H	Me	Me
b	H	$-(CH_2)_3-$	
c	Bu^t	H	H
d	H	H	H
e	Ø	H	H
f	Ø	H	Me
g	H	$-(CH_2)_2-$	



R:Bu^t, Ø

123

a R:Bu^t

b R:Ø

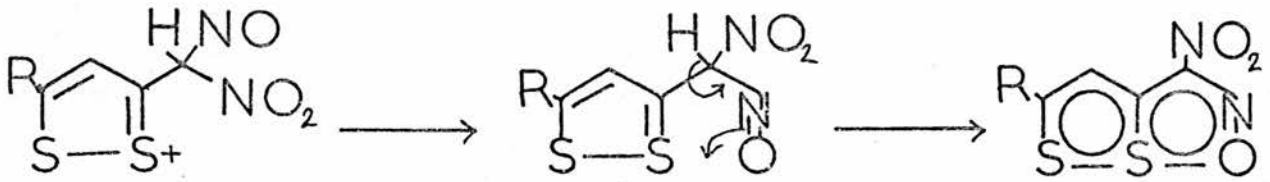
124

125

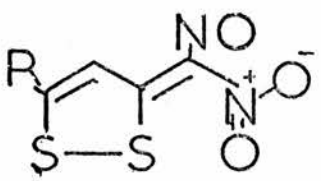
126

required. Previous work in these laboratories has utilised the acidic nature of methylene groups in the 3-position of 1,2-dithiolium salts (Part IA)[14,16]. A simple synthesis of nitromethylene dithioles would involve the nitration of 3-methylene-1,2-dithiolium salts (Scheme XXIII). The reagent chosen was tetranitromethane in boiling ethanol. The dithiolium salt (120a) gave a 76% yield of the nitro compound (121a). This was the only nitromethylene dithiole to be obtained in good yield by this method, using ethanol as solvent. Boiling ethanol as solvent was replaced by N,N-dimethylformamide at 50°. Use of this solvent permitted isolation of the series of nitromethylene dithioles (121a-f). The dithiolium salt (120g) failed to react with tetranitromethane to form the nitro compound (121g). It is noteworthy that this dithiolium salt also failed to yield a 1-oxa-6,6a-dithia-2-azapentalene under reaction conditions[16] which gave other derivatives in its series. The parent compound (121d) was obtained in poor yield (4%) using ethanol at 50°.

Nitrosation of the dithiolium salts (120a,b,e) also occurred. Nitrosation by tetranitromethane has been reported previously[16]. The 1-oxa-6,6a-dithia-2-azapentalenes were produced in low yields (<20%). The t-butyl (121c) and phenyl (121e) compounds were each accompanied by another compound. Analytical and mass spectral data and the simplicity of the nmr spectra of these "unknowns" resulted in the assignment of the structures (124) to these compounds. Two routes to these compounds are possible, nitration of the oxadithia-azapentalenes (125) or nitrosation of the nitro compounds (126). Treatment of the oxadithiaazapentalene (125a) with tetranitromethane in dimethylformamide at 50° failed to nitrate the substrate. Treatment of the nitro compound (126a) with nitrous acid failed to nitrosate the nitro compound. Nitrosation of both nitro compounds (126a,b) was effected by nitrosyl hexafluorophosphate ($NOPF_6$) in methylene chloride in excellent yield (>80%). Nitrosation of the



127 128 129



130

blocked compound (121a) resulted in total destruction of the substrate.

The nitrosation reaction most likely involves an intermediate of type (127) which rearranges to (128) forming the oxadithiaaza-pentalene (129) in preference to a nitromethylene dithiole (130). The phenyl derivative (124b) is a known compound[162]. An Xray structure determination of the known phenyl derivative has shown that compound to have the 3-nitro-1-oxa-6,6a-dithia-2-azapentalene structure[165]. The ready nitrosation of the nitromethylene dithioles shows that these compounds have a high reactivity. One driving force behind this reaction may be the formation of the more stabilised bicyclic oxadithiaazapentalene. High reactivity for nitromethylene dithioles has already been demonstrated by Beer[162].

(vii) Spectral Properties of 3-Nitromethylene-3H-1,2-dithioles and 3-Nitro-1-oxa-6,6a-dithia-2-azapentalenes

The nmr spectra of the nitro compounds (121) have been determined (Table XIV). Data for the nitro compounds (121a,b) have also been included[16]. The upfield shifts of the ring protons in compounds (121a,b) relative to the corresponding protons in compounds (122a,b) have been taken as indicative of greater S-O interaction in the oxadithiaazapentalenes than in the nitro-methylene dithioles[16]. This can be further verified from this present study. All ring protons in 3-nitromethylene-3H-1,2-dithioles resonate upfield of the corresponding protons in 1-oxa-6,6a-dithia-2-azapentalenes (ca 1 ppm) (Table XV). This may be attributed to a greater ring current being present in the oxadithia-azapentalenes and hence greater S-O interaction may be inferred to be present in this system.

The UV spectral data for the nitro compounds (121) are reproduced in Table XVI. The UV spectra of the nitromethylene

dithioles are totally different from those of the corresponding oxadithiaazapentalenes. Three bands are present in the ultraviolet region of the spectra (203-218 nm; 226-244 nm; 255-293 nm). The longer wavelength transitions occur in two forms. The first accounts for the simple alkyl compounds (121a-d) and these show three or four bands, depending on the substitution pattern of the molecule (380-460 nm). The second form occurs in aryl substituted derivatives which show only one long wavelengh transition (ca 450 nm).

The ring protons in the 3-nitro-1-oxa-6,6a-dithia-2-aza-pentalenes (124a,b) experience a downfield shift (ca 1 ppm) relative to the unsubstituted compounds. This may be attributed to the diamagnetic anisotropy of the nitro group. The UV spectra (Table XVI) of these compounds are similar to those of the unsubstituted compounds but are characterised by the presence of an additional band (ca 325 nm). These UV spectra are totally different from those of the nitromethylene dithioles (121c,e) (Table XVI).

The following observations may be drawn from this study of nitrogen-oxygen analogues of 1,6,6a-trithiapentalenes.

a) 1,6-Dioxa-6a-thia-2-azapentalenes are stable bicyclic heterocycles similar in properties to 1,6-dioxa-6a-thiapentalenes.

b) Under favourable circumstances thionation at nitrogen, hitherto unknown, can occur.

c) 1-Oxa-6,6a-dithia-2-azapentalenes can be oxidised, albeit in low yields, to 3-nitromethylene-3H-1,2-dithioles.

d) 3-Nitromethylene-3H-1,2-dithioles are readily available from nitration of 3-methylene-1,2-dithiolium salts.

e) 3-Nitromethylene-3H-1,2-dithioles have a high reactivity.

Table XII

Chemical shift data (δ values in ppm downfield from the tetramethylsilane signal) in the nmr spectra of compounds arising from the study of 1-oxa-6,6a-dithia-2-azapentalenes and 1-oxa-6,6a-diselena-2-azapentalenes (in deuteriochloroform). J values are in Hz.

	Proton Signals (δ)		
Compound	R^5	R^4	R^3
108a	H, 8.93 q $J_{(5,4)}=0.5$	Me, 2.53 d $J_{(4,5)}=0.5$	Me, 2.79
108b	H, 9.24	CH_2, 2.84 m*	CH_2, 3.11 m*
111	H, 9.26 d $J_{(5,4)}=2.2$	H, 8.02 d $J_{(4,5)}=2.2$	CHO, 10.40
110	H, 9.29 q $J_{(5,4)}=0.5$	Me, 2.57 d $J_{(4,5)}=0.5$	Me, 2.85
116	H, 10.30 q $J_{(5,4)}=0.8$	Me, 2.76 d $J_{(4,5)}=0.8$	Me, 2.84
117	H, 9.40 bu	Me, 2.71 d $J_{(4,5)}=0.8$	

* Also β-CH_2, 2.11 m

Values refer to singlet absorptions unless otherwise stated. For multiplets, d = doublet, q = quartet, m = multiplet, bu = broad and unresolved due to weakness.

Table XIII

UV spectral data for the 1,6-dioxa-6a-thia-2-azapentalenes and the 1,6-dioxa-6a-selena-2-azapentalenes

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
108a	216	3.73	108b	201	3.87
	238 infl	3.34		216 infl	3.74
	367	3.87		251 infl	3.19
				385	3.83
111	198	3.77	110	202	3.84
	213	3.99		223	3.68
	279	3.54		249	3.14
	345	3.73		282	3.20
				394	3.93

infl = inflexion

Table XIV

Chemical shift data (δ in ppm downfield from the tetramethylsilane signal) in the nmr spectra of 3-nitromethylene-3H-1,2-dithioles and 3-nitro-1-oxa-6,6a-dithia-2-azapentalenes (in deuteriochloroform) J values are in Hz

	Proton Signals (δ)		
Compound	R^1	R^2	R^3
121a[16,a]	H, 8.03 q $J_{(5,4)}$=0.9	Me, 2.63 d $J_{(4,5)}$=0.9	Me, 2.71
121b[16,a]	H, 7.83t $J_{(5,4)}$=1.1 Hz	CH_2, 2.87 m[b]	CH_2, 2.87 m[b]
121c	Bu^t, 1.45	H, 7.05	H, 7.82
121d	H, 8.18 d $J_{(5,4)}$=5.9	H, 7.21 d $J_{(4,5)}$=6.4	H, 7.90
121e	Ø, 7.4-7.7[c]	H, 7.42	H, 7.92
121f	Ø, 7.4-7.7[c]	H, 7.43	Me, 2.51
124a	Bu^t, 1.60	H, 9.02	NO_2
124b	Ø, 7.58 m[d] 7.90 m[e]	H, 9.35	NO_2

a = This study
b = βCH_2, 2.00 m
c = Complex of multiplets
d = m + p protons
e = o protons

Values refer to singlet absorptions unless otherwise stated.

For multiplets, d = doublet, t = triplet, q = quartet, m = multiplet

Table XV

The change in chemical shift ($\Delta\delta$) of the ring protons in the 3-nitromethylene-3H-1,2-dithioles compared with the corresponding protons in 1-oxa-6,6a-dithia-2-azapentalenes

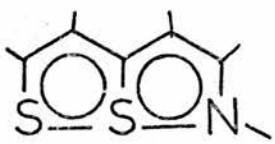
Compound	$\Delta\delta(R^1)$	$\Delta\delta(R^2)$	$\Delta\delta(R^3)$
121a	1.04	-	-
b	1.22	-	-
c	-	0.99	1.26
d	1.23	1.02	1.30
e	-	0.89	1.16
f	-	0.76	-

Table XVI

UV spectral data for the 3-nitromethylene-3H-1,2-dithioles and 3-nitro-1-oxa-6,6a-dithia-2-azapenatlenes

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
121a	215	4.07	121b	218	4.20
	241 infl	3.84		244	3.83
	293	3.41		289	3.48
	415 sh	3.72		415	3.90
	441	4.20		436	4.24
	463	4.31		461	4.34
121c[16]	205	4.14	121d[16]	206	4.09
	232	3.88		226 sh	3.92
	255	3.74		281	3.41
	380 sh	3.84		400 sh	4.02
	400 sh	4.13		415	4.22
	414	4.30		432	4.15
	438	4.32		440	4.26
121e	203	4.32	121f	203	4.33
	226 infl	4.15		235 sh	4.10
	301	4.10		301	4.10
	442	4.24		455	4.28
124a	215	4.18	124b	201	4.40
	244 sh	4.05		225	4.29
	277 infl	3.74		272 sh	3.87
	317	3.66		323 infl	4.03
	397	3.80		334	4.05
				412	4.02

sh = shoulder infl = inflexion



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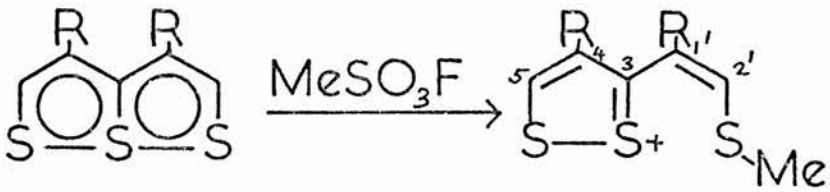
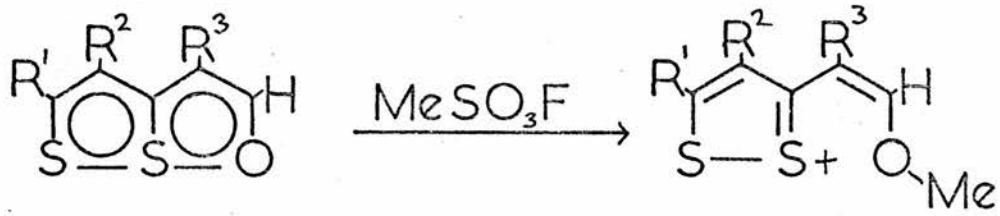


132 133 134

a R-R = $-(CH_2)_2-$

b R-R = $-(CH_2)_3-$



135 136

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

F Methylation of 1,6,6a-Trithiapentalenes and Analogues

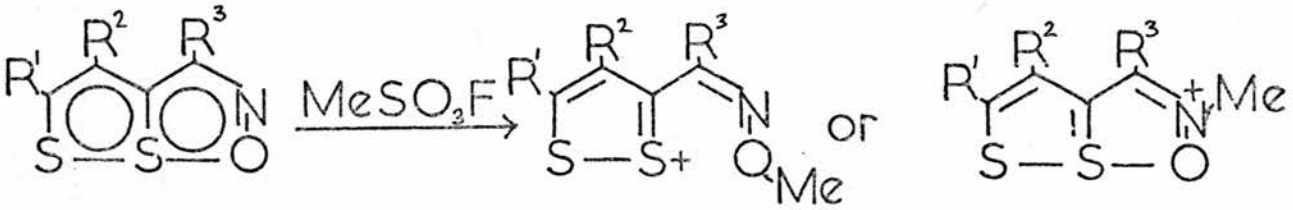
This section describes the results of methylation of 1,6,6a-trithiapentalenes and several analogues. Previous work has shown[107,134,187] that 1,6a-dithia-6-azapentalenes (131) undergo methylation at S-1. 1,6,6a-Trithiapentalenes have also been methylated but few spectroscopic details of the resulting salts, other than UV data, were given. Methylations in this study were performed with methyl fluorosulphonate ($MeOSO_2F$). Elemental analyses of the methylation products (see Experimental section) were occasionally outwith the normally accepted limits (0.3%) for C, H or N. This is due to the very hygroscopic nature of several of the products.

(i) 1,6,6a-Trithiapentalenes

Methylation of the 1,6,6a-trithiapentalenes (132a,b) gave high yields (80-90%) of methylated material. Nmr spectroscopy (Table XVII) shows that compound (132b) gives a mixture of two isomers, (133b) and (134b), in almost equal amounts. The bridged trithiapentalene (132a) gives a product, formulated as (133a), which is almost homogeneous, a small peak (S-Me, the largest in the spectrum) showing the presence of a small quantity of isomer (134a). From the nmr spectra of these compounds, methylation may be said to occur with certainty at sulphur [S-1(6)] . The only other site, C-3(4) may be overlooked on steric grounds.

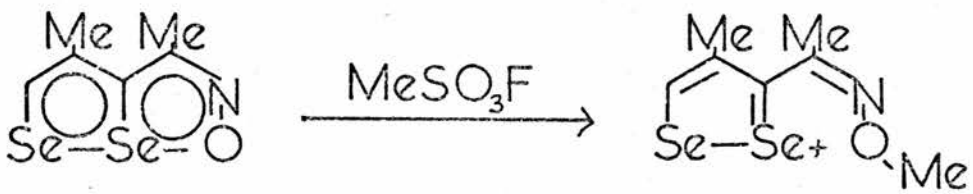
(ii) 1-Oxa-6,6a-dithiapentalenes

Methylation of 1-oxa-6,6a-dithiapentalenes occurs at oxygen (O-1). The nmr spectra of the salts which resulted from methylation (Table XVII) all have a methyl resonance at δ4.2-4.4. S-methylation may be ruled out since the chemical shift for an S-methyl group

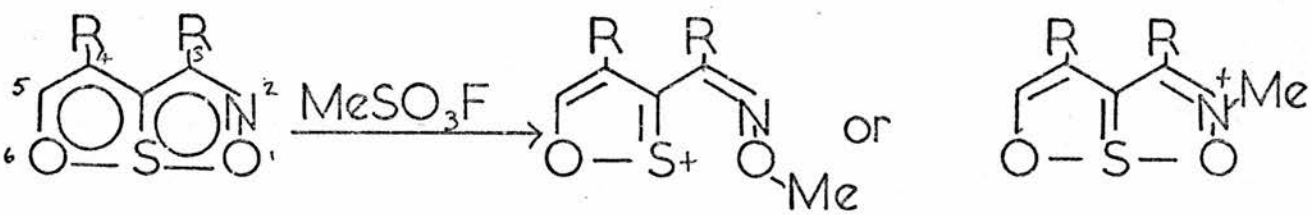


137 138 139

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



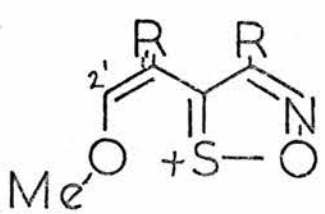
140 141



142 143 144

a R = Me

b R-R = $-(CH_2)_3-$



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normally encountered in compounds of this type lies in the range δ2.6-2.8[134]. C-alkylation was not observed. These salts were unstable to light, air and moisture. Indeed compound (136c) was so unstable as to start decomposing immediately after preparation. Decomposition could be observed readily since the initial pale colour of the salt turned rapidly to dark green. A feature of the nmr spectra of these salts is the absence of coupling between the O-methyl group and either the vinyl protons or methyl groups. The UV spectra (Table XVIII) of the salts are different from the spectra of the starting materials; the long wavelength bands in the starting materials and products occur near the same wavelengths (ca 440 nm). Formulation of these salts as 3-(2-methoxyvinyl)-1,2-dithiolium salts seems reasonable.

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

The 1-oxa-6,6a-dithia-2-azapentalenes (137) methylate readily to give almost quantitative yields of monomethylated salts. The starting materials were orange-to-red and the salts were colourless to pale yellow. The nmr spectra of the salts (Table XVII) show the presence of a methyl resonance at δ4.33 ($\pm$ 0.06 ppm). The position of this peak, as in the previous section, disposes of the possibility of S-methylation having occurred. Two possible positions for methylation remain, O-methylation (138) and N-methylation The nmr spectra of the salts cannot be used to differentiate between O- and N-methylation. The chemical shift of the methyl group might seem to indicate O-methylation but N-methylation cannot be ruled out since N-methyl groups can resonate in this region (eg N-methylpyridinium, δ4.3[216]). An interesting feature of the nmr spectra of the salts is the presence of a coupling between the "added" methyl group and R^3 (138, 139; R^3 = H, Me).

Differentiation between O- and N-methylation thus rests on the only other available evidence, the UV spectra of the salts (Table XVIII). Methylation at nitrogen (139) should make little difference to the UV spectrum, since little change occurs in the system. Methylation at oxygen leads to the production of another heterocyclic system, the product being a derivative of the 1,2-dithiole system. Thus methylation at oxygen should lead to a greatly changed UV spectrum. The UV spectra of 1-oxa-6,6a-dithia-2-azapentalenes (137a-d) show four bands in cyclohexane[16], at 400, 270, 230 and 205 nm and two bands in acetic acid (Table XXII) at 400 and 270 nm (compounds 137a,b,d). The methylated derivatives show four bands in methanol at 380, 290, 230 and 205 nm and two bands in acetic acid at 380 and 290 nm (Table XVIII). The UV spectra of the salts thus appear to be quite different from those of the starting materials. On this basis, methylation at oxygen (O-1) may be presumed to have occurred ie structure (138) is to be preferred. Absolute confirmation is likely to be difficult to obtain unless an Xray structure determination is performed.

3,4-Dimethyl-1-oxa-6,6a-diselena-2-azapentalene (140) was also methylated by methyl fluorosulphonate. The nmr spectrum (Table XVII) of this compound did not differentiate between O- and N-methylation although Se-methylation was ruled out. The UV spectrum of the salt (Table XVIII) is quite different from that of the starting material[16]. Methylation at oxygen (O-1), as was the case for the oxadithiaazapentalenes, seems to be likely in the absence of further information.

(iv) 1,6-Dioxa-6a-thia-2-azapentalenes

Two structures are possible for the methylation products of 1,6-dioxa-6a-thia-2-azapentalenes (142) due to O-methylation (143)

or N-methylation (144). Methylation at O-6 (145) may be ignored since the chemical shift of a 2'-vinyl proton in the nmr spectrum of compounds of this type has already been seen to be at no lower field than δ7.8. The chemical shift of the ring proton in the salts (Table XVII) lies in the range δ9.2-9.3. In the nmr spectrum of the salt from compound (142a) a coupling is observed between the added methyl group and the lower field methyl group. However nmr spectroscopy does not differentiate between O- and N-methylation.

The UV spectra of the salts (Table XVIII) are different from those of the starting materials; the salts show one less band than the starting materials. On this basis there is no hesitation in assigning the 1,2-oxathiolium structure (143) to these salts. They are the first isolated derivatives of this system. The system is isoelectronic with the 1,2-dithiolium system. Replacement of a sulphur atom in the 1,2-dithiolium system by an oxygen atom in the 1,2-dithiolium system by an oxygen atom greatly changes the UV spectrum eg 138b,c ⟶ 143a,b respectively. The dithiolium derivatives have already been seen to have four bands in their UV spectra, at 205, 240, 290 and 400 nm. The corresponding oxathiolium salts have only three bands, at 218, 280 and 355 nm. The long wavelength band undergoes a hypsochromic shift (44 nm) but no comparison can be drawn for the other bands. It is unfortunate that these derivatives are so highly substituted, but, with the newfound knowledge that the system appears to be stable it is to be hoped that simpler derivatives may be prepared.

The results from this study may be summarised as follows:

a) 1,6,6a-Trithiapentalenes undergo methylation at sulphur.

b) 1-Oxa-6,6a-dithiapentalenes undergo methylation at oxygen.

c) 1-Oxa-6,6a-dithia-2-azapentalenes and 1-oxa-6,6a-diselena-2-azapentalenes undergo methylation at oxygen.

d) It is to be noted that the driving force behind these methylations is the production of derivatives of 1,2-dithiolium or 1,2-diselenolium systems, which are known to be stable.

e) 1,6-Dioxa-6a-thia-2-azapentalenes undergo methylation at oxygen (O-1) producing the first known derivatives of the 1,2-oxathiolium system.

Table XVII

Chemical shift data (δ in ppm downfield from the tetramethylsilane signal) in the nmr spectra of the methylation products of trithiapentalenes and analogues (in trifluoroacetic acid). J values are in Hz

Compound	Proton Signals (δ) R^5	R^4	R^1	$R^{2'}$
133a	H, 8.98 t $J_{(5,4)}=1.1$	CH_2, 3.36 m	CH_2, 3.36 m	H, 8.28 t $J_{(2',1')}=2.3$ S-Me, 2.72
133b[a]	H, 9.26 qn	b	b	H, 8.33 m S-Me, 2.73
134b[a]	H, 9.36 qn	b	b	H, 8.02 m S-Me, 2.99
135a	H, 9.29 q $J_{(5,4)}=0.6$	Me, 2.34 d $J_{(4,5)}=0.9$	Me, 2.75b,d[c] $J_{(1',2')}=0.7$	H, 7.81b,q[d] $J_{(2',1')}=0.8$ O-Me, 4.19
135b	H, 9.30 t $J_{(5,4)}\doteqdot 0.8$	CH_2, 3.22 m[e]	CH_2, 2.78 m[e]	H, 7.51 t $J_{(2',1')}\doteqdot 1.1$ O-Me, 4.39
135c	Bu^t, 1.65	H, 8.01	H, 6.64 d $J_{(1',2')}=5.6$	H, 7.55 d $J_{(2',1')}=5.6$ O-Me, 4.39
138a	H, 10.05 d $J_{(5,4)}=5.5$	H, 8.94 d $J_{(4,5)}=5.6$	H, 9.35 q $J_{(1',2')}=0.6$	O-Me, 4.38 d $J_{(2,'1')}=0.6$
138b	H, 9.67 d $J_{(5,4)}=0.5$	Me, 3.10 q $J_{(4,5)}=0.5$	Me, 3.14 q $J_{(1',2')}=0.8$	O-Me, 4.34 q $J_{(2',1')}=0.7$
138c	H, 9.74 b	CH_2, 3.38 m[f]	CH_2, 3.38 m[f]	O-Me, 4.27 b
138d	Bu^t, 1.70	H, 8.76	H, 9.19 q $J_{(1',2')}=0.6$	O-Me, 4.33 d $J_{(2',1')}=0.6$
138e	Ø 7.7 m[g] 8.0 m[h]	H, 8.97	Me, 3.09 q $J_{(1',2')}=0.8$	O-Me, 4.33 q $J_{(2',1')}=0.8$

Table XVII contd

Compound	Proton Signals (δ) R^5	R^4	$R^{1'}$	$R^{2'}$
140	H, 11.30 q $J_{(5,4)}=0.5$	Me, 3.25	Me, 3.25	OMe, 4.21 q $J_{(2',1')}=0.7$
142a	H, 9.22 q $J_{(5,4)}=0.5$	Me, 2.77 b	Me, 3.15 q $J_{(1',2')}=0.8$	OMe, 4.38 q $J_{(2',1')}=0.8$
142a[j]	H, 9.19	Me , 2.76	Me, 3.14	O-Me, 4.36
142b	H, 9.28 b	CH_2, 3.14 m[k]	CH_2, 3.39 m[k]	O-Me, 4.28 b
142b[j]	H, 9.26	CH_2, 3.16	CH_2, 3.40	O-Me, 4.29

a = 133a:134b = 3:4

b = Complex of multiplets, δ2.0-3.5

c = Decoupled at δ7.81

d = Decoupled at δ2.75

e = βCH_2, δ2.06

f = βCH_2, δ2.39

g = m + p protons

h = o protons

j = Perchlorate counter-ion

k = βCH_2, δ2.39

Values refer to singlet absorptions unless otherwise stated.

For multiplets, d = doublet, t = triplet, q = quartet, qn = quintet,

m = multiplet, b = broad

Table XVIII

UV spectral data for the methylation products of trithiapentalenes and analogues (in methanol unless otherwise stated)

Compound	λ_{max} (nm)	log ε	Compound	λ_{max} (nm)	log ε
133a	203	3.78	133/134b	203	3.81
	243 sh	3.72		235 sh	3.79
	260	3.77		258	3.83
	298 sh	3.43		296 sh	3.42
	340 sh	3.11		460	4.26
	469	4.27			
135a	228	3.84	135b	228	4.10
	254 sh	3.51		280 infl	3.07
	302	3.59		427	4.09
	410 infl	3.70		447	4.06
	427	3.72			
	443 sh	3.67			
138a	206	4.04	138a (AcOH)	284	3.20
	232	3.92		384	4.10
	291	3.34			
	383	4.12			
138b	204	3.90	138b (AcOH)	287	3.30
	242	3.99		397	3.96
	397	3.86			
138c	205	3.99	138c (AcOH)	285	3.16
	240	3.97		400	4.05
	288	3.29			
	401	4.04			
138d	207	4.12	138d (AcOH)	295	3.31
	234	3.92		383	3.16
	300	3.26			
	383	3.18			
138e	207	4.40	140	204	4.16
	264	4.10		246	3.86
	350	3.61		320	3.52
	415	4.27		429	3.90

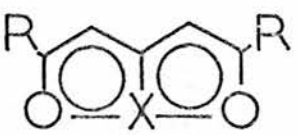
Table XVIII contd.

Compound	λ_{max} (nm)	log ε
142a*	218	3.83
	353	3.91
142b*	218	3.77
	279	3.15
	357	3.92

Compound	λ_{max} (nm)	log ε
142a* (AcOH)	354	3.90
142b* (AcOH)	266	3.06
	357	3.85

* = Perchlorate counter-ion

sh = shoulder, infl = inflexion



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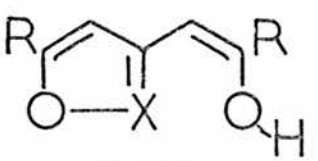

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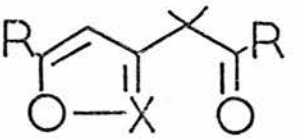
R:H,Me a X:S
b X:Se



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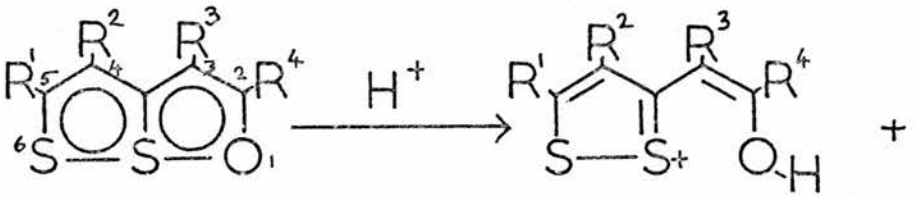

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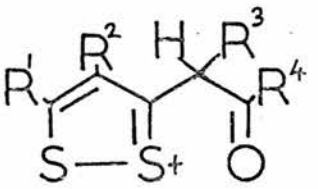

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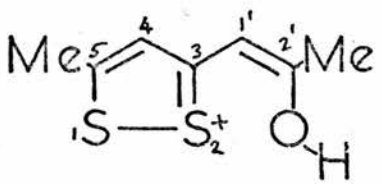
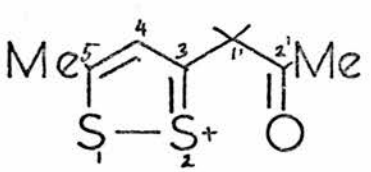
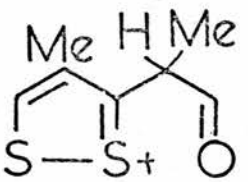
	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	Me	Me	H
c	Bu^t	H	H	H
d	Me	H	H	Me



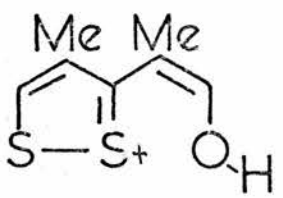
150d



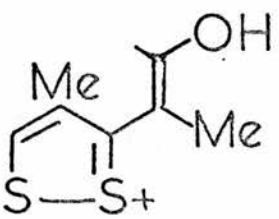
151d



151b



150b



152

G Protonation of 1,6,6a-Trithiapentalenes and Analogues

Since protonation of 1,6-dioxa-6a-thiapentalenes (146a) (Section C) and 1,6-dioxa-6a-selenapentalenes (146b) (Section D) had been shown to occur at oxygen (147) and to a small extent at carbon (148), the latter detectable most easily by H/D exchange, it was of interest to determine whether the protonation of other systems could be interpreted in a similar manner. Three systems were investigated by nmr spectroscopy, 1-oxa-6,6a-dithiapentalenes, 1,6,6a-trithiapentalenes and 1-oxa-6,6a-dithia-2-azapentalenes, since numerous derivatives of each system were available.

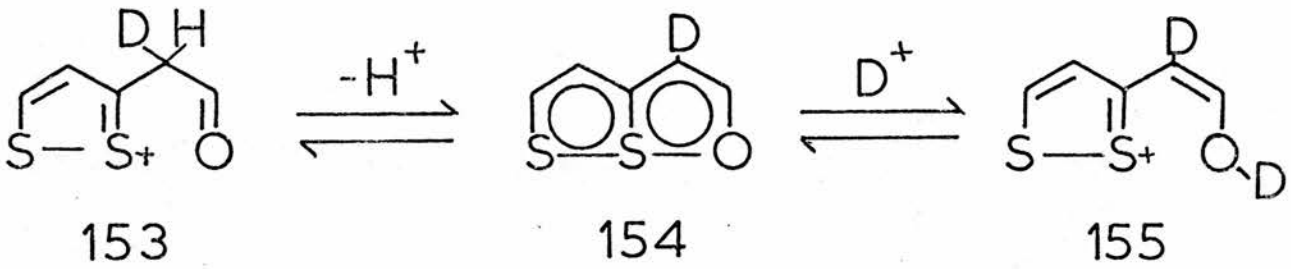
(i) 1-Oxa-6,6a-dithiapentalenes

O-protonation of 1-oxa-6,6a-dithiapentalenes has been inferred in previous studies[24,134,191] and one of these studies obtained some evidence for C-protonation[134]. Pinel and Mollier[105] observed that 3-H in compound (149d) underwent H/D exchange but failed to notice the significance of this fact with respect to the protonation of oxadithiapentalenes. Further evidence for O-protonation will be presented in this study but, more importantly, the presence of C-protonation will be demonstrated conclusively. The nmr spectrum of 2,5-dimethyl-1-oxa-6,6a-dithiapentalene (149d) in trifluoroacetic acid solution clearly demonstrated the presence of both O and C protonation (Table XIX). The signals in the spectrum of this compound were broad, possibly due to exchange of the "added" proton with the solvent medium. This exchange was slowed by obtaining the protonation spectrum from a solution of higher acidity (trifluoroacetic acid - 5% perchloric acid); the peaks were considerably sharper in this medium. Two sets of peaks were observed in almost equal amounts. The O-protonation product (150 d) gives rise to peaks at δ2.43 (2'-Me), 2.89 (5-Me), 6.55 (1'-H) and 7.69 (4-H); the C-protonation product (151d) gives rise to peaks at δ2.58

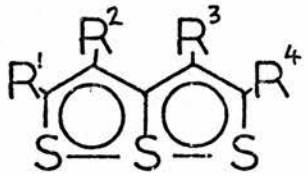
(CH_2COMe), 3.11 (5-Me), 4.92 ($\underline{CH}_2COMe$) and 8.29 (4-H). The presence of a signal at δ4.92 due to a methylene group indicates that C-protonation has occurred. Assignment of the peaks due to the methyl groups in either isomer was facilitated by the presence of a coupling between the dithiolium ring proton (4-H) and one of the methyl groups (5-Me) in each isomer.

The nmr spectrum of the 2-t-butyl derivative (149 c) was obtained in a trifluoroacetic acid-perchloric acid mixture to determine whether or not increasing the acid strength of the spectral medium (from trifluoroacetic acid) could alter the position of protonation in this compound. Only O-protonation was observed, the spectrum being identical to that obtained in trifluoroacetic acid solution. The nmr spectrum of the dimethyl derivative (149b) was also obtained in trifluoroacetic acid-perchloric acid mixture. Protonation occurred to give essentially the same result as was obtained from trifluoroacetic acid solution[134] except that the signals were considerably sharper. C-protonation (151b) and O-protonation (150b,152) were observed to occur together, in almost equal amounts. The product of O-protonation appeared as two isomers (150b, 152), the major of these being (152) (ca 90%).

Although C-protonation was not observed directly in compounds (149 a,c) it could be inferred since the proton at position 3 in these compounds was observed to undergo H/D exchange The spectra of these compounds in deuteriotrifluoroacetic acid show one less signal than the corresponding spectra in trifluoroacetic acid. This can only occur by protonation at C-3 which gives rise to an intermediate of type (153). Since oxadithiapentalenes protonate at oxygen in trifluoroacetic acid solution it must be



153 154 155



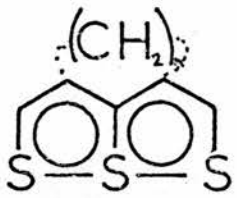
156

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	Me	Me	H
c	H	$-(CH_2)_2-$		H
d	H	$-(CH_2)_3-$		H
e	Bu^t	H	H	H
f	Me	H	H	Me
g	Bu^t	H	H	SMe
h	Bu^t	H	H	NMe_2

assumed that an equilibrium concentration of unprotonated material remains in solution and that this equilibrium concentration is below the limits of detection by nmr spectroscopy. Deuterio-protonation gives rise to the intermediate (153) which then deprotonates (preferential loss of H^+ since $[D^+] \gg [H^+]$); O-deuterio-protonation gives the product (155) from which the spectrum is observed. This mechanism has been taken as representative of the other derivatives in this series (149c,d). The ease with which H/D exchange occurs in these compounds may be demonstrated forcibly. Dissolving any of the oxadithiapentalenes (149a,c,d) in deuterio-chloroform and shaking the solution with a 10% solution of deuteriotrifluoroacetic acid in deuterium oxide for several minutes is sufficient to exchange the 3-proton to such an extent that only a very small residual peak for 3-H remains in the nmr spectrum (Table XIX).

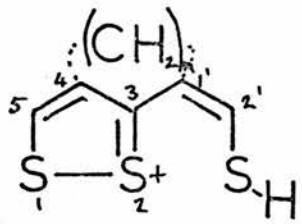
(ii) 1,6,6a-Trithiapentalenes

Protonation of 1,6,6a-trithiapentalenes has not previously been investigated. The trithiapentalenes (156a-h) were employed in this present study. The spectra of the parent compound (156a) and the 2-t-butyl derivative (156e) in trifluoroacetic acid solution were too complex to analyse. Since useful results in previous protonation studies incorporated in this thesis had been obtained from 2,5-dimethyl derivatives the nmr spectrum of compound (156f) in trifluoroacetic acid solution was obtained. 2,5-Dimethyl-1,6,6a-trithiapentalene (156f) was not protonated in trifluoroacetic acid solution; increasing the acidity of the solvent (trifluoroacetic acid-5% perchloric acid) served only to hydrolyse the trithiapentalene to the oxadithiapentalene (149d) which then protonated in the manner already described.

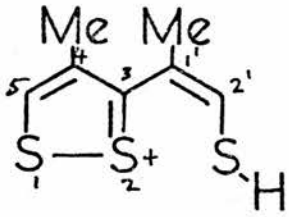


157

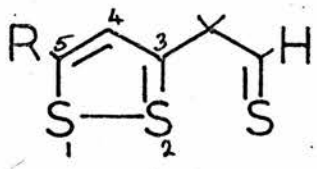
a.n: 2
b.n: 3



158



159



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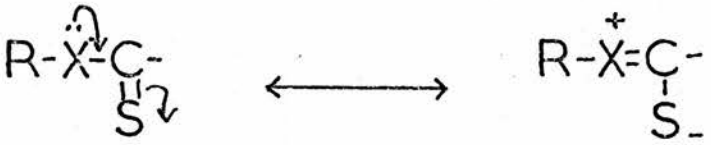
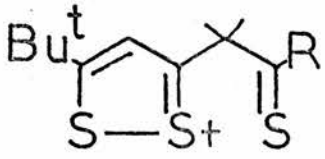


161 X: S, N-R 162

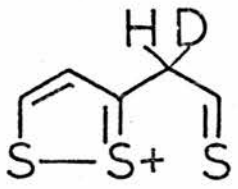


a. R: SMe
b. R: NMe_2

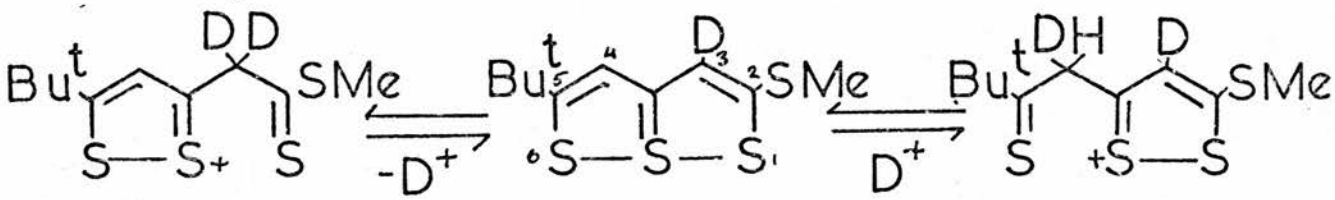
163

Attention was then turned to the 3,4-disubstituted trithiapentalenes (156b,c,d). The first direct evidence for protonation was observed in the spectra of these compounds. The bridged derivatives (156c,d) showed the presence of two species, unprotonated material (157) and a species with an unsymmetrical structure. This latter species arises from S-protonation (158). In trifluoroacetic acid solution the S-H signal was not observed due to the rapid exchange of this proton with the solvent. Increasing the acidity of the spectral medium (trifluoroacetic acid-5% perchloric acid) slowed the rate of exchange. The rate of exchange became even slower when the solution was cooled to 0^{o}. The signal due to the S-H proton then appeared as a doublet ($J \doteqdot 10$ Hz). 3,4-Dimethyl-1,6,6a-trithiapentalene (156b) is unprotonated in trifluoroacetic acid initially but undergoes slow protonation at sulphur. After three days no unprotonated material is left in solution and the nmr spectrum is consistent with S-protonation having occurred. The signal due to the S-H proton was not observed until trifluoroacetic acid-10% perchloric acid was used. In the spectra of these compounds (156b,c,d) the S-H signal was observed to be coupled to 2-H (158,159) which appeared as a doublet ($J \doteqdot 10$ Hz). The signal due to 2-H appeared as a singlet when the solvent was deuteriotrifluoroacetic acid-5% deuterioperchloric acid. Use of fluorosulphonic acid in place of perchloric acid caused the trithiapentalenes (156b,d) to decompose rapidly to a sticky red gum. The same trithiapentalenes were also unstable to acetonitrile-5% perchloric acid and acetonitrile-5% fluorosulphonic acid.

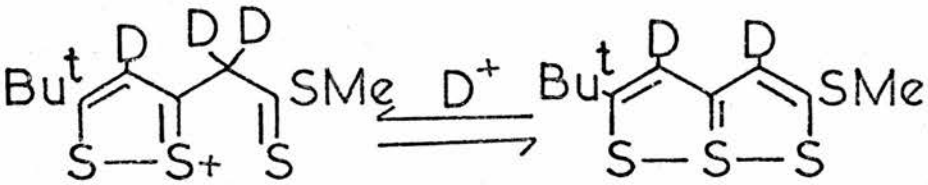
Until this part of the study C-protonation has not been observed. S-protonation has been seen to occur and yields a derivative of the 1,2-dithiolium system. C-protonation of trithiapentalenes (160) has an inbuilt difficulty. The product is



164



165 166 167



169 168

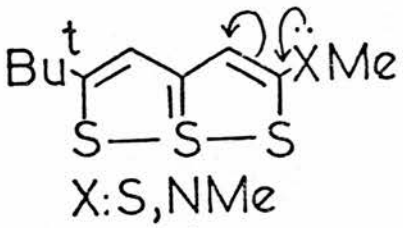
a derivative of the stable 1,2-dithiolium system but the substituent at the 3-position is an alkyl thioaldehyde group. Alkyl thioaldehydes have not yet been isolated due to their instability. Thioformyl compounds are not unknown and the thiocarbonyl group is readily stabilised by the presence of electron releasing groups (161) which polarise the carbon-sulphur double bond (162). It thus became important to determine whether or not C-protonation would occur to any extent in trithiapentalenes which had an electron releasing group in the 2-position. The methylthio and dimethylamino trithiapentalenes (156g,h respectively) were readily available[217] and the spectra of these compounds were recorded in trifluoroacetic acid solution. The spectra of both compounds showed a peak (ca δ5) which integrated for two protons. Singlet peaks were observed for the t-butyl and methyl groups and for the remaining ring proton. C-protonation had occurred and had given rise to a stable intermediate (163). Evidently stabilisation of the thiocarbonyl group is necessary before trithiapentalenes can show C-protonation to any observable extent.

The other test which can be applied in a protonation study to determine whether or not C-protonation has occurred is H/D exchange. The multiplicity of doublets obtained from the spectrum of trithiapentalene (156a) in trifluoroacetic acid was reduced to a multiplicity of singlets in deuteriotrifluoroacetic acid solution. A similar result was obtained for the 2-t-butyl derivative (156e). It is difficult to say with certainty that this has been due to C-protonation and H/D exchange due to the difficulty in analysing the spectrum. However H/D exchange was confirmed with certainty when a deuteriotrifluoroacetic acid solution of trithiapentalene (156a) was quenched with a solution of sodium carbonate in deuterium oxide. The nmr spectrum of the recovered trithiapentalene (in

deuteriochloroform) showed that 3(4)-H had undergone H/D exchange to the extent of 80%. This can only arise by there being a small equilibrium concentration of the C-protonated intermediate (164) in deuteriotrifluoroacetic acid solution.

As a matter of course the spectra of the methylthio (156g) and dimethylamino (156h) trithiapentalenes were also recorded in deuteriotrifluoroacetic acid solution. No analytical difficulties were encountered in the spectrum of the dimethylamino compound (156h). Signals due to the t-butyl and methyl groups and the ring proton were observed. The methylene group due to protonation at C-3 underwent H/D exchange and no signal was observed at the requisite position. The spectrum of the methylthio compound (156g) appeared to be in accord with that of the dimethylamino compound until the spectrum was integrated. The signal due to the ring proton integrated for less than one proton. This signal eventually disappeared. Evidently H/D exchange was occurring. Initially the major species in solution is (165). Dedeuteration leaves a small equilibrium concentration of the monodeuterio derivative (166). Deuterioprotonation at position 4 in (166) gives rise to the C-protonated intermediate (167) which then deprotonates to give the dideuteriotrithiapentalene (168). Deuterioprotonation of this latter compound yields the species (169) which is eventually observed by nmr spectroscopy to be the only species observable in solution.

The fact that the rates of exchange of the protons in the 3- and 4-positions of this compound are different can be seen in another way. Shaking a deuteriochloroform solution of the methylthiothiapentalene (156g) overnight with a 10% solution of deuteriotrifluoro acetic acid in deuterium oxide is sufficient to exchange one proton (3-H) only for deuterium. Protonation and H/D exchange in these



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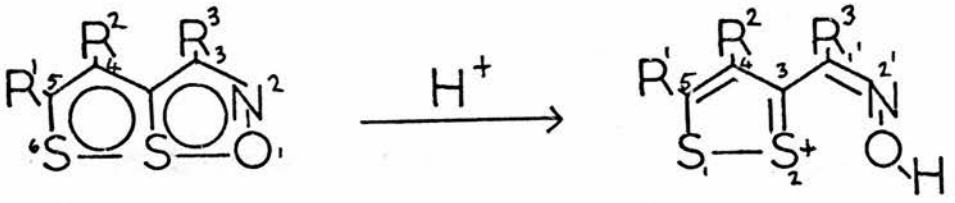
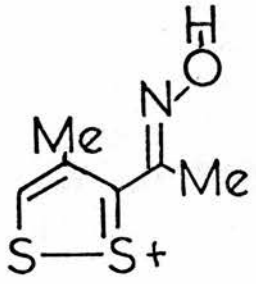


137 171

	R^1	R^2	R^3
a	H	H	H
b	H	Me	Me
c d	Bu^t	H	H



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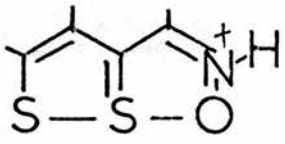


173

trithiapentalenes (156g,h) has been assumed to occur at the 3-position since the presence of the electron releasing group (SMe or NMe_2) will be expected to raise the charge density at this position (170). A t-butyl group is unlikely to have such a strong electronic effect. The data from the protonation spectra of trithiapentalenes are reproduced in Table XIX.

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

1-Oxa-6,6a-dithia-2-azapentalenes (137) dissolve readily in trifluoroacetic acid yielding colourless to pale yellow solutions. The nmr spectra of the solutions (Table XX) show downfield shifts of the ring protons at positions 4 and 5 (ca 0.8 ppm) and little change at position 3 when compared with spectra of the corresponding compounds in deuteriochloroform[16] (Table XXI). The chemical shifts of the ring protons are very similar to those found in the corresponding methylation products (138) (Table XVII). On this basis it seems to be reasonable to assume that O-protonation has occurred (171). After 24 hours the spectrum of compound (137b) in trifluoroacetic acid solution showed the presence of an isomer of the protonated material. This is believed to be (172) and the isomerisation probably occurs to relieve steric clash of the methyl groups; this type of isomerisation was also observed in the protonation of 1-oxa-6,6a-dithiapentalene (149b). No H/D exchange was observed to occur in this class of compounds when their spectra were obtained in deuteriotrifluoroacetic acid solution.

An attempt was made to examine the protonation of 1-oxa-6,6a-dithia-2-azapentalenes by UV spectroscopy. Accordingly the spectra of these compounds were recorded in acetic acid, acetic acid-5% perchloric acid and acetic acid-10% perchloric acid. Two bands were observed when acetic acid was employed as solvent (270, 400 nm).

The presence of perchloric acid (5 or 10%) was observed to have a considerable effect on the spectra since three bands were now observed to be present (280, 350, 380 nm). O-protonation may be inferred from this study since protonation at nitrogen (173) would not disrupt the system and hence the UV spectrum would change by very little from that of the unprotonated material (cf pyridine and pyridinium ion[215]). The spectra of the protonated species do not appear to bear any relation to those of the corresponding methylation products.

The following conclusions may be drawn from this study:

a) 1-Oxa-6,6a-dithiapentalenes undergo preferential protonation at oxygen.

b) 1-Oxa-6,6a-dithiapentalenes with a 2- or 3-methyl group can undergo protonation at C-3.

c) 1-Oxa-6,6a-dithiapentalenes with a free 3-position can protonate at C-3, this being below the limits of detection by nmr spectroscopy but being readily detected by H/D exchange.

d) 1,6,6a-Trithiapentalenes in the absence of electron releasing groups protonate preferentially at sulphur.

e) 1,6,6a-Trithiapentalenes with a free 3-position undergo protonation at C-3, this being below the limits of detection by nmr spectroscopy but being readily detected by H/D exchange.

f) 1,6,6a-Trithiapentalenes with an electron releasing group at position 2 protonate exclusively at C-3.

g) 1-Oxa-6,6a-dithia-2-azapentalenes protonate exclusively at oxygen.

Table XIX

Chemical shift data (δ in ppm downfield from the tetramethylsilane signal) in the nmr spectra of 1-oxa-6,6a-dithiapentalenes and 1,6,6a-trithiapentalenes in trifluoroacetic acid unless otherwise stated J values are in Hz

Compound	Proton signals (δ) R^5	R^4	R^3	R^2
149d(150d)	Me, 2.89 b	H, 6.51 b	H, 7.64 b	Me, 2.47 b
(151d)	Me, 3.08 b	H, 8.23 b	CH_2^a, 4.88 b	Me, 2.47 b
149b[b](152)	H, 9.25 q $J_{(5,4)}=0.6$	Me, 2.36 d $J_{(4,5)}=0.6$	Me, 2.72 b	H, 8.25 b
149b[b](150b)	H, 9.34[c]	Me, 2.86 d $J_{(4,5)}=0.6$	Me, 2.41 d $J_{(1',2')}=1.0$	H, 7.70[c]
149b[b](151b)	H, 9.97 d $J_{(5,4)}=0.6$	Me, 2.78 d $J_{(4,5)}=0.6$	Me, 1.78 d $J_{(1'\text{-Me},1')}=7.8$ H, 5.05 q $J_{(1',1'\text{-Me})}=8$	H, 9.94
149d[b](150d)	Me, 2.89 d $J_{(5,4)}=0.7$	H, 7.69 q $J_{(4,5)}=0.6$	H, 6.55 b	Me, 2.43 b
149d[b](151d)	Me, 3.11 d $J_{(5,4)}=0.5$	H, 8.29 q $J_{(4,5)}=0.6$	CH_2^a, 4.92	Me, 2.58
149a[d](155)	H, 9.54 d $J_{(5,4)}=5.4$	H, 8.12 d $J_{(4,5)}=5.4$	D	H, 8.03 b
149c[d]	Bu^t, 1.65	H, 7.98	D	H, 7.91
149a[e]	H, 8.06 d	H, 7.28 d	D	H, 9.31
149c[e]	Bu^t, 1.41	H, 7.06	D	H, 9.16
149d[s]	Me, 2.43 d $J_{(5,4)}=1.0$	H, 6.81 q $J_{(4,5)}=0.8$	H, 6.63	Me, 2.22
149d[e]	Me, 2.43 d	H, 6.81 q	D	Me, 2.22
156a[j]	Multiplicity of doublets, δ4-5.5 and δ7-10			
156b[fj]	H, 8.5 b	Me, 2.50	Me, 2.50	H, 8.5 b

Table XIX contd.

Compound	Proton Signals (δ) R^5	R^4	R^3	R^2
156b[gj](159)	H, 9.53q $J_{(5,4)}$=0.6	Me, 2.72 d $J_{(4,5)}$=0.7	Me, 2.41 d $J_{(1',2')}$=0.8	H, 7.91 b
156c	H, 8.54 qn $J_{(5,4)}$=0.8	CH_2, 3.53 t $J_{(4,5)}$=0.8	CH_2, 3.53 t	H, 8.54 qn
156c(158a)	H, 9.20 t $J_{(5,4)}$=1.1	CH_2, 3.39 tb $J_{(4,5)}\doteqdot$1.2	CH_2, 3.43 tb $J_{(1',2')}\doteqdot$2.4	H, 8.11 tb $J_{(2',1')}\doteqdot$2.4
156d	H, 8.78 b	h	h	H, 8.78 b
156d(158b)	H, 9.45 m	h	h	H, 8.29 m
156e[j]	Bu^t, 1.65, 1.67, 1.69, 1.71	Multiplicity of signals, δ 4-5.2, 7-8.6		
156f	Me, 2.84	H, 7.70	H, 7.70	Me, 2.84
156g(163a)	Bu^t, 1.67	H, 8.40	CH_2^a, 5.18	SMe, 2.81
156h(163b)	Bu^t, 1.60	H, 8.33	CH_2^a, 4.98	NMe, 3.50 NMe, 3.64
156b[k](159)	H, 9.54 q $J_{(5,4)}$=0.5	Me, 2.73 d $J_{(4,5)}$=0.5	Me, 2.40 d $J_{(1',2')}$=0.8	H, 7.87 dq $J_{(2',1')}$=0.8 $J_{(2',SH)}$=11.4 SH, 4.17 d $J_{(SH,2')}$=9.8
156c[b]	H, 8.54 b	CH_2, 3.56 b	CH_2, 3.56 b	H, 8.54 b
156c[b](158a)	H, 9.22 t $J_{(5,4)}$=0.9	CH_2, 3.40 m	CH_2, 3.40 m	H, 8.15 d $J_{(2'SH)}$=9.2 SH, 4.28 db
156d[b]	H, 8.78 b	m	m	H, 8.78 b
156d[b](158a)	H, 9.46 t	m	m	H, 8.30 dt $J_t\doteqdot$1.4 J_{SH}=9.5 SH, 4.38 db[l] J = 9.5
156g[b](163a)	Bu^t, 1.67	H, 8.42	CH_2^a, 5.19	SMe, 2.81

Table XIX contd.

Compound	Proton Signals (δ) R^5	R^4	R^3	R^2
156h(163b)	Bu^t, 1.61	H, 8.38	CH_2^a, 5.01	NMe, 3.53 NMe, 3.56
$156a^n$	Multiplicity of signals, δ 1.65-1.71, δ 8-8.6			
$156c^o$	H, 8.55	CH_2, 3.55	CH_2, 3.55	H, 8.55
$156c^o$	H, 9.21	CH_2, 3.40	CH_2, 3.40	H, 8.12
$156d^o$	H, 8.79	p	p	H, 8.79
$156d^o$	H, 9.47	p	p	H, 8.29
$156e^o$	Bu^t, 1.65, 1.67, 1.69, 1.71	Multiplicity of signals, δ 8-8.6		
$156f^o$	Me, 2.84	D	D	Me, 2.84
$156g^o$(169)	Bu^t, 1.67	D	CD_2^r	SMe, 2.81
$156g^q$(166)	Bu^t, 1.39	7.28	D	SMe, 2.61
156h	Bu^t, 1.61	8.36	CD_2^r	NMe, 3.64 NMe, 3.68

a - Protonation at C-3

b - In TFA-5% $HClO_4$

c - Too weak to detect multiplicity on 100 MHz scale

d - In dTFA

e - In $CDCl_3$ after shaking with 10% dTFA in D_2O

f - After 30 mins

g - After 3 days

h - $(CH_2)_3$ protons, δ 2.09, 2.73, 3.14 m

j - In TFA or TFA-5% $HClO_4$

k - In TFA-10% $HClO_4$

l - Sharpens on cooling to 0^o

m - $(CH_2)_3$- protons, δ2.08, 2.69, 3.13 m

n - In dTFA

o - In dTFA-5% $DClO_4$

p - $(CH_2)_3$- protons δ2.08, 2.70, 3.12 m

q - In $CDCl_3$ after standing with 10% dTFA in D_2O overnight

r - Deuterioprotonation

s - in $CDCl_3$

Values refer to singlet absorptions unless otherwise stated. For multiplets, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, b = broad

Table XX

Chemical shift data (δ in ppm downfield from the tetramethylsilane signal) in the nmr spectra of 1-oxa-6,6a-dithia-2-azapentalenes in trifluoroacetic acid. J values are in Hz

	Proton Signals (δ)		
Compound	R^5	R^4	R^3
137a(172a)	H, 10.21 d $J_{(5,4)}=5.3$	H, 8.98 d $J_{(4,5)}=5.3$	H, 9.15
137b(172b)	H, 9.82 b	Me, 3.09 b	Me, 3.06
137b[a](173)	H, 9.89	Me, 2.86	Me, 2.58
137b[b](172b)	H, 9.83 q $J_{(5,4)}=0.6$	Me, 3.09 d $J_{(4,5)}=0.6$	Me, 3.06
137b[a,b](173)	H, 9.94 q $J_{(5,4)}=0.6$	Me, 2.87 d $J_{(4,5)}=0.6$	Me, 2.59
137c(172c)	Bu^t, 1.75	H, 8.83	H, 8.98

a = After 24 hours

b = In TFA-5% $HClO_4$

Values refer to singlet absorptions unless otherwise stated.

For multiplets, d = doublet, q = quartet, b = broad

Table XXI

The change in chemical shift ($\Delta\delta$) of the ring protons in 1-oxa-6,6a-dithia-2-azapentalenes on going from deuteriochloroform to trifluoroacetic acid (Increases in deshielding are given positive values)

Compound	$\Delta\delta R^5$	$\Delta\delta R^4$	$\Delta\delta R^3$
137a	0.80	0.75	0.05
137b	0.76		
137c		0.79	-0.10

Table XXII

UV spectral data for 1-oxa-6,6a-dithia-2-azapentalenes

	A		B		C	
Compound	λ_{max}(nm)	log ε	λ_{max}(nm)	log ε	λ_{max}(nm)	log ε
137a	263	3.50	285	3.28	284	3.29
	399	3.74	348	3.82	348	3.83
			378	3.80	376	3.81
137b	265sh	3.44	292	3.32	292	3.47
	410	3.78	364	3.69	351	3.86
			393	3.76	386 sh	3.60
137d	277	3.56	300 sh	3.51	300 sh	3.51
	396	3.83	346	3.89	346	3.92
			376	3.84	376	3.82

A - In acetic acid

B - In acetic acid-5% perchloric acid

C - In acetic acid-10% perchloric acid

sh = shoulder

Introductory Notes

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

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

Infrared spectra were measured with a Perkin-Elmer 621 spectrophotometer. Samples were prepared as KBr discs or as solutions in carbon tetrachloride (0.02 M).

1H Nmr spectra were measured at 31.4°C with a Varian HA 100 operating at 100 MHz. Chemical shifts (δ) are expressed in ppm downfield from the tetramethylsilane signal. Solutions in deuteriochloroform were 0.4 M, in hexadeuteriodimethylsulphoxide 0.5 M and in trifluoroacetic and deuteriotrifluoroacetic acids, 0.6 M except where these concentrations could not be attained, when saturated solutions were employed. Where nmr spectral data are given in the experimental section values refer to singlet absorptions unless otherwise stated, where the symbols have their usual meanings.

Mass spectra were recorded on an AEI MS902 instrument. "Stick" diagrams were prepared with the aid of an IBM 360/44 computer. Molecular Weights were determined by mass spectroscopy.

Thin layer chromatography (tlc) was performed on silica (MN Kieselgel G) coated plates (0.25 mm thick). Plates were eluted with benzene and, when necessary, developed with iodine. Alumina for column chromatography was Spence type H (100/200 mesh) and silica was Sorbsil Silica Gel.

Petrol refers to petroleum ether (40/60 unless otherwise stated) and ether to diethyl ether.

Acetic anhydride, methanol, ethanol, cyclohexane, n-hexane,

40/60 petrol, acetone and dimethylsulphoxide were all redistilled commercial materials.

30/40 Petrol and glacial acetic acid were of Analar grade, the former being alkene free.

Benzene, 30/40 petrol and ether were refluxed over sodium wire for 1 hour and distilled to give the dry solvents. These solvents were stored over sodium wire. Where necessary the crude solvents were predried over calcium chloride for 2 days.

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

Chloroform and methylene chloride were boiled over phosphoric anhydride for 30 minutes, distilled, then percolated through a dry-packed column of alumina (12.5 x 2.5 cm) as required.

Carbon tetrachloride was boiled over potassium hydroxide pellets for 1 hour, then distilled. Spectroscopically pure solvent was obtained as required by percolating this distillate through a dry-packed column of alumina (12.5 x 2.5 cm).

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

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

Bromine was dried over sulphuric acid and distilled.

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

Sodium acetate was dried by fusion immediately before use.

2M-Aqueous sodium hydrogen sulphide solutions were prepared by saturating 2M-aqueous sodium sulphide nonahydrate solutions with

hydrogen sulphide (ca 2 hours).

1M-Aqueous sodium hydrogen selenide solutions were prepared under nitrogen by saturating 1M-aqueous sodium hydroxide solutions with hydrogen selenide. Hydrogen selenide was prepared by dropping hydrochloric acid (5N) onto crushed aluminium selenide.

Methylfluorosulphonate ($MeSO_3F$) was redistilled commercial material and was stored in a polythene bottle.

Thiolacetic acid was redistilled commercial material.

Solutions were dried over anhydrous sodium sulphate and solvents were evaporated at reduced pressure with a rotary film evaporator.

A. Synthesis of 1,6,6a-Trithiapentalene

γ-Pyrone, b.p. 108-110°C at 18 mm Hg, was prepared[202] by the copper catalysed decarboxylation of dry chelidonic acid[201] (225 g in 25 g batches gave 56 g pure γ-pyrone).

Thionation of γ-Pyrone

A stirred mixture of γ-pyrone (24 g, 250 mmol), phosphorus pentasulphide (55.5 g, 250 mmol) and benzene (750 ml) was boiled for one hour. The benzene solution was decanted and the residual solid was extracted with a fresh portion of boiling benzene (100 ml). The extract was decanted and combined with the parent benzene solution. The residual solid was solvolysed with aqueous 0.4M-sodium sulphide (100 ml), and the resulting mixture was extracted with benzene-ether (1:1; 3 x 300 ml). The extracts were added to the parent benzene solution and the combined extracts were washed with water (x 3), dried, and concentrated to 150 ml. Petrol (150 ml) was added and the resulting solution was adsorbed on to a column of alumina (40 x 5.7 cm). Elution with petrol-benzene (1:1) gave red eluates (1.5 l) from which 1,6,6a-trithiapentalene was isolated, identical (nmr spectrum in $CDCl_3$, m.p. 112-114°, lit.[10], 112-113°) with the product of previous syntheses[10]. Continued elution with benzene-ether (9:1) brought through homogeneous (Tlc) purple eluates which yielded 4H-pyran-4-thione (13.65 g, 48%). Crystallisation from acetone-petrol (1:8) gave orange needles, m.p. 47-49° (lit.[23], 44°; lit.[218], 49°).

1-Oxa-6,6a-dithiapentalene

(i) From 4H-Pyran-4-thione

Aqueous 0.8 M-sodium sulphide (125 ml) was added to a solution of 4H-pyran-4-thione (5.610 g, 50 mmol) in dimethylsulphoxide (500 ml)

at room temperature. After 10 minutes, benzene (625 ml) was added to the deep red solution followed by aqueous M-potassium ferricyanide (300 ml) with vigorous swirling. The mixture was diluted with water (500 ml) and filtered through Celite (12 x 1 cm). The Celite was washed with hot benzene (3 x 200 ml) and the washings were added to the two-phase filtrate. The aqueous layer was extracted with benzene (3 x) and the combined extracts were washed with water (6 x), dried and the solvent was evaporated. To a solution of the residue in ether (200 ml) was added a solution of mercury(II)chloride (6.80 g, 25 mmol) in ether (400 ml). 4-Chloromercurithiopyrylium chloride (10) was precipitated as a greenish black powder which was removed by filtration. The filtrate was diluted with benzene (200 ml), washed with water (9 x) (until the washings no longer gave a precipitate with aqueous sodium hydrogen sulphide), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.5 cm). Elution with benzene gave initial colourless eluates which were discarded. Continued elution with benzene gave yellow eluates (800 ml). The residual oil, after evaporation of the solvent was dissolved in benzene-petrol (1:1) and adsorbed on a column of alumina (20 x 2.5 cm). Elution with the same solvent mixture gave colourless-pale yellow eluates (800 ml) which were discarded. Continued elution with benzene gave homogeneous (tlc) yellow eluates which on evaporation of the solvent afforded 1-oxa-6,6a-dithiapentalene (1.673 g, 23%) as a yellow oil, b.p. 115-120°, 0.5 mm Hg (lit.[9], 160-180°, 1.0 mm Hg), [ν ring C$\cdots$O, 1583 cm^{-1} (film)].

Found C 42.0; H 2.9%

$C_5H_4OS_2$ requires C 41.7; H. 2.8%

[Nmr spectrum: $CDCl_3$, 6.86 (1H, d, $J_{(3,2)}$ 1.6, 3-H), δ 7.23 (1H, d, $J_{(4,5)}$ 5.9, 4-H), δ 7.98 (1H, d, $J_{(5,4)}$ 5.9, 5-H)and δ 9.38

(1H, d, $J_{(2,3)}$ 1.6, 2-H]

[UV spectrum: Cyclohexane; λ_{max} 194, 227, 412, 428 sh (log ε 4.10, 4.20, 4.03, 3.95)]

(ii) Attempted Preparation from 4H-Pyran-4-thione

To a solution of 4H-pyran-4-thione (1.122 g, 10 mmol) in acetonitrile (30 ml) was added a solution of thallium(III)trifluoroacetate (5.97 g, 11 mmol) in acetonitrile (30 ml). After 1 minute aqueous 2M sodium hydrogen sulphide (10 ml) was added and the resulting mixture was extracted with ether (3 x). The combined extracts were washed with water (3 x), dried and evaporated. The residue was chromatographed on alumina (15 x 2.2 cm) using benzene for adsorption and elution. Red eluates were collected and afforded only starting material (553 mg, 49%). 1-Oxa-6,6a-dithiapentalene was not detected.

(iii) Attempted Preparation from 4H-thiopyran-4-thione

To a solution of 4H-thiopyran-4-thione (1.280 g, 10 mmol) in acetonitrile (30 ml) was added a solution of thallium(III)trifluoroacetate (5.97 g, 11 mmol) in acetonitrile (30 ml). After 1 minute aqueous M sodium hydroxide (20 ml) was added and the resulting mixture was extracted with ether (3 x). The combined extracts were washed with water (3 x), dried and evaporated. The residue was chromatographed on alumina (15 x 2.2 cm) using benzene for adsorption and elution. Pale mauve dichroic eluates were collected and afforded only starting material (63 mg, 4.9%). 1-Oxa-6,6a-dithiapentalene was not detected.

(iv) Attempted Preparation from 4-Chloromercurithiopyrylium Chloride

To a suspension of 4-chloromercurithiopyrylium chloride (3.837 g, 10 mmol) in acetonitrile (30 ml) was added aqueous 2M sodium hydrogen

sulphide. A black precipitate appeared instantaneously and after 1 minute the mixture was diluted with water and extracted with ether (3 x). The combined extracts were washed with water (3 x), dried and evaporated. The residue was chromatographed on alumina (5 x 2.2 cm) using benzene for adsorption and elution. Red eluates were collected and afforded 4H-pyran-4-thione only (955 mg, 85 %).

1,6,6a-Trithiapentalene

(i) Directly from 4H-pyran-4-thione

Aqueous 0.8M-sodium sulphide (250 ml) was added to a solution of 4H-pyran-4-thione (11.215 g, 100 mmol) in dimethylsulphoxide (1 l) at room temperature. After 10 minutes benzene (1.25 l) was added to the deep red solution, followed by aqueous M-potassium ferricyanide (600 ml) with vigorous swirling. The mixture was diluted with water (1 l) and filtered through Celite (12 x 1 cm). The Celite was washed with hot benzene (3 x 200 ml) and the washings were added to the two-phase filtrate. The aqueous layer was extracted with benzene-ether (9:1, 5 x 500 ml) and the extracts were added to the orange benzene layer. The combined extracts were washed with water (6 x), dried and the solvent was evaporated. A stirred solution of the residue in benzene (1 l) was boiled for 1 hour with phosphorus pentasulphide (22.2 g, 100 mmol). The solution was filtered through Celite (12 x 1 cm) which was then washed with hot benzene (4 x 200 ml). The benzene filtrates were combined and the solvent was evaporated. The residual solid in petrol-benzene (2:1) (a small quantity of material remained undissolved) was adsorbed on a column of alumina (70 x 3.8 cm). Elution with petrol-benzene (3:1) gave colourless sulphur containing eluates (2 l) which were discarded. When red eluates appeared,

elution was continued with benzene and in this manner red eluates were collected (1.5 l). After evaporation of the solvent the residue was rechromatographed in the same manner. Evaporation of the solvent from the final red eluates and recrystallisation from cyclohexane gave 1,6,6a-trithiapentalene (3.901 g, 24%) as red plates, m.p. 113-114° (lit.[10], 112-113°) identical (nmr spectrum in $CDCl_3$) to the product of a previous synthesis[10].

(ii) From 1-Oxa-6,6a-dithiapentalene

A stirred solution of 1-oxa-6,6a-dithiapentalene (1.44 g, 10 mmol) in benzene (100 ml) was boiled for 1 hour with phosphorus pentasulphide (2.22 g, 10 mmol). The solution was filtered through Celite (7.5 x 1 cm) which was then washed with benzene. The combined benzene filtrates were evaporated. Subsequent purification (2 chromatograms; 60 x 2.5 cm) as in the preceding experiment gave 1,6,6a-trithiapentalene (921 mg, 58%).

(iii) Attempted Preparation from 4H-thiopyran-4-thione

To a solution of 4H-thiopyran-4-thione (1.280 g, 10 mmol) in acetonitrile (30 ml) was added a solution of thallium(III)trifluoroacetate (5.97 g, 11 mmol). After 1 minute aqueous 2M sodium hydrogen sulphide (10 ml) was added and the resulting mixture was extracted with ether (3 x). The combined extracts were washed with water (3 x), dried and evaporated. The residue was chromatographed on alumina (15 x 2.2 cm) using benzene for adsorption and elution. Purple dichroic eluates were obtained and afforded only starting material (344 mg, 27%). No 1,6,6a-trithiapentalene was detected.

B. Synthesis of 1,6-Dioxa-6a-thiapentalenes

Thallium(III)nitrate[219] and thallium(III)trifluoroacetate[220] were prepared as in the references cited.

2-Phenylpyrone was prepared and thionated by the method of Pfister-Guillouzo and Lozac'h[23].

2,6-Dimethylpyrone

The following is an adaptation of the method of Pfister-Guilllouzo and Lozac'h[23].

Dehydroacetic acid (100 g, 600 mmol) was boiled in concentrated hydrochloric acid (500 ml) till evolution of carbon dioxide ceased (ca 30 min). The resulting yellow solution was cooled and the acid was evaporated. The residue was dissolved in water (200 ml), neutralised with sodium hydrogen carbonate, and extracted with chloroform (4 x). The extracts were dried and the solvent was evaporated. The residual solid was recrystallised from ethanol to give 2,6-dimethylpyrone (54.58 g, 73%) as colourless spars, m.p. 132-133° (lit.[23], 132°).

2,6-Dimethyl-4H-pyran-4-thione

2,6-Dimethylpyrone has been thionated previously[23] but experimental details are lacking.

A stirred solution of 2,6-dimethylpyrone (18.6 g, 150 mmol) in benzene (500 ml) was boiled for 1 hour with phosphorus pentasulphide (33.3 g, 150 mmol). The mixture was cooled, the red solution was decanted, and the residue was decomposed with water. The aqueous mixture was extracted with benzene (3 x). The red benzene solution was added to the extracts and the combined solution was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on

a column of alumina (15 x 3.8 cm). Red benzene eluates (2 l) were collected, found to be homogeneous (tlc) and the solvent was evaporated. 2,6-Dimethyl-4H-pyran-4-thione was obtained as yellow spars (14.12 g, 67%) from methanol, m.p. 145-146° (lit.[23], 145°).

Esterification of Chelidonic acid

The following is an adaptation of a method of Attenburrow and co-workers[221].

A solution of chelidonic acid (100 g) in ethanolic hydrogen chloride (5%*, 500 ml) was boiled for 3 hours. The hot solution was filtered, cooled and about 200 ml of ethanol were removed under reduced pressure (water bath < 35°). The residual solution was chilled to -20° for 12 hours. The solid which precipitated was filtered off to yield crude monoethyl chelidonate (25.4 g). The mother liquors were evaporated to dryness and the residue was dissolved in benzene. The solution was washed with water (1 x), dilute sodium carbonate (2 x) then water (3 x). The organic layer was dried and the solvent evaporated. The residue was dissolved in benzene and filtered through a column of alumina (10 x 3.8 cm). The colourless eluates were evaporated to small bulk and petrol was then added which precipitated pure colourless diethylchelidonate (41.3 g), m.p. 60-62° (lit.[221], 60-62°).

The crude monoethyl chelidonate was suspended in water (150 ml) and basified with sodium carbonate (ether prevented excess frothing). The brown aqueous solution was extracted with ether (5 x), the ether extracts being discarded. The aqueous layer was acidified (conc HCl) to precipitate the acid, which was filtered off after chilling the suspension to -20° for 1 hour. In this way pure monoethyl chelidonate was isolated as a buff coloured solid which was

dried at 100°C in vacuo (20.7 g).

* Saturated ethanolic hydrogen chloride = 21% HCl (5.85 M).

Decarboxylation of Monoethyl Chelidonate

Monoethyl chelidonate (20.7 g) was heated under vacuum to 250°. When evoluation of gas ceased a liquid distilled from the reaction vessel and solidified on cooling. The distillate was dissolved in benzene and adsorbed on a column of alumina (10 x 2.5 cm). Elution with benzene gave colourless eluates (1 l) which were evaporated to low bulk. Addition of petrol precipitated ethyl comanate (21d) as a colourless solid (12.43 g, 76%), m.p. 97-98° (lit.[221], 96-98°).

2-Carbethoxy-4H-pyran-4-thione

A stirred solution of ethyl comanate (6.72 g, 40 mmol) in benzene (150 ml) was boiled with phosphorus pentasulphide (8.9 g, 40 mmol) for 1 hour. The mixture was filtered through Celite (7 x 1 cm), and the Celite pad was washed well with benzene. The red benzene solution was washed with water (3 x) , dried and the solvent was evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.5 cm). Elution with benzene gave inhomogeneous (tlc) red eluates which after evaporation of the solvent were rechromatographed as already described. The red eluates still had trace impurities but recrystallisation of the residue, after evaporation of the solvent, gave pure 2-carbethoxy-4H-pyran-4-thione (22d) as red needles, m.p. 66-68° (lit.[218], 66-67°) (from n-hexane) (2.88 g, 39%).

[Nmr spectrum: $CDCl_3$, δ 1.39 (3H, t, J_{Et} 7.0, O-CH_2-$\underline{CH_3}$), δ 4.41 (2H, q, J_{Et} 7.0, O-$\underline{CH_2}$-CH_3), δ 7.19 (1H, dd, $J_{(6,5)}$ = 5.2, $J_{(6,3)}$= 0.5, 6-H), δ 7.56 (1H, dd, $J_{(5,6)}$5.2, $J_{(5,3)}$2.2, 5-H), and δ 7.73 (1H, dd, $J_{(3,5)}$2.1, $J_{(3,6)}$0.5, 3-H)].

2,5-Dicarbethoxy-4H-pyran-4-thione

A stirred solution of diethyl chelidonate (12.0 g, 50 mmol) in benzene (150 ml) was boiled with phosphorus pentasulphide (11.1 g, 50 mmol) for 1 hour. The crude thione was isolated by the procedure described in the previous experiment. The residue from the solution was dissolved in benzene and adsorbed on a column of alumina (25 x 2.5 cm). Elution with benzene gave homogeneous (tlc) green eluates which afforded 2,5-dicarbethoxy-4H-pyran-4-thione (22e) as green needles, m.p. 51-52° (lit.[222], 51°) (from petrol) (9.50 g, 74%).

[Nmr spectrum: $CDCl_3$,) 1.45 (6H, t J_{Et} 7.1, O-CH_2-$\underline{CH_3}$), δ4.49 (4H, q, J_{Et} 7.1, O-$\underline{CH_2}CH_3$), δ 7.81 (2H, 3,5-H)].

1,6-Dioxa-6a-thiapentalene

Several methods were investigated and details are given for each.

(i) To a solution of 4H-pyran-4-thione (11.215 g, 100 mmol) in acetonitrile (300 ml) was added a solution of thallium(III)trifluoroacetate (59.7 g, 110 mmol) in acetonitrile (300 ml). After 1 minute water (500 ml) was added and the resulting mixture was extracted with ether (4 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 3.8 cm). Elution with benzene gave impure eluates from which the solvent was evaporated. The residue was dissolved in petrol-benzene (1:1) and adsorbed on a column of alumina (50 x 2.8 cm). Elution with the same solvent mixture gave homogeneous (tlc) colourless eluates (2 l) which afforded a colourless solid (7.804 g, 61%). 1,6-Dioxa-6a-thiapentalene (17a) formed colourless spars, m.p. 61-62.5°, [from petrol (40/50)], b.p. 80-85° at 18 mm (block temperature)

Found C 46.7; H 3.00; S 25.0%

$C_5H_4O_2S$ requires C 46.9; H 3.14; S 25.0%

Molecular Weight: Found 127.9931

$C_5H_4O_2S$ requires 127.9932

(ii) The reaction was performed as in the preceding experiment (i) but with aqueous M-sodium hydroxide (500 ml) in place of the water for hydrolysis. The crude product was dissolved in benzene and adsorbed on a column of alumina (10 x 3.8 cm). Elution with benzene gave colourless, homogeneous (tlc) eluates (1.5 l) which afforded 1,6-dioxa-6a-thiapentalene (17a) (7.188 g, 56%).

(iii) To a solution of 4H-pyran-4-thione (1.120 g, 10 mmol) in acetonitrile (20 ml) was added a solution of thallium(III)nitrate (5.55 g, 12.5 mmol) in acetonitrile (20 ml). After 1 minute aqueous M-sodium hydroxide (50 ml) was added and the resulting mixture was extracted with benzene (3 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and chromatographed on a column of alumina (10 x 2.5 cm) as described in the preceding experiment (ii). The colourless, homogeneous (tlc) eluates afforded 1,6-dioxa-6a-thiapentalene (17a) (443 mg, 35%).

(iv) To a solution of 4H-pyran-4-thione (1.120 g, 10 mmol) in acetonitrile (30 ml) was added a solution of lead(IV)acetate (5.32 g, 12 mmol) in methylene chloride (30 ml). After 1 minute water (50 ml) was added and the resulting mixture was extracted with ether (3 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and chromatographed on a column of alumina (15 x 2.2 cm). The colourless homogeneous (tlc) eluates afforded 1,6-dioxa-6a-thiapentalene (17a) (16 mg, 1.3%).

(v) The preceding reaction was repeated with lead(IV) trifluoroacetate solution (42 ml, 12 mmol), in place of the lead(IV)acetate solution. Chromatography on alumina (15 x 2.2 cm) as previously described afforded 1,6-dioxa-6a-thiapentalene (17a) (99mg, 7.6%).

(vi) Aqueous M-sodium hydroxide (20 ml) was added to a solution of 4H-pyran-4-thione (1.120 g, 10 mmol) in dimethylsulphoxide (100 ml) at room temperature. After 10 minutes benzene (125 ml) was added to the purple brown solution followed by aqueous M-potassium ferricyanide (60 ml). The mixture was diluted with water and extracted with benzene (3 x). The extract was washed with water (6 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (15 x 2.2 cm). Elution with benzene gave colourless homogeneous (tlc) eluates which afforded 1,6-dioxa-6a-thiapentalene (17a) (30 mg, 2.3%).

(vii) A suspension of 4-chloromercurithiopyrylium chloride (10) (3.837 g, 10 mmol) in acetonitrile (30 ml) was treated with aqueous M-sodium hydroxide (20 ml). A black precipitate appeared instantly and after 1 minute the mixture was extracted with ether (3 x). The extract was washed with water (3 x), dried and the solvent evaporated to leave no residue. The reaction was abandoned.

Attempted Preparation of 1-Methyl-1-oxa-6a-thia-2-azapentalene

To a solution of 4H-pyran-4-thione (1.122 g, 10 mmol) in acetonitrile (30 ml) was added a solution of thallium(III)trifluoroacetate (5.97 g, 11 mmol) in acetonitrile (30 ml). After 1 minute aqueous methylamine solution (25 ml) was added and the resulting mixture was extracted with ether (3 x). The combined extracts

were washed with water (3 x), dried and evaporated. The residue was chromatographed on alumina (15 x 2.2 cm) using benzene for adsorption and elution. From the colourless eluates only 1,6-dioxa-6a-thiapentalene was isolated (614 mg, 48%).

The reaction was repeated with molecular sieves in the solutions prior to the addition of the methylamine to prevent hydrolysis of the reactive intermediate. Again only 1,6-dioxa-6a-thiapentalene was isolated but in reduced yield (44 mg, 3.4%).

2,5-Dimethyl-1,6-dioxa-6a-thiapentalene

(i) To a solution of 2,6-dimethyl-4H-pyran-4-thione (14.013 g, 100 mmol)in acetonitrile (300 ml) was added a solution of thallium(III)trifluoroacetate (59.7 g, 110 mmol) in acetonitrile (300 ml). After 1 minute water (500 ml) was added and the resulting mixture was shaken with ether and filtered through Celite (9 x 1 cm). The Celite was washed well with ether and the washings were added to the two-phase filtrate. The aqueous layer was extracted with ether (4 x) and the combined extracts were washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 3.8 cm). Dark eluates were collected which, after evaporation of the solvent, were rechromatographed on alumina (20 x 2.5 cm) with petrol-benzene (1:1) for adsorption. Elution with petrol-benzene (1:1) gave colourless homogeneous (tlc) eluates which afforded a colourless solid (1.148 g, 7.4%). 2,5-Dimethyl-1,6-dioxa-6a-thiapentalene (17b) formed colourless spars, m.p. 70-71° (from petrol).

Found C 53.7; H 5.06%

$C_7H_8O_2S$ requires C 53.8; H 5.16%

Molecular Weight: Found 156.0250

$C_7H_8O_2S$ requires 156.0245

(ii) The reaction was performed as in the preceding experiment (i) but with aqueous M-sodium hydroxide (500 ml) in place of the water for hydrolysis. The crude product was dissolved in benzene and adsorbed on a column of alumina (10 x 3.8 cm). Elution with benzene gave colourless homogeneous (tlc) eluates which afforded 2,6-dimethyl-1,6-dioxa-6a-thiapentalene (17b) (1.365 g, 8.7%).

2-Phenyl-1,6-dioxa-6a-thiapentalene

To a solution of 2-phenyl-4H-pyran-4-thione (3.765 g, 20 mmol) in acetonitrile (60 ml) was added a solution of thallium(III)trifluoroacetate (11.94 g, 22 mmol) in acetonitrile (60 ml). After 1 minute aqueous M-sodium hydroxide was added and the resulting mixture was extracted with ether (4 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.5 cm). Elution with benzene gave yellow eluates (400 ml) from which the solvent was evaporated. The residue was dissolved in petrol-benzene (1:1) and adsorbed on a column of alumina (40 x 2.2 cm). Elution with petrol-benzene (1:1) gave homogeneous (tlc) pale yellow eluates which on evaporation afforded the product (1.996 g, 49%). 2-Phenyl-1,6-dioxa-6a-thiapentalene (17c) formed pale yellow spars, m.p. 97-98° (from n-hexane).

Found C 64.6; H 3.83 %

$C_{11}H_8O_2S$ requires C 64.7; H 3.95 %

Molecular Weight: Found 204.0240

$C_{11}H_8O_2S$ requires 204.0245

2-Carbethoxy-1,6-dioxa-6a-thiapentalene

To a solution of 2-carbethoxy-4H-pyran-4-thione (1.842 g, 10 mmol) in acetonitrile (30 ml) was added a solution of

thallium(III)trifluoroacetate (5.97g, 11 mmol) in acetonitrile (30 ml). After 1 minute water (50 ml) was added and the crude dioxathiapentalene was isolated by extraction as in the preceding experiment. The crude product was dissolved in benzene and adsorbed on a column of Woëlm alumina (Activity 1) (5 x 2.5 cm). The column was eluted rapidly with benzene-ether (4:1). Homogeneous (tlc) yellow eluates were collected and these afforded the product (1.726 g, 86%). 2-Carbethoxy-1,6-dioxa-6a-thiapentalene (17d) formed pale yellow spars, m.p. 43-44° (from petrol, 40/50, after chilling to -20° for 12 hours).

Found C 47.7; H 4.06%

$C_8H_8O_4S$ requires C 48.0; H 4.03%

Molecular Weight: Found 200.0144

$C_8H_8O_4S$ requires 200.0143

2,5-Dicarbethoxy-1,6-dioxa-6a-thiapentalene

(i) This compound was prepared by the method described in the preceding experiment from 2,6-dicarbethoxy-4H-pyran-4-thione (1.646 g, 61%).

2,5-Dicarbethoxy-1,6-dioxa-6a-thiapentalene (17e) formed pale yellow needles, m.p. 97-98.5° (from methanol).

Found C 48.3; H 4.35%

$C_{11}H_{12}O_6S$ requires C 48.5; H 4.44%

Molecular Weight Found 272.0358

$C_{11}H_{12}O_6S$ requires 272.0355.

(ii) With aqueous M-sodium hydroxide in place of the water for hydrolysis in the preceding experiment (i) the yield of 2,5-dicarbethoxy-1,6-dioxa-6a-thiapentalene (17e) was lowered (573 mg, 21%).

C. Reactions of 1,6-Dioxa-6a-thiapentalenes

Halogenation of 1,6-Dioxa-6a-thiapentalene

(i) Bromination

To a solution of 1,6-dioxa-6a-thiapentalene (641 mg, 5 mmol) in carbon tetrachloride (10 ml) was added a 5M solution of bromine in carbon tetrachloride (2 ml, 10 mmol). Hydrogen bromide was seen to stream from the solution and after 5 minutes, benzene (75 ml), then solid sodium carbonate were added. After filtration and evaporation of the solvent the residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.2 cm). Elution with benzene gave homogeneous (tlc) pale yellow eluates (500 ml) which afforded the product (1.134 g, 79%). 3,4-Dibromo-1,6-dioxa-6a-thiapentalene (44) formed pale yellow needles, m.p.133-135^{o} (from petrol).

Found C 21.0; H 0.63%

$C_5H_2Br_2O_2S$ requires C 21.0; H 0.71%.

Molecular Weight: Found 285.8114

$C_5H_2Br_2O_2S$ requires 285.8122

(ii) Iodination

a) With Excess Iodine

To a solution of 1,6-dioxa-6a-thiapentalene (641 mg, 5 mmol) and iodine (5.080 g, 20 mmol) in methylene chloride (200 ml) was added silver acetate (3.565 g, 22 mmol). The mixture was stirred for 1 hour before being poured into water, 200 ml, and extracted with ether (3 x). The extract was washed with water (3 x), dilute aqueous sodium thiosulphate (1 x) and water (3 x) before being dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.2 cm). Elution with benzene gave homogeneous (tlc) pale yellow eluates

(400 ml) which afforded the product (1.128 g, 59%). 3,4-Diiodo-1,6-dioxa-6a-thiapentalene (46) formed pale yellow spars, m.p. 153-156° (from n-hexane).

Found C 15.9; H 0.45%

$C_5H_2I_2O_2S$ requires C 15.8; H 0.53%

Molecular Weight: Found 379.7864

$C_5H_2I_2O_2S$ requires 379.7865

b) With 1 Equivalent of Iodine

To a solution of 1,6-dioxa-6a-thiapentalene (641 mg, 5 mmol) and iodine (1.270 g, 5 mmol) in methylene chloride (50 ml) was added silver acetate (891 mg, 5.5 mmol). The mixture was stirred for 15 minutes before being poured into water and extracted with ether (3 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.2 cm). Elution with benzene gave inhomogeneous (tlc) pale yellow eluates (400 ml) which afforded the crude product on evaporation of the solvent (1.249 g). Recrystallisation gave pure (tlc) 3-iodo-1,6-dioxa-6a-thiapentalene (47) as pale yellow spars, m.p. 74-75° (from n-hexane in 2 crops) (932 mg, 73%).

Found C 23.8; H 1.14%

$C_5H_3IO_2S$ requires C 23.6; H 1.19%

Molecular Weight: Found 253.8894

$C_5H_3IO_2S$ requires 253.8899

(iii) Attempted Cyanogenation

Silver acetate (713 mg, 4.4 mmol) was suspended in a solution of 1,6-dioxa-6a-thiapentalene (128 mg, 1 mmol) in methylene chloride (20 ml). Cyanogen gas was bubbled through the mixture for 15

minutes. The mixture was poured into water and extracted with ether (3 x). The combined extracts were washed successively with water, dilute sodium thiosulphate solution and water before being dried and evaporated. Starting material was recovered as the only product of the residue (103 mg, 80%).

With silver trifluoroacetate (884 mg, 4 mmol) in place of the silver acetate a similar result was obtained (Recovered starting material 100 mg, 78%).

(iv) Attempted Cyanogenation

Silver acetate (713 mg, 4.4 mmol) was added to a stirred solution of 1,6-dioxa-6a-thiapentalene (128 mg, 1 mmol) in methylene chloride (20 ml). A 0.5 M methylene chloride solution (4 ml) of cyanogen bromide was then added. After 1 hour the mixture was poured into water and worked up as in the preceding experiment. Only starting material was isolated (125 mg, 98%).

(v) Attempted Thiocyanogenation

Silver trifluoroacetate (884 mg, 4 mmol) was added to a stirred solution of 1,6-dioxa-6a-thiapentalene (128 mg, 1 mmol) in a 0.06 M acetic acid solution of thiocyanogen. After being stirred for 12 hours the mixture was poured into water and extracted with benzene (3 x). The combined extracts were washed successively with water (3 x), dilute sodium thiosulphate and water before being dried and evaporated. Starting material was recovered (95 mg, 74%).

Attempted Acylations of 1,6-Dioxa-6a-thiapentalene

(i) Vilsmeier Formylation

A solution of phosphoryl chloride (0.2 ml, 2.2 mmol) in dimethylformamide (2 ml) was added dropwise over 15 minutes to a

stirred solution of 1,6-dioxa-6a-thiapentalene (256 mg, 2 mmol) in dimethylformamide (2 ml). The reaction mixture was stirred for a further 45 minutes before being poured into 2M-aqueous sodium hydroxide (10 ml) and extracted with ether (3 x). The extract was washed with water (6 x), dried and the solvent evaporated. No residue was detected.

(ii) Acetylation

a) A solution of 1,6-dioxa-6a-thiapentalene (256 mg, 2 mmol) in acetic anhydride (10 ml) was boiled for 1 hour with sodium acetate (328 mg, 4 mmol). The cooled mixture was poured into water (100 ml) and left for 12 hours before being extracted with ether. The extract was washed successively with water, saturated sodium bicarbonate solution and water before being dried. Evaporation of the solvent returned 1,6-dioxa-6a-thiapentalene (195 mg, 76%).

b) To a stirred solution of 1,6-dioxa-6a-thiapentalene (256 mg, 2 mmol) and acetyl chloride (0.16 ml, 2.2 mmol) in benzene (5 ml) was added a solution of Stannic chloride in benzene (5 ml). After 1 hour the mixture was poured into water and extracted with ether. The colourless extract was washed with water (3 x), dried and the solvent evaporated to afford only starting material (9 mg, 3.5%).

(iii) Trifluoroacetylation

A solution of 1,6-dioxa-6a-thiapentalene (256 mg, 2 mmol), trifluoroacetic anhydride (463 mg, 2.2 mmol) and triethylamine (0.31 ml, 2.2 mmol) in methylene chloride (20 ml) was boiled for 12 hours. The mixture was poured into water and extracted with ether (3 x). The extract was dried and the solvent evaporated to afford starting material only (162 mg, 62%).

Attempted Nitrations of 1,6-Dioxa-6a-thiapentalene

(i) To a solution of 1,6-dioxa-6a-thiapentalene (128 mg, 1 mmol) in acetic anhydride (10 ml) was added nitric acid (0.08 ml). After 10 minutes the solution was poured into water and left for 1 hour before being extracted with ether (3 x). The extract was washed successively with water, saturated sodium bicarbonate solution and water, before being dried and the solvent evaporated. No weighable residue was left.

(ii) The preceding reaction was repeated using a less acidic reagent, "nitronium acetate" solution (from copper nitrate and acetic anhydride[223]) (0.66 ml, 11 mmol) in place of nitric acid. No product was isolated.

(iii) To a solution of 1,6-dioxa-6a-thiapentalene (128 mg, 1 mmol) and pyridine (0.5 ml) in ethanol (5 ml) was added a solution of tetranitromethane (392 mg, 2 mmol). After 30 minutes at room temperature the dark green mixture was poured into water and extracted with ether (3 x). The extract was washed with water (6 x), dried and the solvent evaporated. The residue in benzene was chromatographed on a column of alumina (10 x 2.2 cm) and only 1,6-dioxa-6a-thiapentalene was isolated (102 mg, 80%).

(iv) To a stirred solution of 1,6-dioxa-6a-thiapentalene (128 mg, 1 mmol) in methylene chloride (20 ml) was added calcium carbonate (2 g) then nitronium fluoroborate (399 mg, 3 mmol). After 1 hour the mixture was poured into water and extracted with ether (3 x). The extract was dried and the solvent evaporated to afford 1,6-dioxa-6a-thiapentalene only (43 mg, 34%).

Nitrosation of 1,6-Dioxa-6a-thiapentalene

To a stirred solution of 1,6-dioxa-6a-thiapentalene (641 mg,

5 mmol) in methylene chloride (100 ml) was added calcium carbonate (10 g) followed by nitrosyl hexafluorophosphate (2.640 g, 15 mmol). After 30 minutes the mixture was poured into water and extracted with ether (3 x). The extract was washed successively with water, dilute sodium carbonate solution and water (2 x) before being dried and the solvent evaporated. The residue was sublimed to give 3-formyl-1,6-dioxa-6a-thia-2-azapentalene (51) as pale yellow spars, m.p. 43-46° (724 mg, 92%) (Block temperature 100-105°C, 15 mm Hg) ($\nu_{C=O}$, 1715 cm^{-1}, CCl_4).

Found C 38.4; H 1.88; N 9.20%

$C_5H_3O_3SN$ requires C 38.2; H 1.97; N 8.91%

Molecular Weight: Found 156.9831

$C_5H_3O_3SN$ requires 156.9834

Tritylation of 1,6-Dioxa-6a-thiapentalene

To a stirred solution of 1,6-dioxa-6a-thiapentalene (641 mg, 5 mmol) in methylene chloride (250 ml) was added calcium carbonate (20 g) then trityl perchlorate (8.575 g, 25 mmol). The mixture was stirred for 21 hours at room temperature before being poured into water and extracted with ether (3 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in petrol-benzene (1:1) and adsorbed on a column of alumina (50 x 2.2 cm). Fractions (150 ml) were collected and fractions 4-6 were found to contain the product (tlc). Evaporation of the solvent afforded a colourless solid (1.749 g, 94%). 3-Trityl-1,6-dioxa-6a-thiapentalene (52) which formed colourless microneedles m.p. 201-203° (from benzene-cyclohexane, 1:1).

Found C 78.0; H 4.91%

$C_{24}H_{18}O_2S$ requires C 77.8; H 4.90%.

Diazo Coupling of 1,6-Dioxa-6a-thiapentalene

To a stirred solution of 1,6-dioxa-6a-thiapentalene (641 mg, 5 mmol) in acetonitrile (50 ml) was added p-nitrobenzenediazonium fluoroborate[224] (3.55 g, 15 mmol). After 1 hour the orange mixture was poured into water and extracted with benzene (3 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (20 x 2.2 cm). Elution with benzene gave colourless homogeneous (tlc) eluates which afforded starting material (474 mg, 74%). Elution with ether gave orange homogenous (tlc) eluates which on evaporation of the solvent yielded an orange solid (98 mg, 7.1%; 24 % conversion). 3-Formyl-6-(p-nitrophenyl)-1-oxa-6a-thia-5,6-diazapentalene (54) formed orange microneedles, m.p. 246-252° (dec.) ($\nu_{C=O}$, 1681 cm^{-1}, KBr).

Found C 47.8; H 2.44; N 14.9%.

$C_{11}H_7O_4SN_3$ requires C 47.7; H 2.54; N 15.2%.

Molecular Weight: Found 277.0163

$C_{11}H_7O_4SN_3$ requires 277.0157.

Oxymercuration of 1,6-Dioxa-6a-thiapentalene

To a solution of 1,6-dioxa-6a-thiapentalene (641 mg, 5 mmol) in acetic acid (10 ml) was added a solution of mercury(II)acetate (3.187 g, 10 mmol) in acetic acid (50 ml). A colourless precipitate appeared immediately and after 5 minutes was filtered off and washed well with acetic acid then ether. The remaining solid was dried in vacuo (3.217 g, quantitative). 3,4-bis-(acetoxymercury)-1,6-dioxa-6a-thiapentalene (55) was a colourless amorphous solid which decomposed above 190° without melting.

Found C 17.0; H 1.34%

$C_9H_8O_6SHg_2$ requires C 16.7; H 1.25%.

Deuteration of 1,6-Dioxa-6a-thiapentalenes

(i) 1,6-Dioxa-6a-thiapentalene (256 mg, 2 mmol) was dissolved in deuteriotrifluoroacetic acid (7.7 ml). After 3 minutes at room temperature a solution of sodium carbonate (6 g) in deuterium oxide (20 ml) was added and the mixture was extracted with methylene chloride (3 x). The extract was dried and evaporation of the solvent produced a colourless solid (255 mg, 98%). 3,4-Dideuterio-1,6-dioxa-6a-thiapentalene (61) formed colourless needles, m.p. 61-63° (from petrol, 40/50).

Found C 46.2%

$C_5H_2D_2O_2S$ requires C 46.1%.

Molecular Weight: Found 130.0048

$C_5H_2D_2O_2S$ requires 130.0058

(ii) 2,5-Dimethyl-1,6-dioxa-6a-thiapentalene (312 mg, 2 mmol) was treated as in the preceding experiment. The residue from the extraction was dissolved in benzene and adsorbed on a column of alumina (5 x 1.9 cm). Elution with benzene gave colourless homogeneous (tlc) eluates which on evaporation of the solvent afforded the product (119 mg, 38%). 3,4-Dideuterio-2,5-dimethyl-1,6-dioxa-6a-thiapentalene (64) formed colourless spars, m.p. 70-71° (from petrol).

Found C 53.2%

$C_7H_6D_2O_2S$ requires C 53.1%.

Molecular Weight: Found 158.0380

$C_7H_6D_2O_2S$ requires 158.0371.

Thionation of 1,6-Dioxa-6a-thiapentalene

(i) With Thiolacetic Acid

A solution of 1,6-dioxa-6a-thiapentalene (641 mg, 5 mmol) in thiolacetic acid (25 ml) was boiled for 1 hour. After cooling, the red solution was poured into water and basified with solid sodium

carbonate, before being extracted with ether (3 x). The extract was washed with water (4 x), dried and the solvent evaporated. The residue was dissolved in petrol-benzene (1:1) and adsorbed on a column of alumina (25 x 2.5 cm). Elution with the same solvent mixture gave red eluates which afforded 1,6,6a-trithiapentalene identical (nmr spectrum in $CDCl_3$) with the samples previously prepared (97 mg, 12%). Continued elution with benzene gave a pale yellow fraction which was discarded. Continued elution with benzene-ether (9:1) gave a yellow fraction from which the solvent was evaporated. The residue from this last fraction was dissolved in benzene and adsorbed on a column of alumina (25 x 2.2 cm). Elution with benzene gave pink eluates which were discarded. Elution with benzene-ether (9:1) gave yellow homogeneous (tlc) eluates which afforded 1-oxa-6,6a-dithiapentalene as a yellow oil, identical (nmr spectrum in $CDCl_3$) with the sample previously synthesised (274 mg, 38%).

(ii) With Phosphorus Pentasulphide

A stirred solution of 1,6-dioxa-6a-thiapentalene (1.282 g, 10 mmol) in benzene (200 ml) was boiled for 1 hour with phosphorus pentasulphide (4.44 g, 20 mmol). The cooled mixture was filtered through Celite (5.5 x 1 cm), the filter pad being washed well with benzene. The organic solution was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in petrol-benzene (2:1) and adsorbed on a column of alumina (70 x 2.8 cm). Elution with petrol-benzene (3:1) gave initial colourless eluates which were discarded. Continued elution with the same solvent mixture gave homogeneous (tlc) red eluates which afforded 1,6,6a-trithiapentalene identical (nmr spectrum in $CDCl_3$) with samples previously prepared (324 mg, 20%).

Secondary Reactions of 1,6-Dioxa-6a-thiapentalenes

1-Oxa-6a-thia-6-azapentalenes

The following method was used to convert halogenated 1,6-dioxa-6a-thiapentalenes into 1-oxa-6a-thia-6-azapentalenes.

Aqueous methylamine (25 ml, 30%) was added to a solution of the halogenated dioxathiapentalene (5 mmol) in acetonitrile (50 ml). The solution darkened immediately followed by the appearance of a flocculent precipitate. After 5 minutes the mixture was poured into water and extracted with ether (3 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.2 cm). Elution with benzene gave initial colourless eluates which were discarded. Continued elution with benzene-ether (9:1) gave homogeneous (tlc) pale yellow eluates which afforded the product.

3,4-Dibromo-1,6-dioxa-6a-thiapentalene (1.430 g, 5 mmol) gave 6-methyl-3,4-dibromo-1-oxa-6a-thia-6-azapentalene (83a) (1.434 g, 96%) which formed yellow needles, m.p. 138-139° (from benzene-cyclohexane).

Found C 24.1; H 1.70; N 4.65%.

$C_6H_5OSNBr_2$ requires C 24.1; H 1.69; N 4.69%.

3,4-Di-iodo-1,6-dioxa-6a-thiapentalene (1.900 g, 5 mmol) gave 6-methyl-3,4-di-iodo-1-oxa-6a-thia-6-azapentalene (83 b) (1.416 g, 72%) which formed brown spars m.p. dec. >110° (from benzene-cyclohexane).

Found C 18.4; H 1.34; N 3.66%.

$C_6H_5OSNI_2$ requires C 18.3; H 1.28; N 3.57%.

3-Iodo-1,6-dioxa-6a-thiapentalene (1.270 g, 5 mmol) gave a mixture of 6-methyl-3-iodo-1-oxa-6a-thia-6-azapentalene (85) and 6-methyl-4-iodo-1-oxa-6a-thia-6-azapentalene (86) (2:1 by nmr spectroscopy) which formed yellow needles, m.p. 104-111° (from

cyclohexane). The composition of the mixture was unchanged on repeated chromatography (alumina or silica, 50 x 2.2 cm) or repeated recrystallisation (3 x).

Found C 26.9; H 2.39; N 5.16%

C_6H_6OSNI requires C 27.0; H 2.26; N 5.24%.

Hydrolysis of 2-Carbethoxy-1,6-dioxa-6a-thiapentalene

To a solution of 2-carbethoxy-1,6-dioxa-6a-thiapentalene (400 mg, 2 mmol) in ethanol (40 ml) was added M-aqueous sodium hydroxide (10 ml) whereupon a flocculent yellow precipitate appeared. After 5 minutes the mixture was diluted with water and extracted with ether (3 x). The ether extracts were discarded and the aqueous layer was then acidified (2M HCl) and extracted with ether (3 x). The extract was dried and the solvent evaporated. The residue, 1,6-dioxa-6a-thiapentalene-2-carboxylic acid (87) formed pale yellow spars which decomposed above 180° (from water, with charcoal screening).

Found C 42.2; H 2.45%

$C_6H_4O_4S$ requires C 41.9; H 2.34%.

Molecular Weight: Found 171.9838

$C_6H_4O_4S$ requires 171.9830.

Metalation Reactions

n-Butyl-lithium was prepared in petrol (30/40) by the method of Gilman, Moore, and Baine[224].

The following reactions were performed under dry, oxygen free nitrogen.

Addition of a petrol solution of n-butyl-lithium (7.5 mmol) to a stirred solution of 3-iodo-1,6-dioxa-6a-thiapentalene (1.270 g, 5 mmol) in ether (50 ml) at -70° produced an intense green colouration, due to the unstable metalated species (88). The mixture was stirred

for 1 minute before being used in the following experiments (a fresh mixture was prepared for each reaction).

(i) Carboxylation

Carbon dioxide was bubbled through the mixture for 5 minutes. The mixture was allowed to warm to room temperature before being poured into 2M-hydrochloric acid (50 ml) and extracted with ether (3 x). The extract was dried and the solvent evaporated, leaving an intractible brown tar (71 mg) which was not further investigated.

(ii) Reactions with Aldehydes

(a) Acetaldehyde

Acetaldehyde (1.5 ml) was added rapidly to the mixture. After 5 minutes the mixture was allowed to warm to room temperature and was poured into water and extracted with ether (3 x). The extract was dried and the solvent evaporated leaving an insoluble brown residue (24 mg).

(b) Benzaldehyde

The reaction was performed in the same manner as the preceding reaction with benzaldehyde (0.80 ml, 17.5 mmol) in place of acetaldehyde. The residue from the extraction, an oil (122 mg) showed the presence of 5 compounds (tlc, silica, ether) and an attempt was made to distil the oil. No material had appeared before 200^{o} was reached (Block temperature, 0.5 mm Hg) and the sample had blackened. The reaction was abandoned.

(iii) Ethyl Formate

Ethyl formate (5 ml) was added to the reaction mixture. After 5 minutes work-up as in (iib) gave no residue from the extraction.

(iv) Dimethylformamide

To a solution of the anion, prepared as described, was added a solution of dimethylformamide (5 ml) in ether (50 ml). After 5 minutes the reaction mixture was allowed to warm to room temperature and was poured into water and extracted with ether (3 x). The extract was washed with water (6 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (15 x 2.2 cm). Elution with benzene (200 ml), benzene-ether (1:1, 200 ml) and ether (200 ml) gave colourless homogeneous (tlc) eluates which afforded 3-formyl-1,6-dioxa-6a-thiapentalene (89) (54 mg, 6.9%) which formed straw-coloured needles, m.p. 98-100° (from n-hexane) ($\nu_{C=O}$, 1688 cm^{-1}, CCl_4).

Found C 46.1; H 2.46%.

$C_6H_4O_3S$ requires C 46.1; H 2.58%.

Molecular Weight: Found 155.9873

$C_6H_4O_3S$ requires 155.9881.

The reaction was repeated using phosphoryl chloride (2 ml) in dimethylformamide (20 ml) in place of the dimethylformamide in ether. 3-Formyl-1,6-dioxa-6a-thiapentalene (89) was obtained in similar yield (43 mg, 5.5%), identical (nmr spectrum in $CDCl_3$) to that already prepared.

D. Synthesis of 1,6-Dioxa-6a-Selenapentalenes

(i) Methylation of γ-Pyrones

γ-Pyrone

To a solution of γ-pyrone (9.61 g, 100 mmol) in methylene chloride (200 ml) was added methyl fluorosulphonate (8.8 ml, 110 mmol). A colourless oil separated after 5 minutes and at the end of 1 hour the oil was seeded by "scratching" and crystallised. Excess ether was added and the colourless solid was filtered off, washed well with ether, and dried in vacuo (14.436 g, 69%). 4-Methoxypyrylium fluorosulphonate (100) was a hygroscopic amorphous powder, m.p. 26-30°, for which satisfactory analytical data was not obtained. The corresponding fluoroborate was an oil and the perchlorate (m.p. 77-78°) was explosive.

[Nmr spectrum: TFA, δ 4.44 (3H, 4-OMe), δ 7.67 (2H, m. 3(5)-H), δ 9.06 (2H, m, 2(6)-H)]

2,6-Dimethylpyrone

To a solution of 2,6-dimethylpyrone (12.41 g, 100 mmol) in methylene chloride (200 ml) was added methylfluorosulphonate (8.8 ml, 110 mmol). Colourless crystals separated after 5 minutes and at the end of 1 hour excess ether was added. The solid was filtered off and washed well with ether before being dried in vacuo (23.402 g, 98%). 2,6-Dimethyl-4-methoxypyrylium fluorosulphonate (96, $\bar{X}$ = SO_3F^-) formed colourless micro-prisms, m.p. 123-129° (from methanol with addition of ether).

Found C 40.3; H 4.87%.

$C_8H_{11}FO_5S$ requires C 40.3; H 4.65%.

[Nmr spectrum: TFA, δ 2.77 (6H, 2(6)-Me), δ 4.18 (3H, 4-OMe), δ 7.20 (2H, 3(5)-H)]

(ii) Preparation of 4H-pyran-4-selenoketones

4H-Pyran-4-selenoketone

To an ice-cold solution of 4-methoxypyrylium fluorosulphonate (4.204 g, 20 mmol) in water (40 ml) was added M-aqueous sodium hydrogen selenide (40 ml). After standing at 0^{o} for 2 hours the blue precipitate was filtered off, washed well with water, and dried in vacuo. Five such concurrent experiments produced 4H-pyran-4-selenoketone (101) as blue needles, contaminated with elemental selenium (5.141 g, 32%). Recrystallisation was not practicable due to the compounds instability and, due to the contamination with selenium, neither analytical data nor melting point would be meaningful.

[Nmr spectrum: $CDCl_3$, δ 7.46 (m, 3(5)-H), δ 7.58 (m, 2(6)-H)]

2,6-Dimethyl-4H-pyran-4-selenoketone

To an ice cold solution of 2,6-dimethyl-4-methoxypyrylium fluorosulphonate (23.82 g, 100 mmol) in water (200 ml) was added M-aqueous sodium hydrogen selenide (200 ml). After standing at 0^{o} for 2 hours the red crystalline precipitate was filtered off, washed well with water and dried in vacuo. 2,6-Dimethyl-4H-pyran-4-selenoketone (94) was thus obtained as red needles and was not further purified before use (12.54 g, 67%) (m.p. 137-138^{o}; lit.[70] 137-138^{o}).

[Nmr spectrum: $CDCl_3$, δ 2.07m (6H, 2(6)-Me), δ 7.22 m (2H, 3(5)-H)]

This method is essentially that of Traverso[70] who prepared the selenoketone from 2,6-dimethyl-4-methoxypyrylium perchlorate.

(iii) Preparation of 1,6-Dioxa-6a-selenapentalenes

1,6-Dioxa-6a-selenapentalene

To a solution of 4H-pyran-4-selenoketone (3.98 g, 25 mmol) in acetonitrile (75 ml) was added a solution of TTFA (14.92 g, 27.5 mmol) in acetonitrile (75 ml). After 1 minute the mixture was diluted with water (125 ml) and extracted with ether (4 x). The extract was washed with water (3 x), dried, and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina(20 x 2.2 cm). Elution with benzene gave pale yellow eluates, from which the solvent was evaporated. The residue was sublimed to yield 1,6-dioxa-6a-selenapentalene (103) as colourless crystals, m.p. 43-44° (646 mg, 15%).

Found C 34.2; H 2.27; Se 44.8%.

$C_5H_4O_2Se$ requires C 34.3; H 2.30; Se 45.1%

Molecular Weight: Found 175.9373

$C_5H_4O_2Se$ requires 175.9377

2,5-Dimethyl-1,6-Dioxa-6a-selenapentalene

To a solution of 2,6-dimethyl-4H-pyran-4-selenoketone (18.71 g, 100 mmol) in acetonitrile (300 ml) was added a solution of TTFA (59.7 g, 110 mmol) in acetonitrile (300 ml). After 1 minute the mixture was diluted with water (500 ml) and extracted with ether (3 x). The extract was washed with water (3 x), dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (15 x 3.8 cm). Elution with benzene gave yellow eluates from which the solvent was evaporated. The residue was dissolved in petrol-benzene (1:1) and adsorbed on a column of alumina (25 x 2.2 cm). Pale yellow eluates were collected (300 ml) and after evaporation of the solvent the residue was rechromatographed on a column of alumina (50 x 2.2 cm) using petrol-benzene (3:1) for adsorption and elution. Pale

yellow eluates were collected (400 ml) and the residue after evaporation of the solvent was sublimed on to a "coldfinger" to give 2,5-dimethyl-1,6-dioxa-6a-selenapentalene (98), m.p. 55-56^{o} (391 mg, 1.9%) (Block temperature 145-150^{o}, 16 mm Hg).

Found C 41.6; H 4.03%

$C_7H_8O_2Se$ requires C 41.4; H 3.97%.

Molecular Weight: Found 203.9686

$C_7H_8O_2Se$ requires 203.9690.

E. Desulphurisation of 1-Oxa-6,6a-dithia-2-azapentalenes and Deselenisation of 1-Oxa-6,6a-diselena-2-azapentalenes

Two sets of experimental conditions were used, but the isolation procedure was identical in each.

Method A

A solution of the substrate (5 mmol) in chloroform-acetic acid (50 ml:25 ml) was boiled for 30 minutes with mercury(II)acetate (1.595 g, 5 mmol). A further portion of mercury(II)acetate (1.595 g, 5 mmol) was then added and the mixture was boiled for a further period of 1 hour. After cooling, the mixture was poured into water and extracted with benzene (3 x). The extract was washed successively with water (2 x), dilute sodium carbonate solution and water, dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (25 x 2.2 cm). Details of eluates are given in individual cases.

Method B

A solution of the substrate (5 mmol) in acetic acid (50 ml) was boiled for 15 minutes with mercury(II)acetate. After cooling, the reaction mixture was worked up as in Method A.

1-Oxa-6,6a-dithia-2-azapentalene

(726 mg, 5 mmol) Method A

Elution with benzene-ether (9:1) gave starting material only (79 mg, 11%).

5-t-Butyl-1-oxa-6,6a-dithia-2-azapentalene

(1.007 g, 5 mmol) Method A

Elution with benzene-ether (9:1) gave starting material only (620 mg, 62%).

3,4-Dimethyl-1-oxa-6,6a-dithia-2-azapentalene

Method A (867 mg, 5 mmol)

Elution with benzene gave homogeneous (tlc) pale yellow eluates which afforded 3,4-dimethyl-1,6-dioxa-6a-thia-2-azapentalene (108a) (740 mg, 92%). Continued elution with benzene-ether gave orange eluates which afforded starting material (42 mg, 4.7%).

Method B (867 mg, 5 mmol)

In the same way as the preceding experiment 3,4-dimethyl-1,6-dioxa-6a-thia-2-azapentalene (108a) (648 mg, 82%) and starting material (74 mg, 8.5%) were isolated.

3,4-Dimethyl-1,6-dioxa-6a-thia-2-azapentalene (108a) formed pale yellow spars, m.p. 117-118° (from n-hexane).

Found C 46.0; H 4.59; N 9.03; S 20.2%.

$C_6H_7O_2SN$ requires C 45.7; H 4.49; N 8.91: S 20.4%.

Molecular Weight: Found 157.0200

$C_6H_7O_2SN$ requires 157.0198.

3,4-Propano-1-oxa-6,6a-dithia-2-azapentalene

Method A (926 mg, 5 mmol)

Elution with benzene gave homogeneous (tlc) pale yellow eluates which afforded 3,4-propano-1,6-dioxa-6a-thia-2-azapentalene (108b) (105 mg, 12%). Continued elution with benzene-ether (9:1) gave orange eluates which afforded starting material (278 mg, 30%).

Method B (926 mg, 5 mmol)

Elution with benzene gave pale yellow eluates which afforded 3,4-propano-1,6-dioxa-6a-thia-2-azapentalene (108b) as the only product from this reaction (499 mg, 59%).

3,4-Propano-1,6-dioxa-6a-thia-2-azapentalene (108b) formed pale yellow spars, m.p. 73-75° (from petrol).

Found C 49.9; H 4.36; N 8.34; S 18.7%.

$C_7H_7O_2SN$ requires C 49.6; H 4.17; N 8.28; S 18.9%.

Molecular Weight: Found 169.0192

$C_7H_7O_2SN$ requires 169.0198.

3,4-Dimethyl-1-oxa-6,6a-diselena-2-azapentalene

Method B but boiled for 5 minutes only (1.305 g, 5 mmol)

Elution with benzene-ether (9:1) gave homogeneous (tlc) pale yellow eluates which afforded the product (110) (911 mg, 89%). 3,4-Dimethyl-1,6-dioxa-6a-selena-2-azapentalene (110) formed small yellow plates, m.p. 126.5-127.5° (from cyclohexane).

Found C 35.4; H 3.48; N 6.65; Se 38.7%

$C_6H_7O_2SeN$ requires C 35.3; H 3.46; N 6.86; Se 38.7%.

Molecular Weight: Found 204.9634

$C_6H_7O_2SeN$ requires 204.9642.

Attempted Nitrosation of 3,4-Dimethyl-1,6-dioxa-6a-thia-2-azapentalene

To a stirred solution of 3,4-dimethyl-1,6-dioxa-6a-thia-2-azapentalene (157 mg, 1 mmol) in methylene chloride (20 ml) was added calcium carbonate (2 g) followed by nitrosyl hexafluorophosphate (528 mg, 3 mmol). After 1 hour the mixture was poured into water and extracted with benzene (3 x). The extract was dried and the solvent evaporated to leave starting material only (138 mg, 88%).

F. Thionation of 1-Oxa-6,6a-dithia-2-azapentalenes and Related Compounds

General Procedure

A stirred solution of the substrate in benzene (15 ml/mmol) was boiled for the stated time with phosphorus pentasulphide (1 mmol/mmol of substrate). The mixture was poured into water and extracted with benzene (3 x). The extract was washed with water (3 x), dried and the solvent evaporated. Further details are given in individual cases.

3,4-Dimethyl-1-oxa-6,6a-diselena-2-azapentalene (1.335 g, 5 mmol) was thionated by the general procedure (15 minutes). The residue was dissolved in benzene and adsorbed on a column of alumina (40 x 2.2 cm). Elution with benzene gave red eluates which, after evaporation of the solvent, were rechromatographed on a column of alumina (65 x 2.2 cm) with petrol-benzene (3:1) for adsorption and elution. The homogeneous (tlc) red eluates, on evaporation of the solvent, afforded a mixture of 3,4-dimethyl-1-thia-6,6a-diselena-2-azapentalene (116) (A) and 3,4-dimethyl-1,6-dithia-6a-selena-2-azapentalene (117) (B) (198 mg). Recrystallisation of the mixture from n-hexane (3 x) failed to alter the composition of the mixture. Reducing the reaction time to 5 minutes also failed to alter the composition of the mixture but lowered the yield (55 mg). The mixture formed red needles, m.p. 94-102° (from n-hexane).

Molecular Weights: (A) Found 284.8621
$C_6H_7SSe_2N$ requires 284.8630.
(B) Found 236.9177
$C_6H_7S_2SeN$ requires 236.9185

2-Phenyl-1-oxa-6,6a-diselena-2-azapentalene (315 mg, 1 mmol) was treated as in the general procedure (15 minutes). The residue

amounted to only 14 mg and by tlc showed the presence of at least six compounds. This experiment was abandoned.

3,4-Dimethyl-1-oxa-6,6a-dithia-2-azapentalene (173 mg, 1 mmol) was treated as in the general procedure (15 minutes). The residue (19 mg) as in the preceding experiment was a mixture of several compounds and the experiment was abandoned.

3,4-Dimethyl-1,6-dioxa-6a-thia-2-azapentalene (157 mg, 1 mmol) was treated as in the general procedure but using xylene (15 ml) in place of benzene (5 hours). The residue afforded starting material only (32 mg, 20%) after chromatography on alumina (15 x 2.2 cm) using benzene for adsorption and elution.

3,4-Dimethyl-1,6-dioxa-6a-selena-2-azapentalene (204 mg, 1 mmol) was treated as in the general procedure but using xylene (15 ml) in place of benzene (5 hours). The residue afforded starting material only (39 mg, 19%) after chromatography on alumina (15 x 2.2 cm) using benzene for adsorption and elution.

G. Oxidation of 1-Oxa-6,6a-dithia-2-azapentalenes

The m-chloroperoxybenzoic acid used in the following reactions was determined to be 80% peracid. The following general method was used.

To a solution of the 1-oxa-6,6a-dithia-2-azapentalene (5 mmol) in methylene chloride (50 ml) was added m-chloroperoxybenzoic acid (1.19 g, 7.5 mmol equivalents). After 30 minutes the mixture was poured into water (100 ml) and extracted with ether (3 x). The extract was washed successively with water, dilute aqueous sodium carbonate and water, dried and the solvent evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (20 x 2.2 cm). Elution with benzene gave red eluates which afforded starting material. Elution with ether-ethanol (99:1) gave bright yellow eluates which afforded 3-nitromethylene-3H-1,2-dithioles.

1-Oxa-6,6a-dithia-2-azapentalene (726 mg, 5 mmol) afforded starting material (216 mg, 30%) and 3-nitromethylene-3H-1,2-dithiole (121d) (56 mg, 7.6%) identical (nmr spectrum in $CDCl_3$) with an authentic sample.

3,4-Dimethyl-1-oxa-6,6a-dithia-2-azapentalene (867 mg, 5 mmol) afforded starting material (245 mg, 28%) and 4-methyl-3-(1-nitroethylidene)-3H-1,2-dithiole (121a) (45 mg, 4.9%) identical (nmr spectrum in $CDCl_3$[16]) with an authentic sample.

5-t-Butyl-1-oxa-6,6a-dithia-2-azapentalene (1.007 g, 5 mmol) afforded starting material (372 mg, 37%) and 5-t-butyl-3-nitromethylene-3H-1,2-dithiole (121c) (54 mg, 5.0%).

H. Synthesis of 3-Nitromethylene-3H-1,2-dithioles

3-Methyl-[14], 3-ethyl-4-methyl-[17], 3-methyl-5-t-butyl[228], 3-methyl-5-phenyl[14], 3-ethyl-5-phenyl-[14] and 4,5,6,7-tetrahydrobenzo[c][1,2]dithiolium perchlorate[16] were prepared as described in the references cited.

The following general method was used, variations being given in individual cases.

The dithiolium salt (5 mmol) was added to a solution of tetranitromethane (1.230 g, 6.25 mmol) in dimethylformamide (50 ml). The solution was swirled at 50° for 3 minutes. The solution was cooled, poured into water (200 ml) and extracted with benzene (3 x). The extract was washed with water (6 x), dried and the solvent evaporated. Details of the purification procedure are given in individual cases.

3-Nitromethylene-3H-1,2-dithiole

3-Methyl-1,2-dithiolium perchlorate (1.083 g, 5 mmol) was treated as in the general procedure and the residue was dissolved in benzene and adsorbed on a column of alumina (20 x 2.5 cm). Elution with benzene-ether (9:1) gave orange eluates which afforded 1-oxa-6,6a-dithia-2-azapentalene identical (nmr spectrum in $CDCl_3$[16]) with an authentic sample.[16] Continued elution with ether-ethanol (99:1) gave bright yellow eluates which afforded 3-nitromethylene-3H-1,2-dithiole (121d) (7 mg, 0.9%).

The reaction was repeated using ethanol in place of dimethylformamide. The residue from the extracts was dissolved in benzene and adsorbed on a column of alumina (10 x 2.5 cm). Elution with ether-ethanol (99:1) gave homogeneous (tlc) bright yellow eluates (1 l) which after evaporation of the solvent and rechromatography as described afforded 3-nitromethylene-3H-1,2-dithiole (121d) (30 mg,

3.7%). The compound formed yellow needles, m.p. 168-170° (with decomp.) (from benzene).

Found C 29.9; H 1.88; N 8.70%

$C_4H_3O_2S_2$ requires C 29.8; H 1.87; N 8.69%.

4-Methyl-3-(1-nitroethylidene)-3H-1,2-dithiole

3-Ethyl-4-methyl-1,2-dithiolium perchlorate (1.224 g, 5 mmol) underwent reaction according to the general procedure. The residue was dissolved in benzene and adsorbed on a column of alumina (15 x 2.5 cm). Elution with benzene gave homogeneous (tlc) yellow eluates (150 ml) which afforded 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene, identical (nmr spectrum in $CDCl_3$[16]) with an authentic sample (18 mg, 2.1%). Elution with ether-ethanol (99:1) gave homogeneous (tlc) bright yellow eluates (2 l) which afforded the product (718 mg, 76%). 4-Methyl-3-(1-nitroethylidene)-3H-1,2-dithiole formed orange needles, m.p. 191-193° (lit.[16], 191-192°) (from benzene) and was identical (nmr spectrum in $CDCl_3$[16]) with a previously isolated sample[16].

The reaction was repeated with refluxing ethanol (50 ml) in place of dimethylformamide and a reaction time of 5 minutes. By the chromatographic procedure described already 3,4-dimethyl-1-oxa-6,6a-dithia-2-azapentalene (13 mg, 1.5%) and 4-methyl-3-(1-nitroethylidene)-3H-1,2-dithiole (718 mg, 76%) were isolated.

5,6-Dihydro-7-nitro-4H-benzo[c][1,2]dithiole

4,5,6,7-Tetrahydrobenzo[c][1,2]dithiolium perchlorate (1.284 g, 5 mmol) underwent reaction according to the general procedure. The residue was dissolved in benzene and adsorbed on a column of alumina (15 x 2.5 cm). Elution with benzene-ether (19:1) gave yellow eluates (400 ml) which, after rechromatography in the same way, afforded 3,4-propano-1-oxa-6,6a-dithia-2-azapentalene identical

(nmr spectrum in $CDCl_3$) with an authentic sample[16]. Elution with ether-ethanol (99:1) gave bright yellow eluates (1.2 l) which, after rechromatography in the same way, afforded 5,6-dihydro-7-nitro-4H-benzo[c][1,2]dithiole (506 mg, 50%). The latter product, whose nmr spectrum (in $CDCl_3$) was identical with a previously prepared sample[16] formed orange prisms, m.p. 214-215° (lit.[16], 213.5-214.5°) (from benzene).

The reaction was repeated with refluxing ethanol (50 ml) in place of dimethylformamide and a reaction time of 5 minutes. By the chromatographic procedure described already, 3,4-propano-1-oxa-6,6a-dithia-2-azapentalene (241 mg, 26%) and 5,6-dihydro-7-nitro-4H-benzo[c][1,2] dithiole (173 mg, 17%) were isolated.

5-t-Butyl-3-nitromethylene-3H-1,2-dithiole

3-Methyl-5-t-butyl-1,2-dithiolium perchlorate (1.364 g, 5 mmol) underwent reaction according to the general procedure. The residue was dissolved in benzene and adsorbed on a column of alumina (25 x 2.5 cm). Initial pale yellow eluates (benzene, 100 ml; benzene-ether, 9:1, 150 ml) were discarded. Elution with benzene-ether (9:1) gave orange eluates which, after rechromatography on alumina (15 x 2.5 cm) in the same way as described, affored 3-nitro-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene (124a) (174 mg, 14%). This product formed red plates, m.p. 150-152° (from cyclohexane).

Found C 39.0; H 4.06; N 11.2%

$C_8H_{10}O_3S_2N_2$ requires C 39.0; H 4.09; N 11.4%.

Molecular Weight: Found 246.0137

$C_8H_{10}O_3S_2N_2$ requires 246.0133.

Continued elution with benzene-ether (1:1) on the original column gave pale yellow eluates which were discarded. Elution with ether gave yellow eluates which, after rechromatography on alumina

(15 x 2.5 cm) in the same way as described, afforded 3-nitromethylene-5-t-butyl-3H-1,2-dithiole (121c) (457 mg, 42%). This product formed yellow needles, m.p. 161-163° (from benzene-cyclohexane).

Found C 44.5; H 5.27; N 6.54%

$C_8H_{11}O_2S_2N$ requires C 44.2: H 5.10; N 6.45%.

3-Nitromethylene-5-phenyl-3H-1,2-dithiole

3-Methyl-5-phenyl-1,2-dithiolium perchlorate (1.464 g, 5 mmol) underwent reaction according to the general procedure. The residue was dissolved in benzene and adsorbed on a column of alumina (15 x 2.5 cm). Elution with benzene-ether (9:1) gave pale yellow eluates (300 ml) which were discarded. Elution with benzene-ether (9:1, 300 ml; 1:1, 200 ml) gave yellow eluates which, after evaporation of the solvent, were purified as described below. Elution with ether (400 ml) and ether-ethanol (99:1) (400 ml) gave bright yellow eluates which, after rechromatography on alumina (15 x 2.5 cm) in the same way, afforded 3-nitromethylene-5-phenyl-3H-1,2-dithiole (121e) (413 mg, 35%). This product formed yellow needles, m.p. 158-161° (from benzene).

Found C 50.8; H 3.03; N 5.61%

$C_{10}H_7O_2S_2N$ requires C 50.6; H 2.98; N 5.90%.

The residue from the benzene-ether eluates was dissolved in benzene and adsorbed on a column of silica (40 x 2.2 cm).

Initial benzene (400 ml) and benzene-ether (99:1, 400 ml) eluates were discarded. Elution with benzene ether (99:1) gave yellow eluates which, after rechromatography (40 x 2.2 cm, silica) in the same way afforded 5-phenyl-3-nitro-1-oxa-6,6a-dithia-2-aza-pentalene (124b) (103 mg, 7.7%). This product formed dark red needles, m.p. 186-188° (from cyclohexane).

Found C 45.1; H 2.47; N 10.4%

$C_{10}H_6O_3S_2N_2$ requires C 45.1; H 2.27; N 10.5%.

Molecular Weight: Found 265.9823

$C_{10}H_6O_3S_2N_2$ requires 265.9820.

Continued elution of the first silica column with benzene-ether (99:1) gave yellow eluates which, after rechromatography (silica, 40 x 2.2 cm) in the same way, afforded 5-phenyl-1-oxa-6,6a-dithia-2-azapentalene (119 mg, 11%) identical (nmr spectrum in $CDCl_3$) with an authentic sample[16].

3-(1-Nitroethylidene)-5-phenyl-3H-1,2-dithiole (with A.S. Ingram)

3-Ethyl-5-phenyl-1,2-dithiolium perchlorate (1.538 g, 5 mmol) underwent reaction according to the general procedure. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.8 cm). Elution with benzene-ether (3:2) gave homogeneous (tlc) orange eluates which afforded the product. 3-Nitroethylidene-5-phenyl-3H-1,2-dithiole (121f) formed orange needles, m.p. 171-172° (1.160 g, 93%) (from benzene-cyclohexane).

Found C 52.8; H 3.69; N 5.58%

$C_{11}H_9O_2S_2N$ requires C 52.6; H 3.61; N 5.58%.

Attempted Nitration of 5-t-Butyl-1-oxa-6,6a-dithia-2-azapentalene

5-t-Butyl-1-oxa-6,6a-dithia-2-azapentalene (201 mg, 1 mmol) was added to a solution of tetranitromethane (246 mg, 1.25 mmol) in dimethylformamide (5 ml). The solution was swirled at 50° for 3 minutes before being poured into water and extracted with benzene. The combined extracts were washed with water (6 x), dried and evaporated. The residue was chromatographed on a column of alumina (10 x 2.2 cm) using benzene for adsorption and elution. Starting material was recovered (200 mg, 99%).

I. Nitrosation of 3-Nitromethylene-3H-1,2-dithioles

General Method

Nitrosyl hexafluorophosphate (528 mg, 3 mmol) was added to a stirred solution of the "nitro" compound (1 mmol) in methylene chloride (20 ml) in which there was suspended calcium carbonate (2 g) After 1 hour the mixture was poured into water and extracted with benzene. The extract was washed with water, dried and evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (5 x 2.2 cm). Elution with benzene-ether (9:1) gave homogeneous (tlc) red eluates which afforded the product. Variations are given in individual cases.

5-t-Butyl-3-nitromethylene-3H-1,2-dithiole (217 mg, 1 mmol) gave 3-nitro-5-t-butyl-1-oxa-6,6a-dithia-2-azapentalene, identical (nmr spectrum in $CDCl_3$) with the sample previously prepared (219 mg, 89%).

5-Phenyl-3-nitromethylene-3H-1,2-dithiole (237 mg, 1 mmol) gave 3-nitro-5-phenyl-1-oxa-6,6a-dithia-2-azapentalene identical (nmr spectrum in $CDCl_3$) with the sample previously prepared (223 mg, 84%).

4-Methyl-3-(1-nitroethylidene)-3H-1,2-dithiole (189 mg, 1 mmol) underwent reaction according to the general procedure. The residue from the extract was dissolved in benzene and adsorbed on a column of alumina (25 x 2.2 cm). Elution with benzene-ether (4:1) gave pale orange eluates which were inhomogeneous (tlc) and on evaporation afforded only 12 mg of material. Elution with ether-ethanol (19:1) gave starting material (1 mg). The reaction was abandoned.

J. Methylations with Methyl Fluorosulphonate

General Method

To a solution of the substrate (5 mmol) in dry methylene chloride (25 ml) was added methyl fluorosulphonate (0.44 ml, 5.5 mmol). The solution was allowed to stand at room temperature for 1 hour, during which time a solid separated. Dry ether was then added and the precipitated solid was filtered off and washed well with ether. The resulting salts were dried in vacuo. Some of the salts were very unstable.

The following substrates were employed:

(i) 1,6,6a-Trithiapentalenes

3,4-Propano-1,6,6a-trithiapentalene (1.007 g, 5 mmol) gave 7-methylthiomethylene-4,5,6,7-tetrahydrobenzo[c][1,2]dithiolium fluorosulphonate [(133b), (134b), 1:1] as dark red microneedles m.p. 174-176° (1.460 g, 93%).

Found C 34.1; H 3.60%

$C_9H_{11}FO_3S_4$ requires C 34.4; H 3.53%.

3,4-Ethano-1,6,6a-trithiapentalene (931 mg, 5 mmol) gave 6-methylthiomethylenecyclopenta[c][1,2]dithiolium fluorosulphonate (133a) as dark red needles, which decomposed >190° without melting (1.226 g, 82%) (from acetic acid).

Found C 31.1; H 2.89%

$C_8H_9FO_3S_4$ requires C 32.0; H 3.02%.

(ii) 1-Oxa-6,6a-dithiapentalenes

Methylation of 3,4-disubstituted 1-oxa-6,6a-dithiapentalenes required a reaction time of 12 hours.

3,4-Dimethyl-1-oxa,6,6a-dithiapentalene (861 mg, 5 mmol) gave 4-methyl-3(2-methoxy-1-methylvinyl)-1,2-dithiolium fluorosulphonate (136a) as a pale yellow solid which decomposed >110° (1.047 g, 73%).

This product was very sensitive to light, air and moisture.

Found C 32.9; H 3.94%

$C_8H_{11}FO_4S_3$ requires C 33.6; H 3.87%.

3,4-Propano-1-oxa-6,6a-dithiapentalene (920 mg, 5 mmol) gave 7-methoxymethylene-4,5,6,7-tetrahydrobenzo[c][1,2]dithiolium fluorosulphonate (136b) as yellow microneedles which decomposed >90° (1.003 g, 69%). This product was very sensitive to light, air and moisture.

Found C 35.7; H 3.41 %

$C_9H_{11}FO_4S_3$ requires C 36.2; H 3.72%

5-t-Butyl-1-oxa,6,6a-dithiapentalene (1.007 g, 5 mmol) gave 5-t-butyl-3-(2-methoxyvinyl)-1,2-dithiolium fluorosulphonate (136c) as an unstable tacky green solid (807 mg, 51%). This compound, due to its instability was characterised by nmr spectroscopy only.

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

1-Oxa-6,6a-dithia-2-azapentalene (726 mg, 5 mmol) gave 3-methoxyiminoformyl-1,2-dithiolium fluorosulphonate (138a) as pale yellow needles which decomposed >190° (1.295 g, 100%) (from acetonitrile).

Found C 23.3; H 2.52; N 5.46%

$C_5H_6FO_4S_3N$ requires C 23.2; H 2.33; N 5.40%.

3,4-Dimethyl-1-oxa-6,6a-dithia-2-azapentalene (866 mg, 5 mmol) gave 4-methyl-3-methoxyiminoacetyl-1,2-dithiolium fluorosulphonate (138b) as yellow needles, m.p. 141-146° (1.361 g, 95%).

Found C 29.3; H 3.79; N 4.90%

$C_7H_{10}FO_4S_3N$ requires C 29.3; H 3.51; N 4.87%

3,4-Propano-1-oxa-6,6a-dithia-2-azapentalene (926 mg, 5 mmol) gave 7-methoxyiminoformyl-4,5,6,7-tetrahydrobenzo[c][1,2]dithiolium

fluorosulphonate (138c) as yellow spars, m.p. 129-136° (1.447 g, 97%).

Found C 32.1; H 3.22; N 4.74%

$C_8H_{10}FO_4S_3N$ requires C 32.1; H 3.37; N 4.68%.

5-t-Butyl-1-oxa-6,6a-dithia-2-azapentalene (1.007 g, 5 mmol) gave 5-t-butyl-3-methoxyiminoformyl-1,2-dithiolium fluorosulphonate (138d) as yellow plates, m.p. 170-175° (1.504 g, 96%).

Found C 34.4; H 4.76; N 4.50%

$C_9H_{14}FO_4S_3N$ requires C 34.3; H 4.47; N 4.44%.

3-Methyl-5-phenyl-1-oxa-6,6a-dithia-2-azapentalene[226] (1.176 g, 5 mmol) gave 5-phenyl-3-methoxyiminoacetyl-1,2-dithiolium fluorosulphonate (138e) as yellow microneedles, m.p. 202-203° (1.687 g, 97%).

Found C 41.2; H 3.48; N 3.97%

$C_{12}H_{12}FO_4S_3N$ requires C 41.2; H 3.46; N 4.01%.

3,4-Dimethyl-1-oxa-6,6a-diselena-2-azapentalene (1.335 g, 5 mmol) gave 4-methyl-3-methoxyiminoacetyl-1,2-dieselenolium fluorosulphonate (141) as yellow prisms, which decompose >200° (1.764 g, 93%).

Found C 22.0; H 2.67; N 3.76%

$C_7H_{10}FO_4SSe_2N$ requires C 22.1; H 2.39; N 3.69%.

(iv) 1,6-Dioxa-6a-thia-2-azapentalenes

A reaction time of 12 hours was employed with this class of compounds.

3,4-Dimethyl-1,6-dioxa-6a-thia-2-azapentalene (786 mg, 5 mmol) gave 4-methyl-3-methoxyiminoacetyl-1,2-oxathiolium fluorosulphonate (143a) as a hygroscopic pale yellow solid (1.079 g, 79%). A sample

of this salt (543 mg, 2 mmol) was dissolved in acetic acid (5 ml) and treated with perchloric acid (0.84 ml). Addition of ether precipitated a fawn solid which on recrystallisation gave fawn needles of 4-methyl-3-methoxyiminoacetyl-1,2-oxathiolium perchlorate, m.p. 118-122° (523 mg, 96%) (from acetic acid-ether).

Found C 30.9; H 3.80; N 5.22%

$C_7H_{10}ClO_6SN$ requires C 31.0; H 3.71; N 5.16%.

3,4-Propano-1,6-dioxa-6a-thia-2-azapentalene (846 mg, 5 mmol) gave 7-methoxyiminoformyl-4,5,6,7-tetrahydrobenzo[c][1,2]dithiolium fluorosulphonate (143b) as a tacky brown solid (912 mg, 64%). [The corresponding perchlorate (m.p. 115-121°) was explosive.]

Found C 32.9; H 3.69; N 4.77%

$C_8H_{10}FO_5S_2N$ requires C 33.9; H 3.56; N 4.95%.

K. The Stability of 1,6,6a-Trithiapentalenes Towards Acid

The 1,6,6a-trithiapentalene (1 mmol) was dissolved in trifluoroacetic acid (5 ml). After standing for 2 hours at room temperature the solution was poured into aqueous saturated sodium bicarbonate solution and extracted with benzene (3 x). The combined extracts were dried and evaporated. The residue was chromatographed on alumina (10 x 2.2 cm) with benzene for adsorption and elution. Red eluates were collected from which starting material was isolated.

3,4-Propano-1,6,6a-trithiapentalene (200 mg, 1 mmol) returned starting material (198 mg, 99%).

3,4-Ethano-1,6,6a-trithiapentalene (186 mg, 1 mmol) returned starting material (180 mg, 97%).

2,5-Dimethyl-1,6,6a-trithiapentalene (188 mg, 1 mmol) returned starting material (13 mg, 6.9%). Continued elution with benzene-ether (9:1) gave yellow eluates which afforded 2,5-dimethyl-1-oxa-6,6a-dithiapentalene (154 mg, 90%).

L. The Preparation of 3,4-Dideuterio-1,6,6a-trithiapentalene

1,6,6a-Trithiapentalene (320 mg, 2 mmol) was dissolved in deuteriotrifluoroacetic acid (7.7 ml) and left for 15 minutes at room temperature. A solution of sodium carbonate (6 g) in deuterium oxide (20 ml) was then added and the resulting mixture was extracted with dry benzene (3 x). The combined extracts were dried and evaporated. The residue was dissolved in benzene and adsorbed on a column of alumina (10 x 2.2 cm). Elution with benzene gave homogeneous (tlc) red eluates which afforded 3,4-dideuterio-1,6,6a-trithiapentalene as red plates, m.p. 112-113^{o} (262 mg, 81%) (from n-hexane).

Found C 36.8%

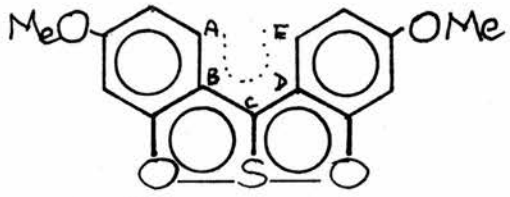
$C_5H_2D_2S_3$ requires C 37.0%.

Molecular Weight: Found 161.9598

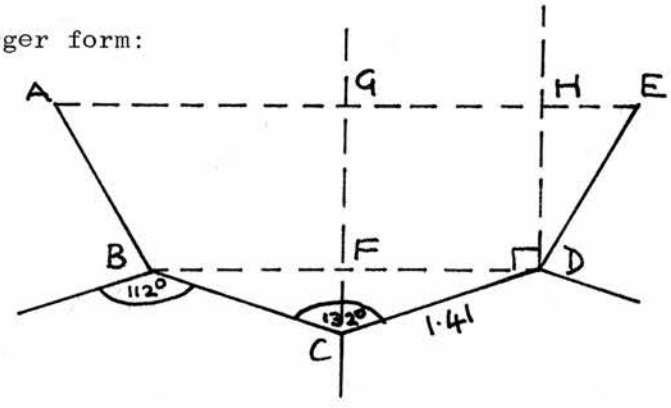
$C_5H_2D_2S_3$ requires 161.9601.

Appendix A

The approximate separation of halogen atoms in the 3,4-positions of 1,6-dioxa-6a-thiapentalenes, based on the geometry of



The important part of the molecule is shown dotted and is reproduced in a larger form:



$BC = CD = 1.41$ Å

$\hat{BCD} = 132^{\circ}$

$\therefore \hat{CBD} = \hat{CDB} = \frac{1}{2}(180-132)^{\circ} = 24^{\circ}$

$\therefore BD = 2FD = 2CD\cos\hat{FDC}$

$= 2 \times 1.41 \cos 24^{\circ}$

ie $BD = 2.57$ Å

If the assumed lengths C-Br and C-I bonds are 1.91 Å and 2.10 Å respectively[42], then using the angles found for the dibenzo compound, the separation of the halogen atoms may be calculated:

Separation of halogens $= AE$

$= 2(GH + HE)$

$= 2.57 + 2DE\sin\hat{HDE}$

$\hat{HDE} = (130-90-24)^{\circ}$

$= 16^{\circ}$

$\therefore$ Separation of bromine atoms $= 2.57 + 3.82 \sin 16^{\circ}$

$= \underline{3.64}$ Å

$\therefore$ Separation of iodine atoms $= 2.57 + 4.20 \sin 16^{\circ}$

$= \underline{3.75}$ Å

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