New 1,2-Dithiole Chemistry

A thesis presented by

Anita Margaret de La Motte

in partial fulfilment for
the degree of
Doctor of Philosophy
of the
University of London

Hofmann Laboratory,
Department of Chemistry,
Imperial College of Science, Technology and Medicine,
London, SW7 2BG

November 1990

To Mummy, Daddy, Amanda, and Gillian,
with love

Abstract

The introduction section of this thesis is divided into two parts; the first deals with the synthesis and properties of poly(sulphurnitride) and approaches to other polymers containing sulphur nitrogen chains in their backbone. The second part reviews 1,2-tetrathiafulvalenes and the role of 1,2-dithioles in charge transfer complexes.

The reactions between sulphur dichloride or disulphur dichloride with certain active methylene compounds is shown to give 1,2-dithiolium-4-olates, a type B mesoionic ring system. The scope of this reaction and some chemistry of the resultant compounds are described.

The reactions of amines and carbanions with 3,4,5-trichloro-1,2-dithiolium chloride lead to neutral 5-substituted *5H* -1,2-dithioles. The reactions of phenols and naphthols with 3,4,5-trichloro-1,2-dithiolium chloride give salts in which the phenols are bonded to the dithiole ring through carbon rather than oxygen. Reaction of 3,4,5-trichloro-1,2-dithiolium chloride with thioacetamide gives 4,5-dichloro-1,2-dithiol-3-thione in excellent yield.

Further reactions of the neutral 5-substituted 5*H* -1,2-dithioles with nucleophiles leads to displacement of the chlorine in position 3. Displacement of the less reactive chlorine in position 4 has been effected intramolecularly to give the new [1,2]dithiol[4,5-*b*][1,4]benzoxazine ring system.

Treatment of 4,5-dichloro-1,2-dithiol-3-one with the same range of nucleophiles usually results in displacement of the chlorine in position 5 but with the carbanion of dimedone a highly substituted pyrone is formed.

Acknowledgements

There are many people to whom I am indebted for help during my time at Imperial College. First of all I would like to thank my supervisor Professor C.W. Rees for constant encouragement, advice, and boundless enthusiasm for the subject.

I also thank John Bilton, Geoff Tucker, and the SERC Mass Spectrometry Service, University College, Swansea for mass spectra; Dick Sheppard and Paul Hammerton for NMR spectra and help in using the NMR spectrometers; Ken Jones for microanalysis of the compounds and Pete Sulsh for invaluable technical advice and help.

Warm thanks go to my friends and colleagues, both past and present, in the Hofmann Laboratory and on the seventh floor, for advice and friendship. I would especially like to thank Dr. Kulsum Rahimtoola for painstakingly proof-reading this thesis.

Last, but by no means least, I would like to thank my parents, sisters, grandparents and friends for their continual support, interest and encouragement in all I have undertaken.

Anita de La Motte
London 1990

Contents

ONE Sulphur nitrogen polymers and 1,2-dithioles in charge transfer complexes

TWO Reaction of sulphur chlorides with organic compounds

THREE 3,4,5-Trichloro-1,2-dithiolium chloride

FOUR Experimental

Abbreviations

Å	Angstrom unit
BOC	*t* -butoxycarbonyl
n -BuLi	*n* -butyllithium
CS	carbon monosulphide
$(CS)_n$	poly(carbonmonosulphide)
DBU	1,8-diazabicyclo-[5.4.0]undecene-7
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMAP	dimethylaminopyridine
DMF	dimethylformamide
ESR	electron spin resonance
IR	infra-red
NMR	nuclear magnetic resonance
S_2N_2	disulphur dinitride
S_4N_4	tetrasulphur tetranitride
$(SN)_x$	poly(sulphurnitride)
THF	tetrahydrofuran
TLC	thin layer chromatography
UV	ultra-violet

Chapter One

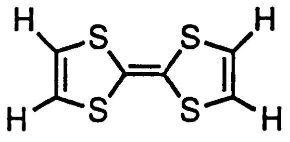
Sulphur nitrogen polymers and 1,2-dithioles in charge transfer complexes

1.1 Introduction

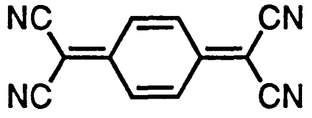
It was suggested as long ago as 1911 that it may be possible 'to prepare composite metallic substances from non-metallic constituent elements'.[1] In the past two decades much research has been carried out on 'organic metals' and is the subject of many excellent reviews.[2-5]

Organic metals fall broadly into two categories - conducting polymers and charge transfer complexes. Conducting polymers are highly conjugated, and conduction is believed to occur along the conjugated chain. This means the electronic transport is highly anisotropic and so conducting polymers are one-dimensional metals.

Charge transfer complexes consist of a donor molecule and an acceptor molecule. One or both of these components must be a planar molecule with a delocalised π-electron system. In the crystal lattice the component molecules must segregate into two types of stack; one of donor molecules and one of acceptor molecules. These stack closely face to face which favours extensive π-overlap and forms an energy band along the stacking axis; again this conductivity is highly anisotropic. The first charge transfer complex of this type was made in 1973 which consisted of 1,3-tetrathiafulvalene (TTF, **1**) as the donor, and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, **2**) as the acceptor, and was found to be metallic in character.[6]



1

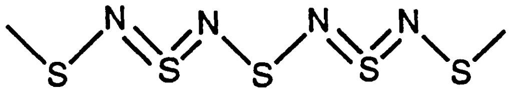


2

In the Hofmann laboratory, a group are studying the synthesis and chemistry of various sulphur-nitrogen heterocycles with particular reference to their possible use as organic metals. The work I have undertaken involves synthesis and modification of 1,2-dithioles, with a view to preparing monomers to give conducting polymers. Thus this review will consider the preparation and properties of conducting polymers which contain a large proportion of sulphur and/or nitrogen, and synthetic approaches to these. Charge transfer complexes which involve 1,2-dithiole rings, including the less known 1,2 -tetrathiafulvalene are also reviewed.

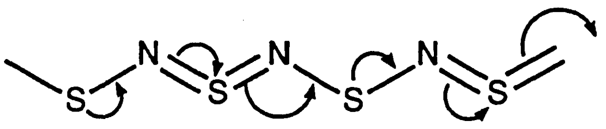
1.2 **Poly(sulphur-nitride)**

Poly(sulphur-nitride) (**3**) was first synthesized as bronze coloured crystals by Burt in 1910 and is the first example of a polymeric metal.[7] Becke-Goehring carried out some systematic work on the formation and properties of $(SN)_x$ in the 1950s and noted that it behaved as a semi-conductor.[8] Labes *et al.* studied the electrical conductivity and discovered that along the polymer chain the material was metallic over the entire temperature range investigated (4.2-300 K).[9] The exciting observation that $(SN)_x$ is superconducting at 0.26 K was made in 1975 by Greene, Street, and Suter.[10] This latter discovery stimulated a lot of interest in $(SN)_x$; however only crystals of high purity, which are prepared and maintained *in vacuo* , are stable at room temperàture indefinitely.[11]



3

As can be seen from the diagram above, the $(SN)_x$ polymer consists formally of alternating sulphur and nitrogen atoms, with sulphur existing in the oxidation states two and four when a valence bond model is used. Conduction occurs along the SN chain and can be viewed, very simplistically, in terms of electron movement as follows:



1.2.1. *Synthesis of $(SN)_x$*

The $(SN)_x$ polymer was originally synthesized from tetrasulphur tetranitride, S_4N_4, which is prepared from ammonia and disulphur dichloride.[12] Tetrasulphur tetranitride is cleaved by passing the hot vapour *in vacuo* through heated silver gauze, a fairly precarious proceeding considering the explosive nature of S_4N_4. Apart from a few modifications this is still the method used for the preparation of $(SN)_x$. Microcrystalline $(SN)_x$ has been prepared by treatment of bistrimethylsilylsulphurdiimine with sulphur dichloride; however the conductivity of this material is five orders of magnitude lower than for solid state polymerized $(SN)_x$.[13]

It is thought that the cleavage of S_4N_4 vapour occurs in two stages; the first being reaction of S_4N_4 with silver to give silver sulphide and nitrogen. Then the silver sulphide formed in the first stage catalyzes the thermal splitting of S_4N_4 (Scheme 1.1):[11]

$$S_4N_4 + 8Ag \longrightarrow 4Ag_2S + 2N_2$$

$$S_4N_4 \xrightarrow{Ag_2S} S_2N_2$$

Scheme 1.1

Disulphur dinitride is recognized to be the important intermediate in the preparation of $(SN)_x$.[14] It is a clear, colourless crystalline solid at room temperature, however it is stable only at low temperatures and polymerizes in the solid state to $(SN)_x$.[8] Modern methods of preparing $(SN)_x$ involve the synthesis and trapping of disulphur dinitride, followed by controlled solid state polymerization. Formation of good quality crystals of disulphur dinitride seems very important; this is achieved by transport of S_2N_2 to a trap at 0 °C where crystal growth is allowed to take place. Polymerization has been effected in various ways, at room temperature for several weeks, or by annealing at 75 °C for 2 h to cite just two examples.[15, 16] Crystal quality is very important in terms of the electrical properties of $(SN)_x$ and there has been much debate about the best method to give consistently good quality crystals.[17]

Well-formed crystals of $(SN)_x$ are usually several millimetres in length, and are bright golden and lustrous in appearance. These crystals consist of highly oriented parallel fibre bundles. The fibres themselves are made up of parallel (SN) chains and are in the order of several hundred angstroms in diameter. The ends of the crystals are blue-black due to the fibre bundle tips.[11]

A common way of improving the conductivity of a polymer is to use a procedure termed doping. This is a chemical manipulation, which involves adding either an oxidizing or reducing agent to the polymer. It is not understood why this improves the conductivity. Hence when $(SN)_x$ is treated with bromine a new substance is formed having a formula $(SNBr_{0.4})$. Street *et al.* prepared this and reported its conductivity to be an order of magnitude higher than that for $(SN)_x$.[18] However this is not a new material since it has been mentioned earlier by Goehring in a 1956 review.[8]

1.3 Oligomeric analogues of poly(sulphur-nitride)

Since the discovery that $(SN)_x$ is superconducting, several groups have tried to prepare analogues in order to obtain materials with superior conducting properties and better processing qualities as well as improved stability.

One area of this research was to build up chains of SN units *i.e.* oligomers of $(SN)_x$ with suitable end groups in order to study their properties. Sulphurdiimines (**4**) are the most common members of this group.[19] Also well established are the trisulphur diimines (**5**).[20]

$$[RNSNR^1] \qquad [RSNSNSR]$$

4 **5**

R, R^1 = Aryl

The longest chains of SN units (apart from $(SN)_x$) reported prior to 1974 were found in compounds (**6**).[21]

$$[R^2\,NSNSNSNR^2]$$

6

R^2 = *t*-Bu, Me_3Si, diphenylmethylene

In 1977, Kuyper and Street published a paper on oligomeric analogues of $(SN)_x$ *i.e.* $[R(SN)_nR^1]$ and $[R(SN)_nSR^1]$.[22] They treated bis(trimethylsilyl)sulphurdiimine (**7**) with arylsulphenyl chlorides; when a 1:1 ratio of these reactants was used the 1-aryl-4-trimethylsilyldisulphurdinitride (**8**) was obtained. If a 2:1 ratio of arylsulphenyl chloride to (**7**) was used the corresponding symmetrical 1,5-diaryltrisulphurdinitride (**9**) was obtained in high yield (70-90%). The mixed aryl derivatives could also be prepared although yields were lower.

$$Me_3SiNSNSiMe_3 \xrightarrow{ArSCl} ArSNSNSiMe_3 + Me_3SiCl$$

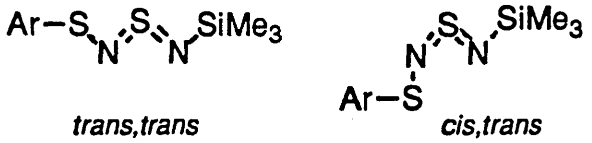
7 **8**

$$Me_3SiNSNSiMe_3 \xrightarrow{2ArSCl} ArSNSNSAr + 2Me_3SiCl$$

9

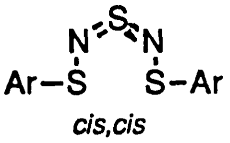
9a Ar = $4\text{-}ClC_6H_4$;
9b Ar = $4\text{-}NO_2C_6H_4$;
9c Ar = $2\text{-}NO_2C_6H_4$;
9d Ar = $2,4\text{-}(NO_2)_2C_6H_3$;
9e Ar = $4\text{-}MeOC_6H_4$;
9f Ar = $4\text{-}MeC_6H_4$.

There are two configurations proposed for compounds (**8**), *trans,trans* and *cis,trans*. In the case of compounds (**9**), an X-ray has been reported for the 4-chlorophenyl analogue which shows a *cis,cis* configuration.[23] It is known that there is some form of bonding between the 1,5 sulphurs as the distance between them is less than the sum of their van der Waals radii.



trans,trans *cis,trans*

8



cis,cis

9

In a similar way the 4-methoxyphenyl compound (**9e**) was prepared by Chien *et al.* and conductivity measurements were carried out on this and the 4-nitrophenyl compound (**9b**).[24] They were found to have high resistivities; however when doped with bromine they became semi-conductors. It was noted that there was a marked disparity in doping rates, the 4-nitrophenyl compound being much slower; this is attributed to the fact that a positive charge is formed by the *p* -type bromine dopant which is stabilized by the electron-donating methoxy group but destabilized by the electron-withdrawing nitro group.

In the case of the aryl groups being 4-chlorophenyl (**9a**) or 4-methylphenyl (**9f**) an unusual reaction took place when these were treated with another equivalent of arylsulphenyl chloride . Golden needles with a metallic appearance were formed in high yield and found to be a tetrasulphurtrinitride salt (**10**).[25] 4-Methyldiphenyldisulphide (**11**) was observed also.

$$\underset{\textbf{9b}}{2(\text{4-MePhSNSNSPhMe-4})} + \text{4-MePhSCl}$$

$$\downarrow$$

$$\underset{\textbf{10}}{(\text{4-MePhSNSNSNSPhMe-4})\text{Cl}} + \underset{\textbf{11}}{(\text{4-MePhS})_2} + N_2$$

Some examples of trisulphur tetranitrides have been made. Appel *et al.* obtained compound (**13**) by treating *N* -*t* -butyl-*N'* -trimethylsilylsulphurdiimine (**12**) with sulphur dichloride:[26]

$$2\ t\text{-BuNSNSiMe}_3 + \text{SCl}_2 \longrightarrow t\text{-BuNSNSNSNBu-}t$$

12 **13**

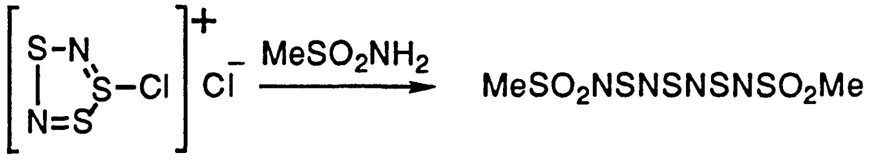
If two moles of bistrimethylsilylsulphurdiimine (**7**) were reacted with one mole of sulphur dichloride the corresponding trisulphur tetranitride compound (**14**) was obtained which had trimethylsilyl groups as end groups.[27]

$$2\ \text{Me}_3\text{SiNSNSiMe}_3 + \text{SCl}_2 \longrightarrow \text{Me}_3\text{SiNSNSNSNSiMe}_3$$

14

When (**14**) was treated with another mole of sulphur dichloride, instead of getting another coupling reaction as hoped, tetrasulphur tetranitride was the only product observed.

Pentasulphur tetranitride chains have also been made. In two examples the sulphurs adjacent to the end groups are present as sulphone moieties. However their preparations were very different; bis(methylsulphonyl)trisulphur tetranitride (**15**) resulted from chlorotrithiadiazolium chloride (**16**) and methylsulphonylamine;[28] whereas bis(tosyl)trisulphur tetranitride (**17**) arises from *N* -sulphinyltrimethylsilylamine (**18**) and *S*,*S* -dichloro-*N* -tosyliminosulfurane (**19**).[29]



16 **15**

$$\text{Me}_3\text{SiN=S=O} + \text{R-N=SCl}_2 \longrightarrow \text{RNSNSNSNR}$$

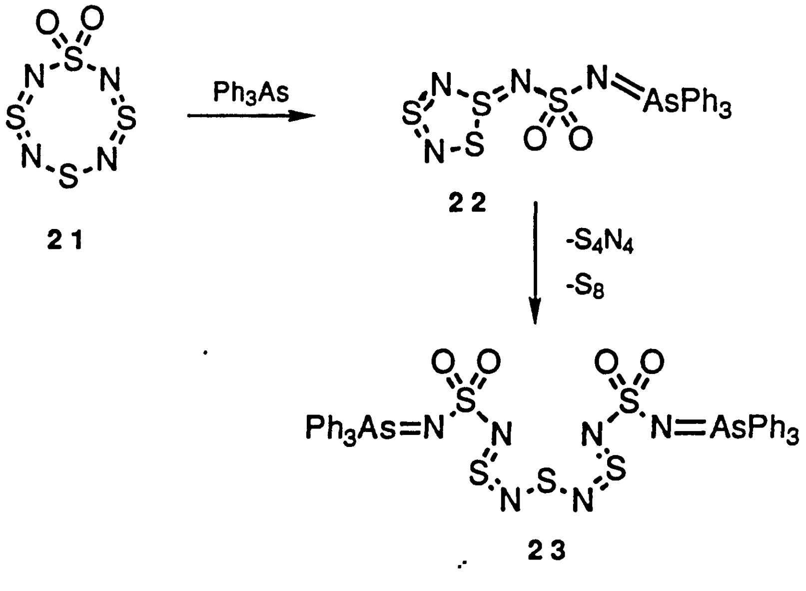
18 **19** **17**

R = tosyl

Kuyper and Street also made pentasulphur tetranitride compounds (**20**) by reaction of (**8**) with sulphur dichloride in a 2:1 ratio.[22] These compounds were golden metallic in appearance. They used UV-visible absorptions as a measure of the extent of electron delocalization in the series of oligomeric SN compounds they had prepared and observed an increase in red shift with increasing SN chain length.

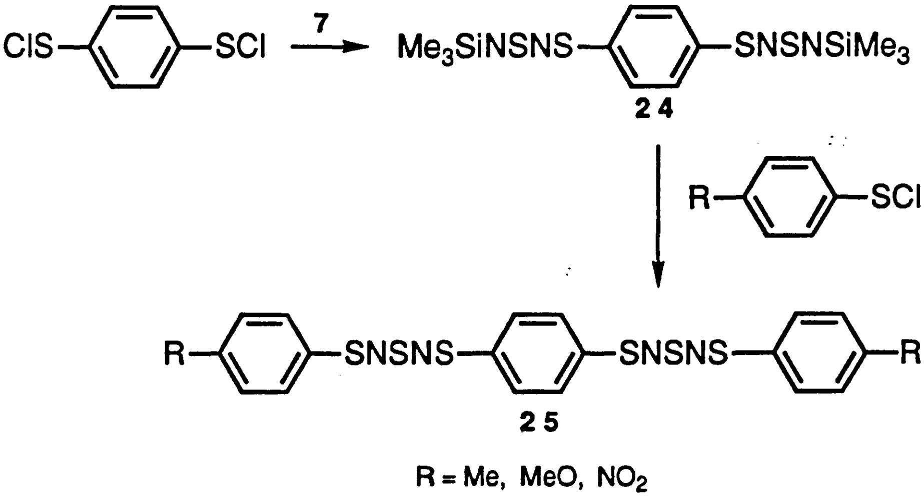
$$\underset{\mathbf{8}}{2ArSNSNSiMe_3} + SCl_2 \longrightarrow \underset{\mathbf{20}}{ArSNSNSNSNSAr}$$

The longest non-polymeric sulphur-nitrogen chain synthesized has eleven alternating atoms.[30] It was found that the *S,S* -dioxide of tetrasulphur tetranitride (**21**) with triphenylarsane undergoes a ring contraction to give an adduct (**22**) which is stable to air and hydrolysis. In acetone solution however (**22**) slowly loses sulphur and tetrasulphur tetranitride to give the product (**23**) which contains a pentasulphur hexanitride chain.



21 **22** **23**

Chien and his group extended the work by making oligomers of $(SN)_x$ with a phenyl group between two trisulphur dinitride chains.[24] By treating *p* -phenylenedisulphenyl chloride with two equivalents of bistrimethylsilylsulphurdiimine (7), compound (24) was obtained. This in turn, when treated with a suitable substituted sulphenyl chloride, gave the oligomer (25).

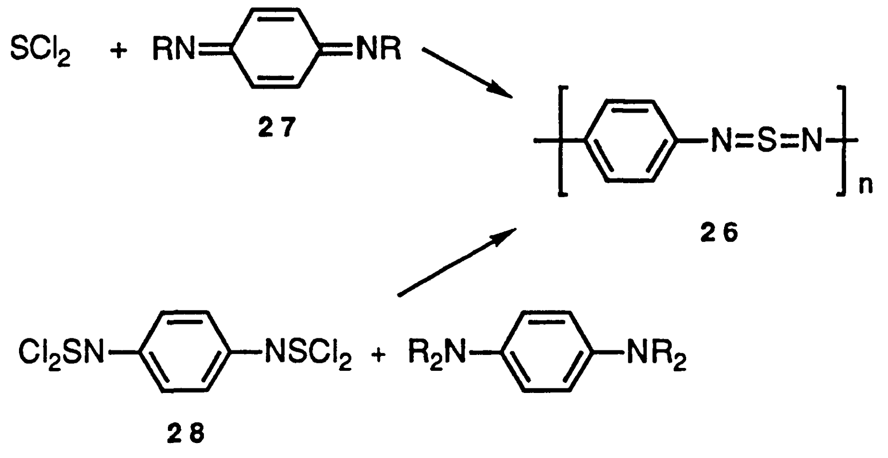


The conductivities of these compounds (25) were also measured, and it was observed that the order of conductivity in the undoped compounds was MeO > Me > NO_2. When doped the conductivity was at least one order of magnitude higher than the corresponding compounds (9) and the order upon doping was MeO ~ Me > NO_2.

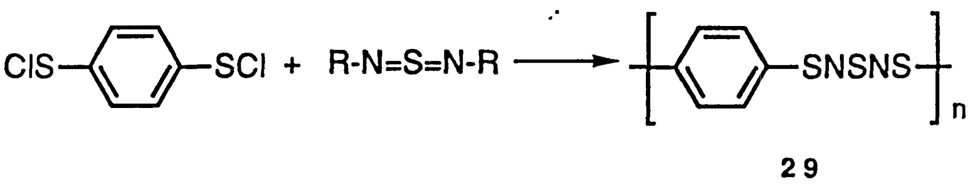
1.4 SN polymers with spacer groups

1.4.1 *SN polymers with aromatic spacer groups*

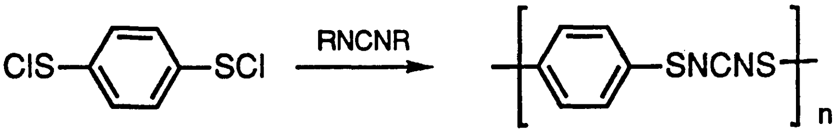
The first polymers containing SN units and spacer groups was published by Scherer *et al.* in 1982.[31] Their strategy was to use either sulphur dichloride or *p* -phenylenedisulphenyl chlorides with silylated diamines and diimines to give several polymers. The longest SN chain present in any of these polymers was a trisulphur tetranitride unit. All the SN units were situated *para* to each other on the phenyl rings. The simplest example had a sulphur diimine group between the phenylene rings (**26**). It was prepared in two ways, either by treating disilyldiiminoquinone (**27**) with sulphur dichloride, or, by reaction of *p* -phenylenediamine or its tetratrimethylsilyl derivative with the reagent (**28**).



By taking *p* -phenylenedisulphenyl chloride with bistrimethylsilylsulphurdiimine an analogous polymer was formed which had a trisulphurdinitride group between the phenyl rings (**29**):

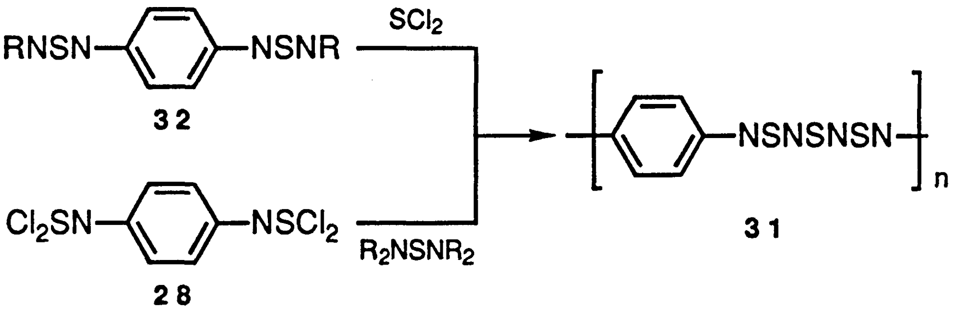


If bistrimethylsilylcarbodiimine is taken with *p*-phenylenedisulphenyl chloride a very similar polymer (**30**) is formed:



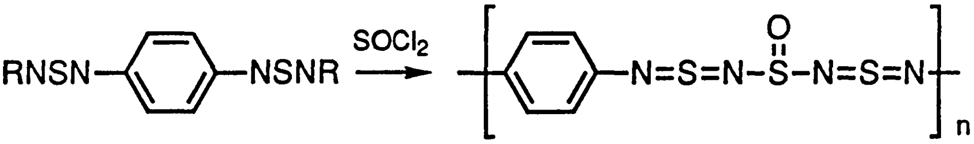
30

The longest chain of alternating sulphur nitrogen atoms between phenyl rings was a trisulphur tetranitride unit (**31**) and was prepared in two ways; by reaction of (**28**) with tetra(trimethylsilyl)sulphurdiamine and also by treatment of compound (**32**), where R is TMS, with sulphur dichloride.



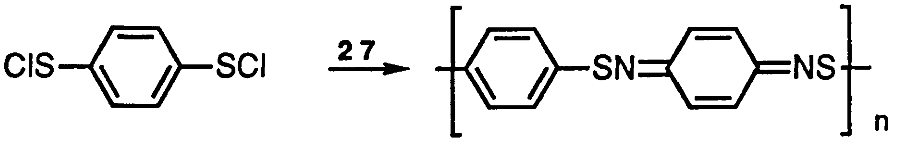
32
28
31

If thionyl chloride was used instead of sulphur dichloride above, the polymer obtained (**33**) had a sulphoxide group in the centre of the SN chain *i.e.*

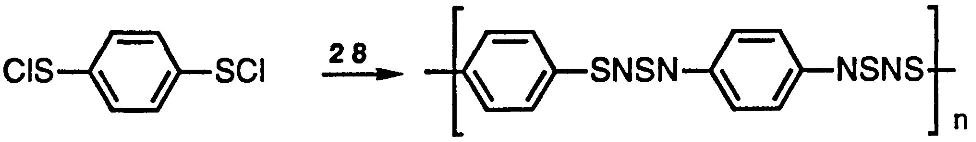


33

In each of the above cases there has been an odd number of sulphur atoms between the phenyl rings. Examples with just one SN unit (**34**) and also two SN units *i.e.* SNSN (**35**) between phenyl rings have also been prepared. *p*-Phenylenedisulphenyl chloride with bistrimethylsilyldiiminoquinone (**27**) gave (**34**), whereas use of (**32**) resulted in (**35**).

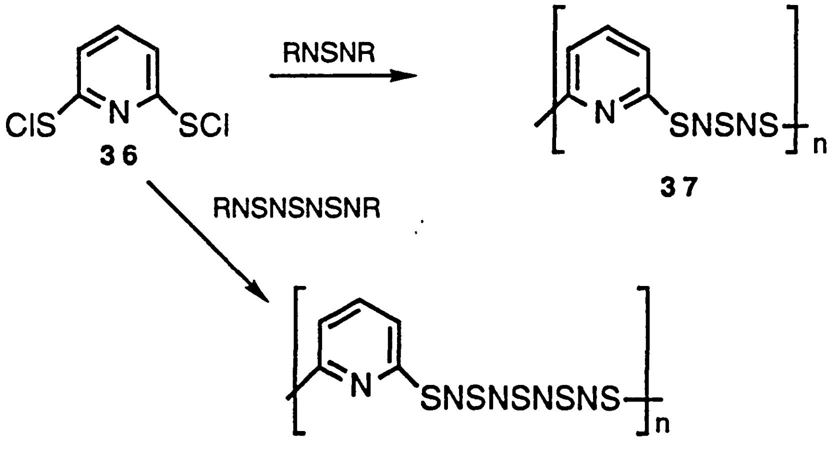


34



35

This work was extended to incorporate heterocyclic spacer units rather than benzene rings.[32] Using bistrimethylsilylsulphurdiimine (**7**) and bistrimethylsilyltrisulphurtetranitride (**14**) to supply the sulphur nitrogen chains, the heterocyclic units were based on thiophene, pyridine and thiadiazole. Thus pyridine-2,6-bis(sulphenyl) chloride (**36**) was used to give the two polymers [(**37**) and (**38**)] shown below:

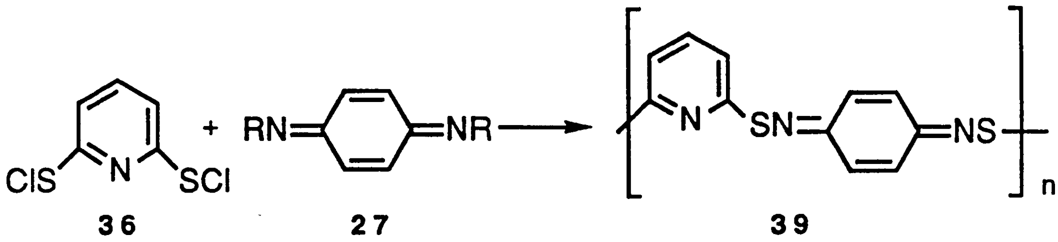


36

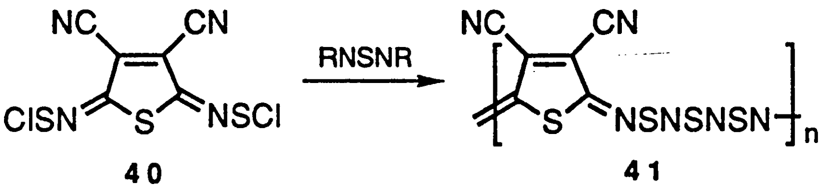
37

38

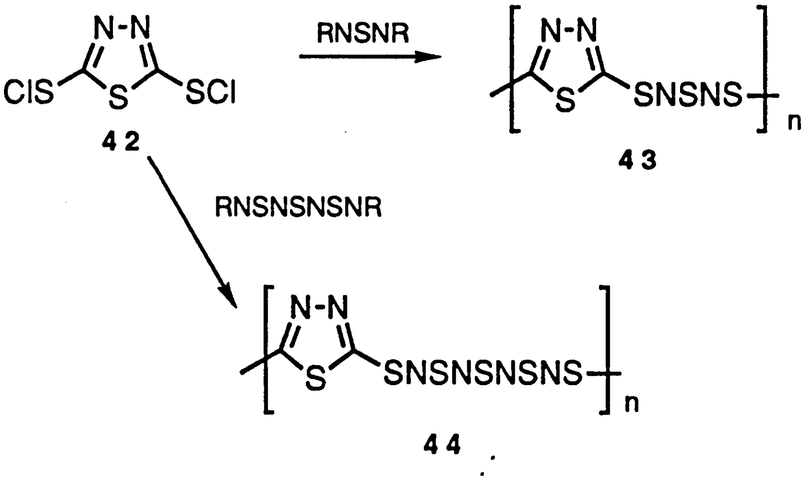
This pyridine reagent was also reacted with bistrimethylsilyldiiminoquinone (**27**) to give a polymer (**39**) with a much lower proportion of sulphur and nitrogen compared to those already described.



The thiophene reagent used (**40**) was first prepared by Wudl by treating 2,5-diamino-3,4-dicyanothiophene with an excess of sulphur dichloride.[33] Wolmerhauser and his group only report the reaction of this reagent with bistrimethylsilylsulphurdiimine to give the polymer (**41**) shown.



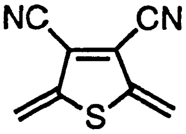
The final reagent used by Wolmershauser was the thiadiazole (**42**) which was reacted with both (**7**) and (**14**) to give the corresponding polymers [(**43**) and (**44**)]:



Both these polymers were obtained as black or highly coloured powders and are presumably microcrystalline. Only (**44**) is not stable to air and is stored in a dry nitrogen atmosphere, and was not tested for conductivity. Of the other polymers synthesized, all were found to be insulators in the pristine state except for

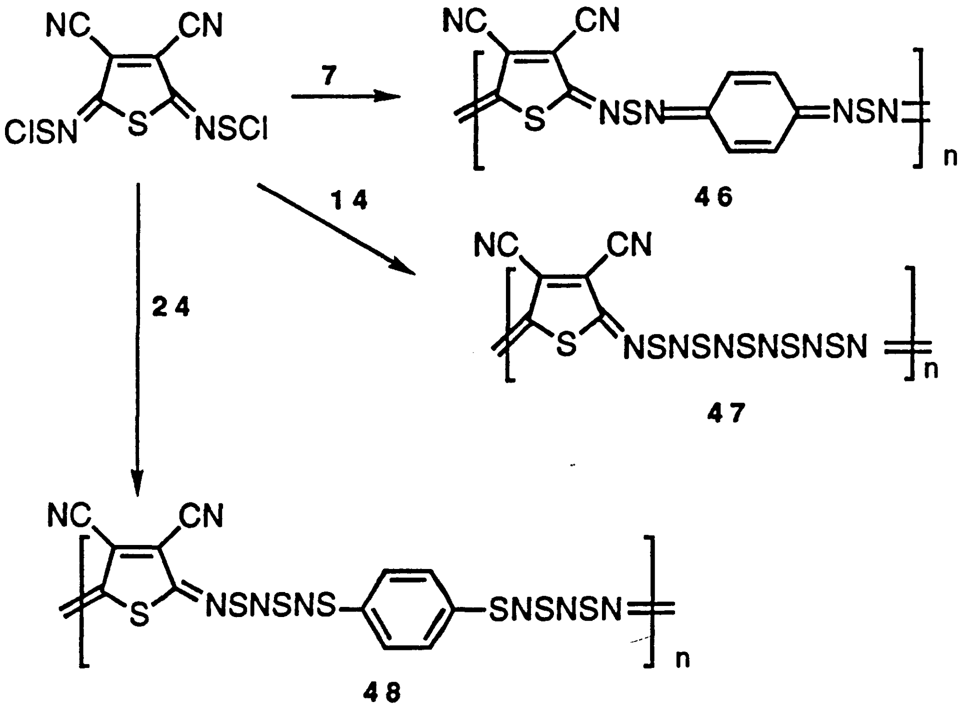
(**41**) which was found to have a comparatively high conductivity. Doping with iodine had no effect on the conductivity of (**41**), but increased the conductivity of (37) and (**43**) by several orders of magnitude; a colour change from red to black was also observed. The latter two polymers were similar in that they both contain a trisulphur dinitride chain. The conductivity of (**41**) was six orders of magnitude higher than any of the other undoped polymers and it was postulated that the electronegative cyano groups present were causing this effect.

Wolmershauser *et al.* published an overview of their work, and drew some conclusions about the conductivity of the polymers they had made.[13] First of all they noted that conductivity was higher when nitrogen was the link between the organic group and sulphur nitrogen chain; conversely sulphur links gave low conductivity. The highest conductivity values were shown by polymers containing the group (**45**); this was attributed to intrinsic doping *i.e.* the highly electronegative cyano groups reduce the electron density in the conjugated chain hence acting as an intramolecular dopant. This explanation also accounts for the inability to increase the conductivity of these polymers containing such a 'thiophene' unit by use of an extrinsic dopant *e.g.* iodine.



45

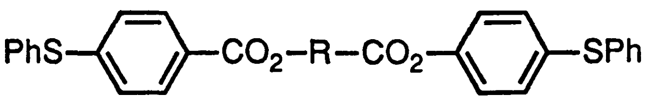
Chien *et al.* made a series of polymers [(**41**), (**46**), (**47**), and (**48**)] with (**45**) being the common spacer unit and varying the SN units by using reagents (**7**), (**14**), and (**24**) respectively.[34] Conductivity measurements on their sample of (**41**) were found to be smaller than those reported by Wolmershauser *et al.* [13] However the conductivity reported for (**46**) was the same for both groups. When the measured



conductivities for these polymers were compared it was found that (**46**) and (**48**) have lower conductivity than (**41**) and (**47**), with (**48**) being the lowest. Hence it seems that the presence of the quinonoid moiety reduces conductivity and phenylene rings separating the SN segments even more so.

Different doping agents were tried with these polymers. AsF_5 is commonly used as the dopant with conducting polymers such as polyacetylene, poly-(*p* -phenylene) and poly(phenylene sulphide). However (**41**) degrades rapidly if treated with AsF_5, the colour of the polymer going from black to brown. Iodine is another commonly used dopant but has been shown to have no effect on SN polymers. Bromine when used as the dopant had a marked effect, if conductivity was measured immediately after doping, with a rise in conductivity of five orders of magnitude. However, after evacuation, the values of conductivity were very similar to the original undoped samples showing the doping process to be reversible. It was also noted that conductivity does not depend solely on chemical composition of the polymer but also on morphology; all these polymers are microcrystalline powders similar to $(SN)_x$ made from bistrimethylsilylsulphurdiimine and sulphur dichloride.

All the polymers described so far are insoluble, which makes their characterization and application complicated. Chien and Ramakrishnan prepared some polymers with alkyl spacers to try to obtain soluble polymers with a high sulphur-nitrogen content.[35] The spacers they used were more flexible than any used previously and consisted of a diester with either an alkyl or ether linkage:

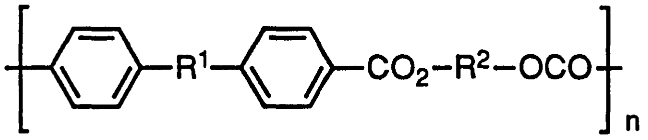


$R = (CH_2)_{10}$, $CH_2CH_2OCH_2CH_2$, $(CH_2CH_2O)_2CH_2CH_2$.

49

It had been observed previously that electron-donating groups on the phenylthiazyl segments enhanced the charge transfer complexing when doped with bromine.[24] However the weakly electron-withdrawing ester linkage was used to link the phenylthiazyl and spacer units for two reasons, both synthetic. First of all sulphuryl chloride which is used to chlorinolyze the benzyl sulphide also chlorinates the aromatic ring if it contains electron-releasing groups. Also in sulphenyl chlorides with electron-releasing groups a side reaction occurs leading to the formation of a salt which would preclude the formation of a uniform high polymer.[22]

Hence polymers (**50**) were made from (**47**) using sulphuryl chloride to remove the benzyl protecting group and form the sulphenyl chloride. This was followed by reaction of the bis(sulphenyl) chloride with bistrimethylsilylsulphurdiimine, or in one case using the reagent (**24**).



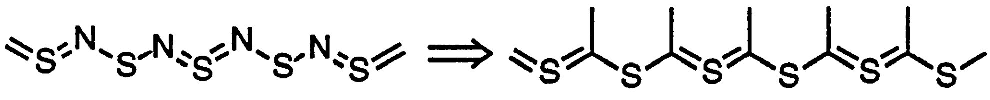
50

R^1 = SNSNS $R^2 = (CH_2)_{10}$, $CH_2CH_2OCH_2CH_2$,
or $(CH_2CH_2O)_2CH_2CH_2$.
$R^1 = SNSNSC_6H_4SNSNS$ $R^2 = (CH_2CH_2O)_2CH_2CH_2$.

It was found that the polymer with the triethylene glycol spacer and phenyltrisulphurdiimine as the SN unit was soluble and fusible. However when the SN unit was *p* -phenylenedithiobis(phenyldithiazyl) the polymer was insoluble; this was attributed to stronger interactions between the longer thiazyl segments. The conductivity of these polymers upon doping with bromine was comparable to those mentioned previously.

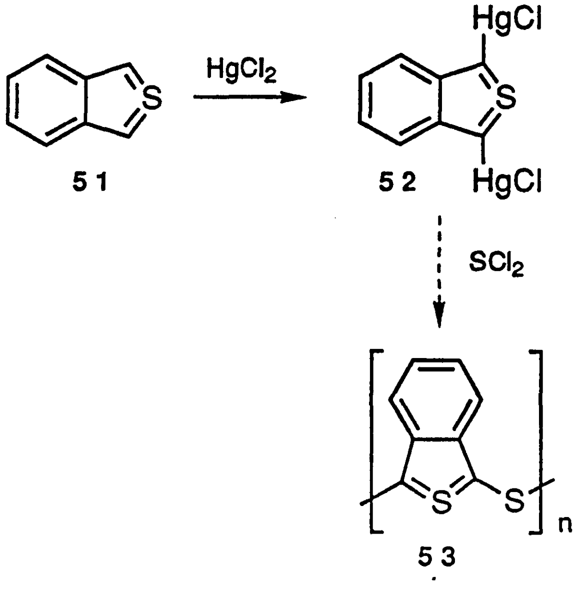
1.4.2 *Alternative approaches to SN polymers*

As early as 1977 Wudl had suggested that the future of organic metals, from a conductivity point of view, lay in σ-bonded systems with π-delocalization.[36] Using $(SN)_x$ as a model he envisaged a polymeric system where the nitrogen atoms were replaced by carbon (Scheme 1.2).

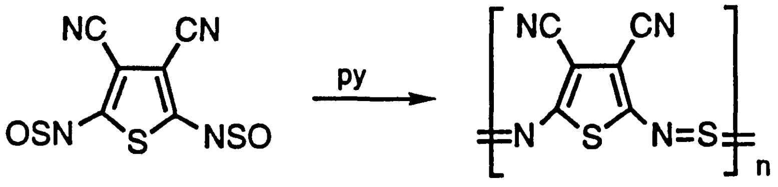


Scheme 1.2

Some work was undertaken to attempt to produce such a polymer (53) via isobenzothiophene (51) which was chloromercurated to give (52) in quantitative yield. This was treated with sulphur dichloride, however the product obtained was shown still to contain mercury.

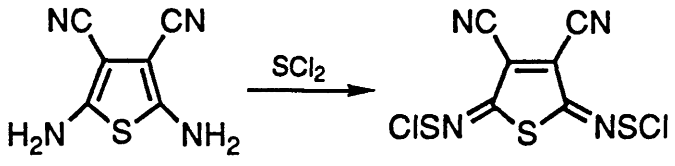


Later Wudl extended this idea by making polymers from diaminothiophenes using cyano substituents to try to stabilize the electron-rich heterocyclic ring.[33] One precursor was 3,4-dicyano-2,5-bis(sulphinylamino)thiophene (54) which was prepared by prolonged reaction of 2,5-diamino-3,4-dicyanothiophene with neat thionyl chloride. When treated with pyridine a black polymeric substance (55) was obtained which was assumed to have the structure shown, but elemental analysis indicated that pyridine had also been incorporated.



54 **55**

Other attempts to polymerize this monomer using heat or aluminum chloride resulted in black intractable tars. Thus Wudl prepared (40) as red crystals from 2,5-diamino-3,4-dicyanothiophene and an excess of sulphur dichloride.



40

Treatment of (40) with an excess of tetrabutylammonium iodide afforded complete dechlorination and reduction to a radical anion with tetrabutylammonium as a counter ion. This is another example where the reagent has become incorporated into the polymeric product.

Thus it can be seen that several examples of polymers containing a high proportion of sulphur and nitrogen in a conjugated chain analogous in structure to $(SN)_x$ have been prepared. However there has been very little work on the morphology of these polymers which appears to have a pronounced effect on the conductivity, whereas much research on the synthesis of $(SN)_x$ has been devoted to this.

1.5 Polymerization of CS

The formation of CS was first reported by Loew in 1868 and Sidot in 1872 who observed the formation of a brown precipitate when carbon disulphide was exposed to sunlight.[37, 38] Dewar and Jones produced CS by treatment of nickel tetracarbonyl with thiophosgene which gave a non-conductive brown black powder.[39] They also trapped monomeric CS at -196 °C from an electrical discharge of CS_2. It was obtained as a crystalline colourless solid or a glassy, amorphous condensate which slowly turned brown giving the polymer.[40] (Scheme 1.3)

$$CS_2 \xrightarrow{h\nu} (CS)_n$$

$$Ni(CO)_4 + CSCl_2 \longrightarrow (CS)_n + NiCl_2 + CO$$

$$CS_2 \longrightarrow CS \longrightarrow (CS)_n$$

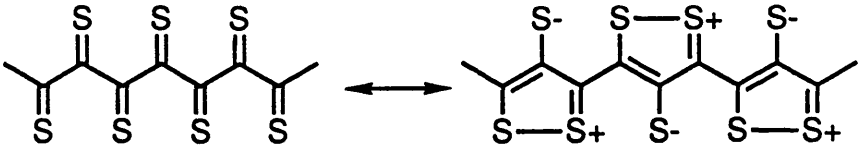
Scheme 1.3

The polymerization of monomeric CS does not take place readily in the gas phase; a surface is required, usually provided by carbon, which helps to control the polymerization process. Otherwise the polymerization is violent.

$(CS)_n$ was found to be readily soluble only in concentrated sulphuric or nitric acid, and solutions of sodium hydroxide or ammonia in water or alcohol. The polymer could be precipitated by adding water to the acidic solutions and acid to the basic solutions.

The polymer is stable to heat; only a slight evolution of hydrogen sulphide was observed at 360 °C. Above 360 °C carbon disulphide was evolved leaving mainly carbon. Elemental analysis showed a C:S molar ratio of 1:1. X-ray analyses of the CS polymer showed that the material was amorphous. X-ray photoelectron spectroscopy studies of the polymer showed that there were two types of carbon at values which were suggestive of aromatic-like carbons. IR shows weak bands due to C-S, C=S and C=C. No ^{13}C signals were found in the NMR (solid state).[41]

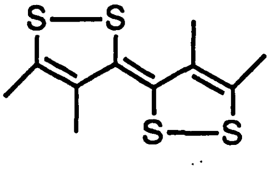
There have been several structures postulated for this polymer. However it has proved difficult to reproduce the polymer synthesis to give the same properties and stoichiometry. One possible structure is given below based on a 1,2-dithiol ring system (Scheme 1.4), though it is possible that the actual structure of $(CS)_n$ is far more complex than this.



Scheme 1.4

1.6 1,2-Tetrathiafulvalenes

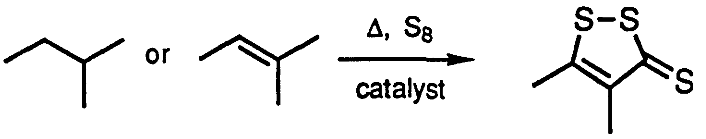
1,3-Tetrathiafulvalenes have been known for many years and their synthesis and chemistry is well developed. Conversely 1,2-tetrathiafulvalene (**56**) was first made in 1975 and the chemistry is poorly developed.[42] Most pathways to 1,2-TTF start from 1,2 -dithioles, the syntheses of which are reviewed very briefly.



56

1.6.1. Syntheses of 1,2-dithioles

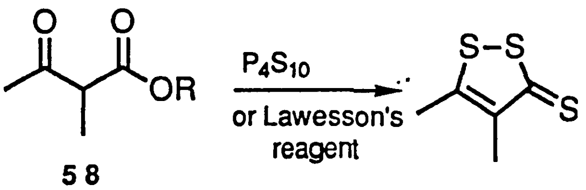
a) 1,2-Dithiol-3-thiones (**57**): High temperature sulphurization (200-500 °C) of hydrocarbons yields 1,2-dithiol-3-thiones (trithiones). The yields are good in some cases and may be increased by the use of basic catalysts *e.g.* diphenylguanidine (Scheme 1.5).[43]



57

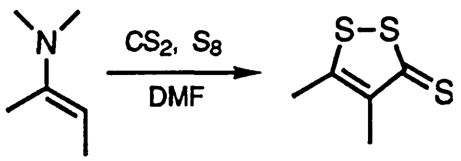
Scheme 1.5

Sulphurization of β-ketoesters (**58**) and their derivatives with phosphorous pentasulphide in the presence of sulphur also gives these trithiones very efficiently.[44] Use of the 2,4-diphospha-1,3-dithietane (Lawesson's reagent) as the sulphurizing agent increases the yield in most cases.[45]



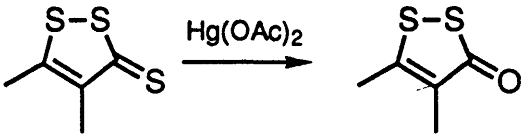
58

Trithiones can also be obtained from enamines, carbon disulphide and sulphur (Scheme 1.6):[46]



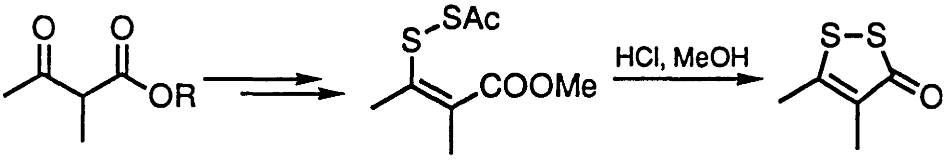
Scheme 1.6

b) 1,2-Dithiol-3-ones: Desulphurization of the corresponding 1,2-dithiol-3-thiones using mercuric acetate gives the 1,2-dithiol-3-ones (**59**):[47]



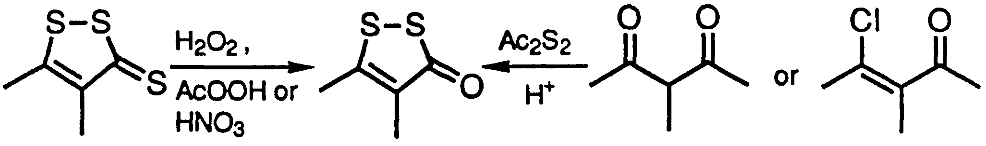
59

They can also be synthesized from acyclic compounds *e.g.* the sulphurization of cinnamic esters with sulphur at 250 °C gives 5-phenyl-1,2-dithiol-3-one in 65% yield.[48] A more versatile method of making 1,2-dithiol-3-ones is from β-keto esters and proceeds via the β-acetyldithioacrylic esters (Scheme 1.7).[49]



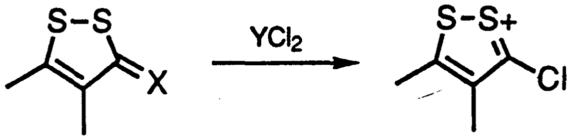
Scheme 1.7

c) 3*H* -1,2-dithiolium salts: these are obtained from the trithiones by oxidation using a suitable oxidizing agent *e.g.* peracetic acid, hydrogen peroxide or nitric acid.[50] They are also available from simple acylic precursors such as 1,3-diketones or from β-ketoallyl chlorides with diacetyl disulphide in the presence of strong acids (Scheme 1.8).[51]



Scheme 1.8

d) 3-Chloro-1,2-dithiolium salts: These are prepared from either the corresponding 1,2-dithiol-3-thiones or 1,2-dithiol-3-ones by treatment with halogen transfer agents *e.g.* phosphorous pentachloride, oxalyl chloride or phosphorous oxychloride (Scheme 1.9).[52]

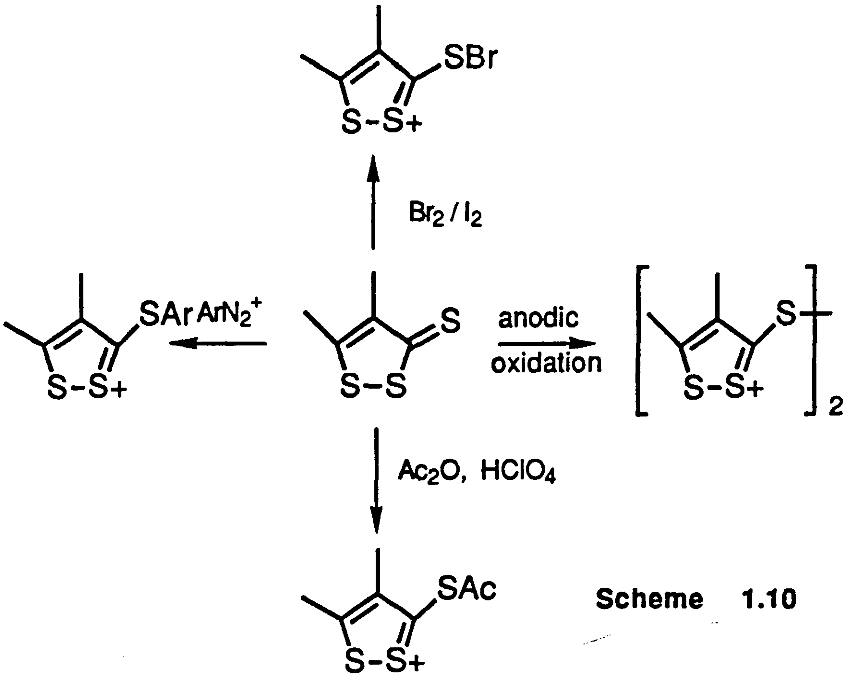


Y = PCl_3, POCl, SO, CO.

X = O, S.

Scheme 1.9

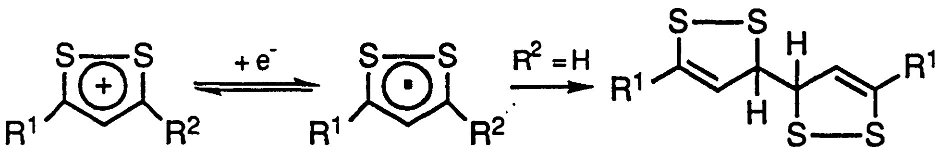
e) Organylthio-1,2-dithiolium salts: The thione group in 1,2-dithiol-3-thiones is strongly polar and is easily attacked by electrophiles. Sulphenyl halides are formed if the trithiones are treated with halogens, anodic oxidation affords the disulphides.[53, 54] Acylation of the sulphur occurs with a suitable acylating agent and perchloric acid;[55] arylation of the sulphur occurs with aryldiazonium salts (Scheme 1.10).[56] As these organylthio groups can easily be replaced by nucleophiles and are readily available they are of great synthetic interest.



Scheme 1.10

1.6.2. Synthesis of 1,2-TTF

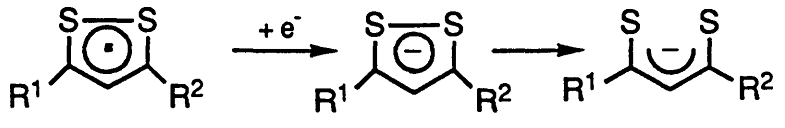
The most successful and widely applicable method of forming 1,2 TTF has been by reductive dimerization of 1,2-dithiolium salts. Cathodic reduction of the dithiolium salts gives the corresponding 1,2-dithiolium radical (**59**) which can then dimerize to give the dihydro-1,2-TTF derivative (**60**).[57]



59

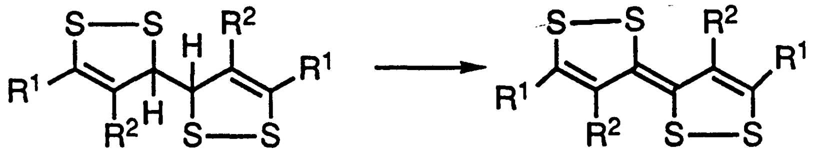
60

The stability of the radical and the dimerization step depend on both the nature of R^1 and R^2 and also the temperature. In the case shown where R^2 is hydrogen the equilibrium lies on the side of the dimers and conversely when R^2 is phenyl the equilibrium lies to the side of the radical. If the radical receives another electron during the reduction process then the dithiolium anion is formed; this step is irreversible due to the formation of the dithidiketonate anion (Scheme 1.11).



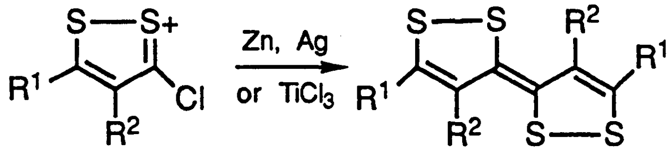
Scheme 1.11

The usual reagents for the preparative reduction of the dithiolium salts to the dimers are zinc and aqueous titanium (III) chloride solutions although silver has been used.[58] Several different oxidizing agents have been used to obtain the 1,2-TTF (**61**) from the dihydro compound including air, DDQ, and selenium oxide.[42] Oxidation of the dimers using iodine, bromine or electrochemical oxidation results in dithiolium salts.[59]



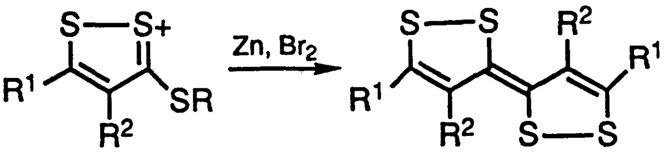
60 **61**

Reduction of 3-chloro-1,2-dithiolium salts with zinc, silver or aqueous titanium (III) chloride gives 1,2 TTF directly (Scheme 1.12):[58]



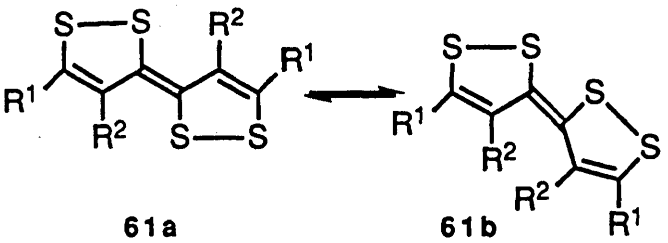
Scheme 1.12

The dimerization of 3-alkylthio-1,2-dithiolium salts requires zinc as a reducing agent and sometimes the presence of bromine to act as an oxidative 'extractor' for the alkylthio groups (Scheme 1.13).[59]



Scheme 1.13

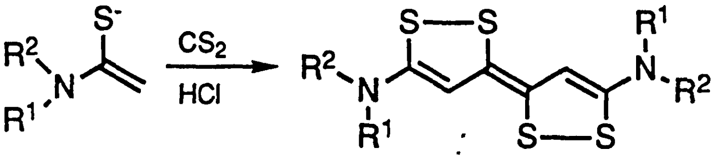
In certain cases *i.e.* where R^1 is phenyl and R^2 is hydrogen and where R^1 and R^2 are $(CH{=}CH)_2$, two isomers of 1,2-TTF are obtained, the *trans* (**61a**) and *cis* (**61b**) forms. These are characterized by their different UV-visible spectra and conversion of one form to the other is carried out either thermally or photochemically. In the cases where R^2 is methyl or phenyl only one isomer is obtained.[59]



61a **61b**

In all the above reactions not only is the relevant 1,2-TTF formed but also the corresponding trithiones and in some cases also the 1,2-dithiol-3-ones and thieno[3,2-*b*]thiophenes.

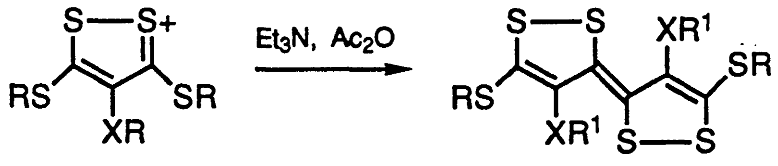
Another method of synthesizing 1,2-TTF has been reported which uses the thiolates, which are treated successively with carbon disulphide and hydrochloric acid. This gives amino substituted 1,2-TTF in 7-30% yields (Scheme 1.14).[60]



$R^1 = Me$; $R^2 = Me, Ph$
$R^1\ R^2 = (CH_2)_5,\ (CH_2)_2O(CH_2)_2.$

Scheme 1.14

A procedure was also reported to synthesize 1,2 TTF with alkylthio and acetyloxy-substituted groups. This was achieved by refluxing the substituted 1,2-dithiolium salts or 3,5-bis(alkylthio)-1,2-dithiolium-4-olates in acetic anhydride in the presence of a base *e.g.* triethylamine (Scheme 1.15).[61]

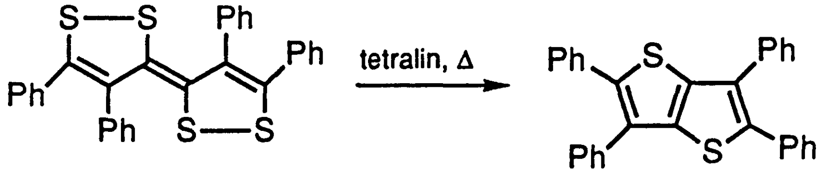


Where X = S, O and R = H, alkyl, acetyl.

Scheme 1.15

1.6.3. Properties of 1,2-tetrathiafulvalenes.

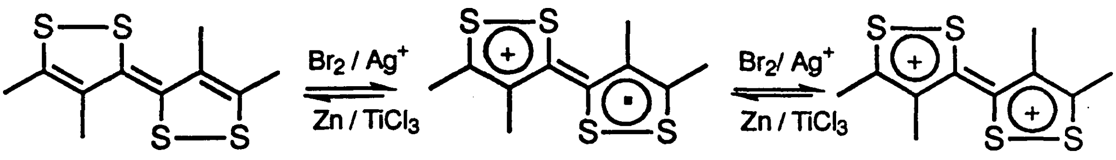
1,2 -TTF are deeply coloured except the amino substituted analogues which are reported to be yellow, and are sparingly soluble in common organic solvents. 1,2-TTF are less thermally stable than 1,3-TTF, for example in boiling tetraline 1,2-TTF (where R^1 and R^2 are phenyl **62**) is converted to the thieno[3,2-*b*]thiophene (**63**) in 80% yield.[42]



62

63

1,2-TTF are very similar to 1,3-TTF in their redox properties. Oxidation to the radical cation or the di-cation can be achieved by using an appropriate oxidizing agent. The neutral 1,2-TTF can proportionate with the di-cations to the radical cation. Zinc or titanium (III) chloride reduces the cations back to neutral 1,2-TTF, hence 1,2-TTF are typical reversible redox systems (Scheme 1.16).[62]



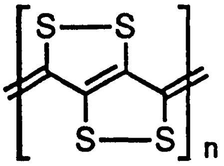
Scheme 1.16

1.6.4. Charge transfer complexes of 1,2-TTF

Charge transfer complexes of 1,2-TTF with several acceptors *e.g.* DDQ, TCNQ, tetracyanoethylene, and tetrafluorotetracyanoquinodimethane have been prepared. Only 1:1 donor-acceptor complexes have been isolated and the donor and acceptor radical ions have been identified in the electron spectra. However the experimental data available is very limited so general conclusions cannot be drawn.

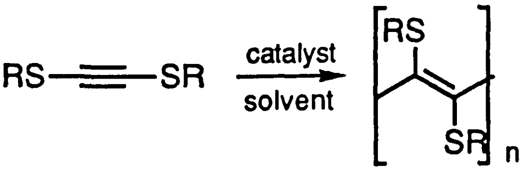
1.6.5. Towards polymeric 1,2-TTF

Poly(acetylene) is known to be a semi-conductor; in 1977 it was noted that if poly(acetylene) is doped with bromine, iodine or AsF_5, then its resistance decreases dramatically and gives polymers with metal-like properties.[63] If a polymeric form of 1,2-TTF (**64**) is considered then it can be seen to consist of a poly(acetylene) backbone with the carbon atoms substituted with sulphur. Such a polymer could be expected to have high electrical conductivity and is also a possible stucture for $(CS)_x$.[64]



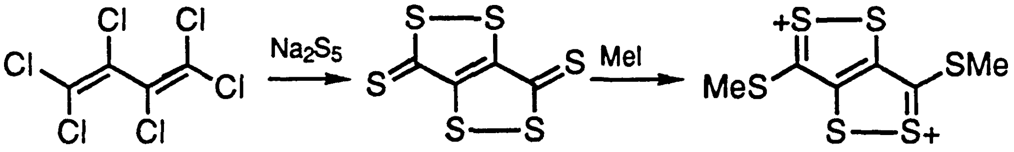
64

There were two approaches to the synthesis of this polymer, The first would be to synthesize the polyacetylenes (**65**), remove the protecting alkyl groups and then connect the 1,3 sulphur atoms. Several examples of the acetylenes (**65a**) were made and polymerized, however reductive alkylation failed as the sulphur-polymer backbone bonds were cleaved as well as the sulphur-alkyl bonds.



65a **65**

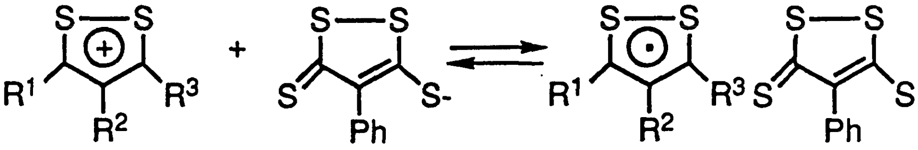
The second strategy was to synthesize monomeric dithiolo-dithioles (**66**) which was achieved by reaction of perchlorobutadiene with sodium pentasulphide in DMF. Salts were made from this dithione in the usual way. However reduction of the di-cation (**67**) gave many products which could not be isolated.



66a **66** **67**

1.7 1,2-Dithioles in charge transfer complexes.

The first report of 1,2-dithioles acting as charge transfer agents came from Pedersen and Loayza in 1975.[65] They found that a mixture of the anion of 4-phenyl-3-thiol-1,2-dithiol-3-thione and 1,2 dithiolium salts formed charge transfer salts (Scheme 1.17).



Scheme 1.17

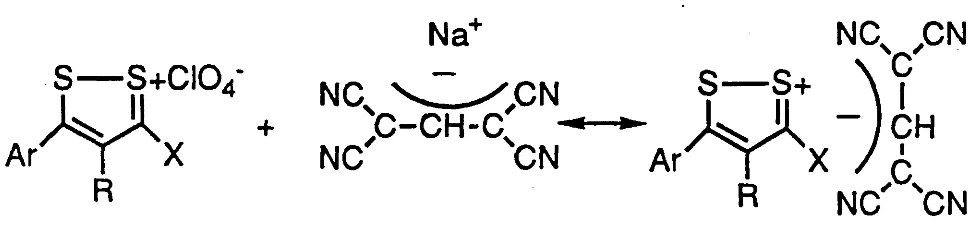
Only in the case where R^1 and R^3 are phenyl and R^2 is hydrogen is the resultant charge transfer complex semi-conducting. It was postulated that the formation of the neutral radical was due to the action of the thiolate anion as an electron donor. These charge transfer salts with an ionic ground state and and an excited state of two neutral radicals are known.[66]

A more detailed paper was published by the same authors in 1977 in which a series of radical ion salts were synthesized from 1,2-dithiolium salts and 4-phenyl-3-thiolate-1,2-dithiol-5-thione, and characterized.[67] All these salts are dark coloured and no charge transfer bands were observed in the UV-visible spectra. However this was probably because any charge transfer bands were being obscured by the intense absorption bands. Charge transfer was deduced to have taken place as the extinction coefficient of the complex at any given wavelength was higher than the sum of the extinction coefficients of the starting ions at the same wavelength..

Support for the complex being the pair of radicals shown was supplied by ESR measurements. The complex containing the 3,5-diphenyl-1,2-dithiolium ion had a weak ESR signal in the solid phase with a *g* value of 2.00 compared to the *g* value of 2.003 measured for the electrochemically generated radical in acetonitrile.

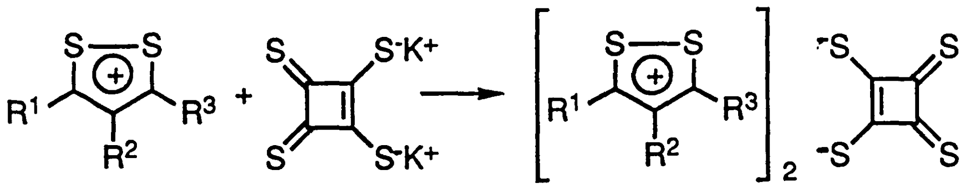
The conductivity of these complexes was investigated. All complexes except for those of the 3,5-diphenyl-1,2-dithiolylium ion had high resistance. The crystal structure of this complex was determined. It is known that for good conductivity in charge transfer complexes the crystals must be highly ordered and consist of segregated stacks. In the 3,5-diphenyl-1,2-dithiolylium complex where there is the highest packing density (the *a* and *b* axes) the stacks are made up of alternating donor and acceptor molecules. Packing in the *c* axis has isolated stacks but the distance between the dithiole rings is 8.47 Å compared to the distance between TTF molecules in the TTF-TCNQ complex which is 3.47 Å. These factors explain the low conductivity of this complex.

Catel and Mollier made a series of charge transfer complexes using tetracyanopropene anion and the 1,2-dithiolium rings as the cation.[68] (Scheme 1.18) They did not carry out any conductivity studies on the resultant compounds but measurement of the UV spectra showed a band due to charge transfer. The position and intensity of this band was dependent upon the polarity of the solvent.



Scheme 1.18

There has also been a report of complexes being formed between 1,2-dithiolium salts and TCNQ.[69] The complexes formed have 1:2 stoichiometry (dithiole:TCNQ) and conductivities comparable to other complexes involving two molecules of TCNQ. When TCNQ was exchanged for dipotassium tetrathiosquarate (**68**), black shiny 2:1 complexes were obtained in the micro crystalline state (Scheme 1.19). Dipotassium tetrathiosquarate complies with the requirements for acceptor salts *i.e.* high symmetry, high polarizability, small molecular size and molecular planarity. However the conductivity was found to be low, this could be attributed to considerable electrostatic repulsion in the solid thus increasing the distance between the molecules.

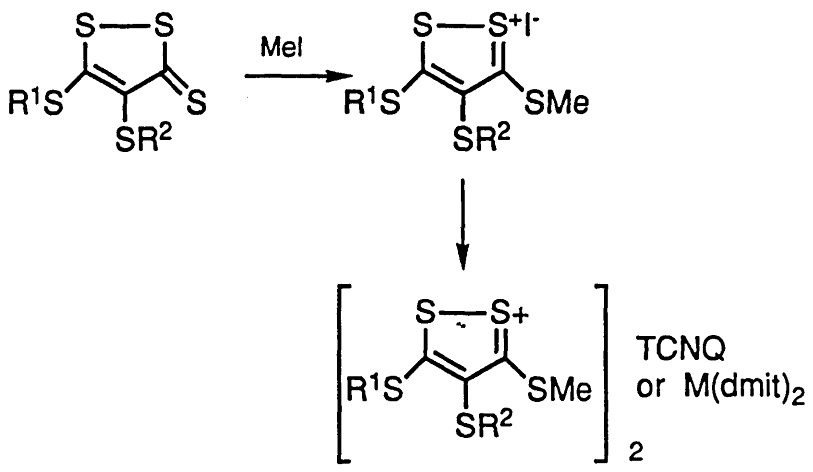


R¹	R²	R³
Ph	H	H
Ph	H	Ph
H	Ph	H

68

Scheme 1.19

Complexes of 1,2-dithiolium salts were also made using TCNQ or metal bis(dimercaptoisotrithione) where the metal is nickel, platinum or palladium.[70] The substituents on the dithiolium ring were alkylthio groups. The dithiolium salts were obtained by treatment of the 1,2-dithiol-3-thiones with methyl iodide and then the complexes were prepared (Scheme 1.20). The D.C. conductivity was measured and was found to be low when metal bis(dimercaptoisotrithione) was the acceptor. However when TCNQ was the acceptor and R^1 and R^2 = Me or R^1 and R^2 = -$(CH_2)_3$-, the complexes were found to be semi-conductors at room temperature. Moreover, conductivity temperature studies indicated that the complexes may undergo a semiconductor / metal phase change above room temperature. It also appears that they are 2D or 3D semiconductors as the conductivity of the polycrystalline compressed discs did not differ significantly from that of single crystals.



Scheme 1.20

1.8 Summary

There have been two approaches to organic conducting metals, polymers with a high level of conjugation, or complexes made up of discrete molecules, which have extensive π-overlap. In both areas interest has been shown in compounds which contain a high proportion of nitrogen and/ or sulphur and some of the materials tested have shown promising results.

Chapter Two

Reaction of sulphur chlorides with organic compounds

2.1 Introduction

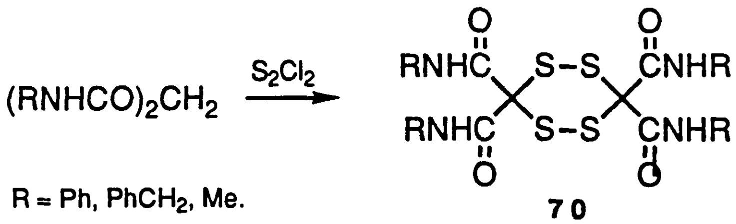
A series of papers was published by Naik in the early 1920's which dealt with the reactions between disulphur dichloride and organic amides as well as active methylene compounds. The work in these papers was based on a thesis written by Naik for a Diploma of Imperial College.[71] He claimed some unusual structures for the products that he obtained, based on microanalytical data and molecular weight measurements. Some reinvestigation of these reactions had been carried out, but not comprehensively; hence it was decided to look at disulphur dichloride as a reagent to introduce sulphur into organic compounds and to see if any of the unusual products claimed by Naik could be obtained.

In the first of the papers published by Naik,[72] he claimed to have synthesized 'thiosulphines' (**69**) by reacting active methylene compounds with disulphur dichloride *i.e.*

$$(RNHCO)_2CH_2 + S_2Cl_2 \longrightarrow (RNHCO)_2C{=}S{=}S$$

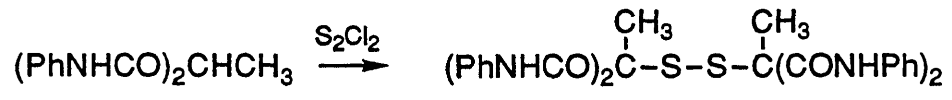
R = Ph, PhCH$_2$, Me. **69**

This reaction was later repeated by Kutney and Still and they showed that when *N,N'*-substituted malondiamides were treated with disulphur dichloride, the corresponding tetrathianes (**70**) were obtained:[73]



70

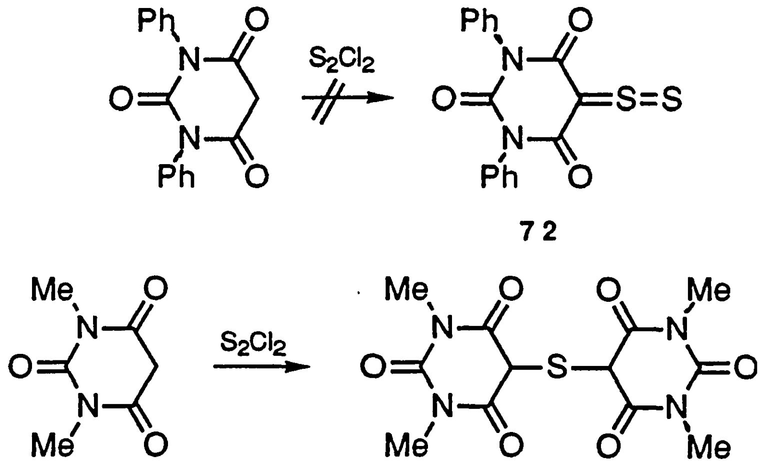
Naik investigated the reaction between disulphur dichloride and *N,N'*-diphenylmethylmalondiamide and also *N,N'*-diphenyldimethylmalondiamide which he claimed to give thiosulphoxides but later he demonstrated that they were non-branched disulphides (**71**).[74]



$$(PhNHCO)_2CHCH_3 \xrightarrow{S_2Cl_2} (PhNHCO)_2\overset{CH_3}{C}-S-S-\overset{CH_3}{C}(CONHPh)_2$$

71

N,N′ -Diphenylbarbituric acid was reported by Naik to give a 'thiosulphine' (72) with disulphur dichloride. When Gompper *et al.* repeated this work using *N,N′* -dimethylbarbituric acid they found that the sulphide (73) was formed; however they used different conditions to those used by Naik.[75] The reaction was repeated by us using both sets of conditions on *N,N′* -dimethylbarbituric acid. When Gompper's method was used, with acetic acid as the solvent and heating at 100 °C the sulphide (73) was obtained in 27% yield. Using Naik's method only starting material and sulphur was obtained in the case of *N,N′* -diphenylbarbituric acid whereas in the case of *N,N′* -dimethylbarbituric acid the corresponding sulphide was obtained (42%). Barbituric acid did not react under either set of conditions possibly due to its insolubility.

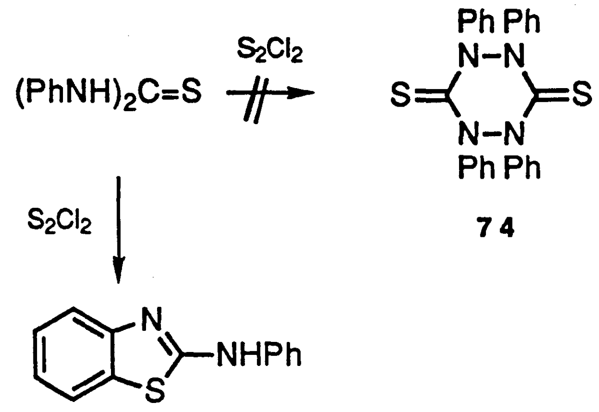


72

73

When Naik treated *N,N′* -diphenylthiourea with disulphur dichloride in refluxing benzene he claimed to have a dimeric product (74) where disulphur dichloride had acted as an oxidizing agent.[76] When we repeated this under the same conditions the only product isolated was shown to have the structure (75)(6%). Thus no sulphur from the disulphur dichloride had been incorporated

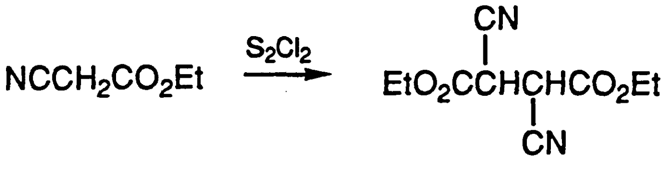
When Naik treated *N,N'* -diphenylthiourea with disulphur dichloride in refluxing benzene he claimed to have a dimeric product (**74**) where disulphur dichloride had acted as an oxidizing agent.[76] When we repeated this under the same conditions the only product isolated was shown to have the structure (**75**)(6%). Thus no sulphur from the disulphur dichloride had been incorporated into the product and oxidative cyclization had occurred to give the aromatic benzothiazole. With thiourea itself, only starting material and sulphur were recovered.



74

75

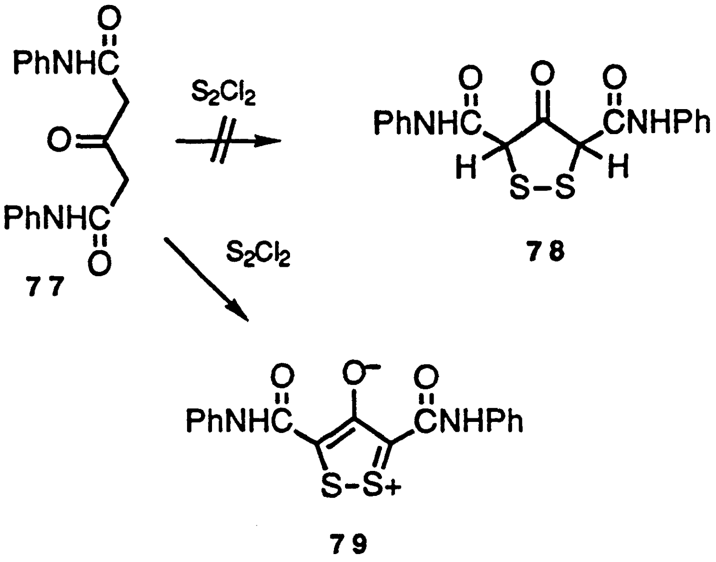
This was not the only instance where disulphur dichloride was shown to behave as an oxidizing agent. When ethyl cyanoacetate was treated with disulphur dichloride and heated in the absence of solvent the product obtained was identified as being diethyl dicyanosuccinate (**76**):[77]



$$\mathrm{NCCH_2CO_2Et} \xrightarrow{S_2Cl_2} \mathrm{EtO_2C}\overset{\mathrm{CN}}{\mathrm{C}}\mathrm{H}\underset{\mathrm{CN}}{\mathrm{C}}\mathrm{HCO_2Et}$$

76

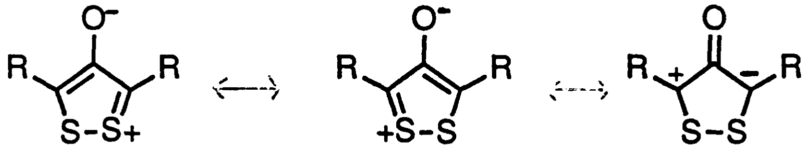
The dianilide of acetone-1,3-dicarboxylic acid (**77**) was prepared by the method of Besthorn and Garben from diethyl acetone-1,3-dicarboxylate and aniline.[78] When this was treated with disulphur dichloride in refluxing benzene a red solid formed. This was found to have an M^+ in the mass spectrum which was two units less than expected for the product (**78**) Naik had claimed. On the basis of this, its deep colour and very polar nature it was deduced to have the five membered mesoionic ring structure (**79**).



This was a pleasing result which warranted further investigation.

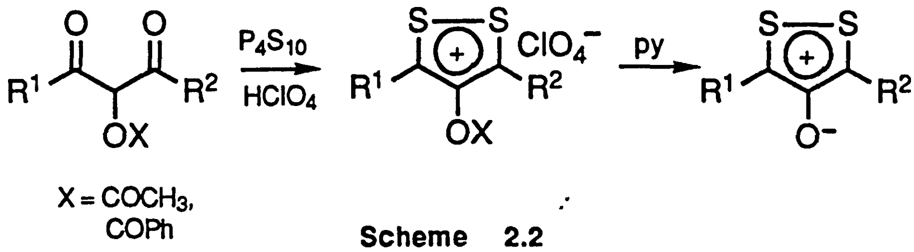
2.2 1,2-Dithiolium-4-olates

The 1,2-dithiolium-4-olate ring is termed a type B mesoionic. According to Newton and Ramsden "*a compound may be appropriately called mesoionic if it is a five-membered heterocycle which cannot be represented satisfactorily by any one covalent or polar structure and possesses a sextet of electrons in association with the five atoms comprising the ring* ".[79] They are sub-divided further into types A and B according to the origin of the sextet of electrons. There are eight π -electrons involved in this system , two are contributed from each sulphur atom, one from each carbon atom and one from the oxygen atom. There are also three valence bond structures which can be regarded to contribute to the overall structure (Scheme 2.1):



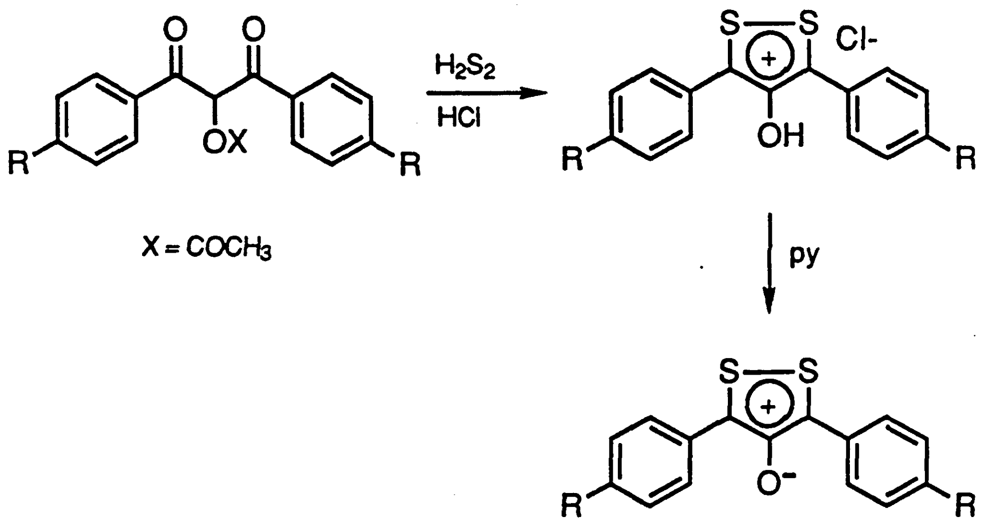
Scheme 2.1

To date, seventeen examples of this particular ring system have been published, most of which have phenyl or substituted benzene rings as the groups in the 3- and 5- positions. The usual method of preparation involves converting a suitably protected 2-hydroxy-1,3-diketone into the dithione followed by treatment with a suitable base. In the case shown below phosphorus pentasulfide is used as the sulphurizing agent (Scheme 2.2):[80]



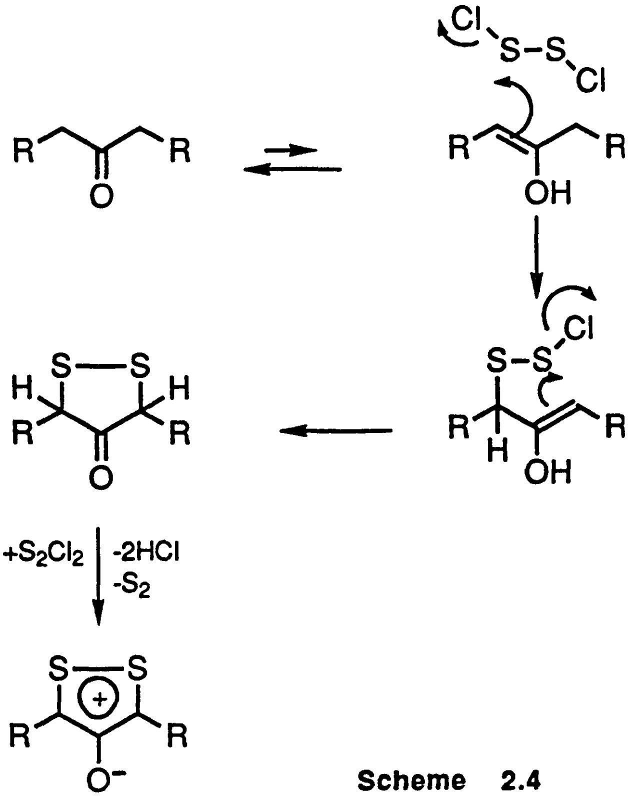
Scheme 2.2

Many symmetrical examples were prepared from the acetyl protected 2-hydroxy-1,3-diketone using hydrogen disulphide and hydrogen chloride as the sulphurizing agent. Again pyridine was used as the base to give the 1,2-dithiolium-4-olate (Scheme 2.3):[81]



Scheme 2.3

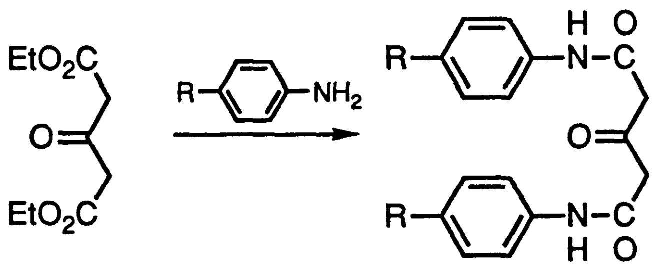
In all the previous syntheses of these 1,2-dithiolium-4-olates trifunctionality of the starting material is required and a source of sulphur which is nucleophilic. In the present synthesis of the 1,2-dithiolium-4-olates using disulphur dichloride the sulphur is electrophilic and requires attack by a nucleophile which is provided by the monofunctional active methylene compound. The postulated mechanism of the reaction is outlined overleaf (Scheme 2.4).



Scheme 2.4

Initial attack on the electrophilic sulphur could be by the π-electrons of the double bond of the enol form of the ketone, with subsequent loss of HCl. The same process occurs at the other side of the carbonyl function giving the dihydro form of the 1,2-dithiolium-4-olate. This could be oxidized by another molecule of disulphur dichloride, which has been shown to act in this manner in the previous section, as excess of disulphur dichloride is present.

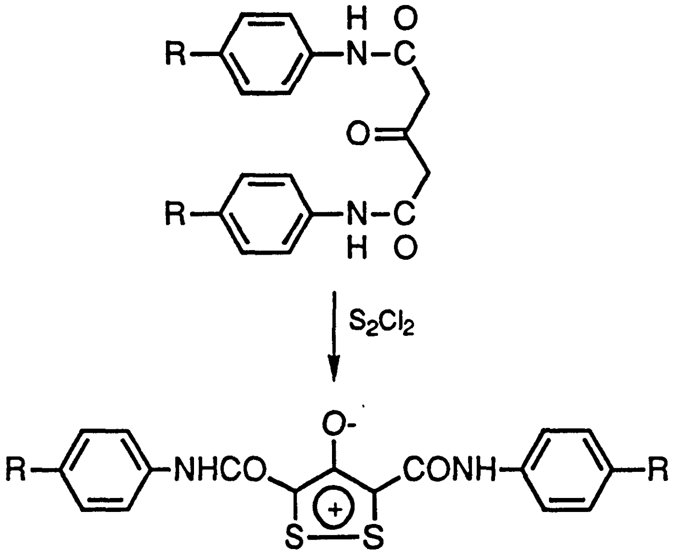
The product (79) from the dianilide (77) was obtained in only 23% yield when carried out using Naik's conditions of refluxing benzene for 2 h. The yield was improved dramatically (70%) by increasing the temperature to 110 °C by using toluene as the solvent. The dianilide starting material (77) was obtained by the method of Besthorn and Garben in poor yield (23%). If p -toluidine was used in place of aniline the yield was better (45%) (Scheme 2.5).



R = H, yield 23%
CH$_3$, yield 45%

Scheme 2.5

With disulphur dichloride in refluxing benzene the corresponding 1,2-dithiolium-4-olate (**80**) was obtained in moderate yield (40%). Use of toluene as solvent improved the yield slightly (50%). These results are summarized below (Scheme 2.6).

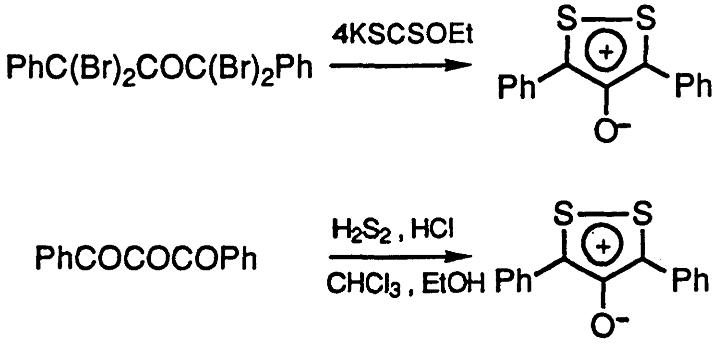


R	solvent	yield
H	benzene	23%
H	toluene	70%
CH$_3$	benzene	40%
CH$_3$	toluene	50%

79 R = H
80 R = CH$_3$

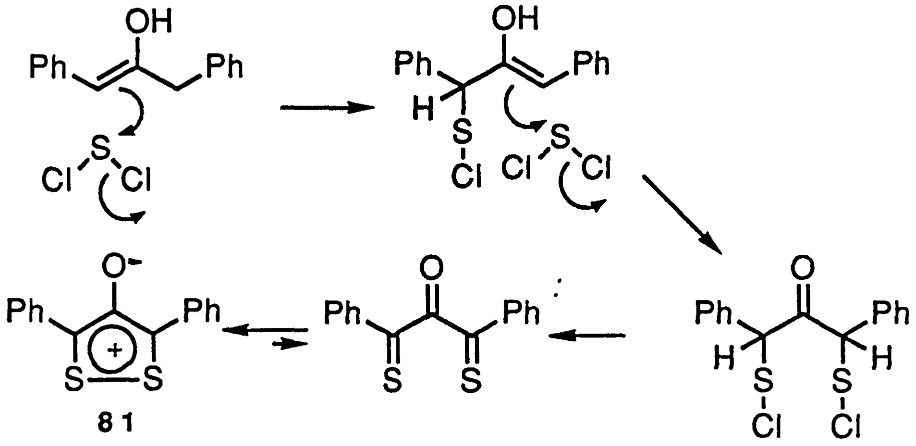
Scheme 2.6

With these results in mind, simpler ketones were considered, in particular 1,3-diphenylpropan-2-one. The corresponding 3,5-diphenyl-1,2-ditholium-4-olate is known and was first synthesized by Schonberg and Frese in 1969 and obtained as brown crystals.[82] Apart from the syntheses already outlined, two others had also been used to make this compound; again all the starting materials were trifunctional (Scheme 2.7).[83]



Scheme 2.7

The reaction between 1,3-diphenylpropan-2-one and disulphur dichloride was tried under various conditions. The best conditions were using THF as the solvent and refluxing for two hours gave the hydrochloride salt as a yellow oil, which when treated with pyridine gave 3,5-diphenyl-1,2-dithiolium-4-olate (**81**) (25%) as purple crystals. This yield was improved to 40% by using two equivalents of freshly distilled monosulphur dichloride. By analogy to the mechanism postulated for the reaction with disulphur dichloride; sulphur dichloride can react with loss of four moles of hydrogen chloride to give the dithiolium ring (Scheme 2.8):

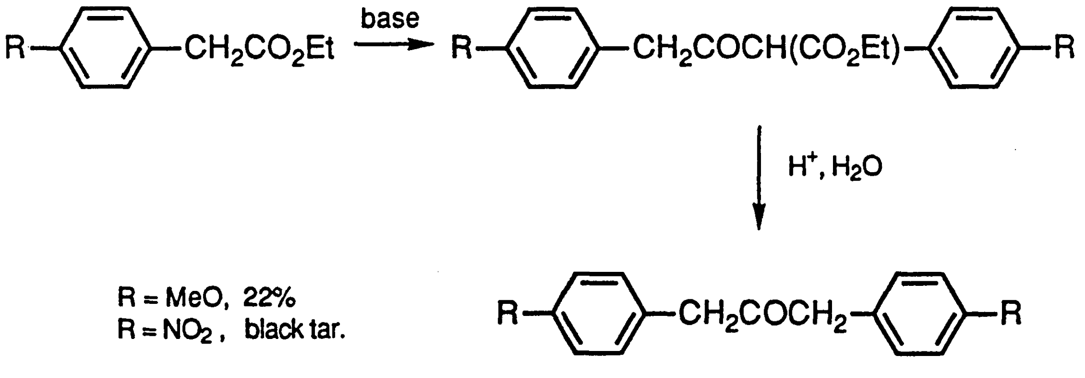


Scheme 2.8

The use of sulphur dichloride was also tried with the acetone-1,3-dicarboxyanilides (Scheme 2.5), the corresponding dithiolium-4-olates were obtained but in poor yield (20% and 15%); this was due at least partly to purification problems.

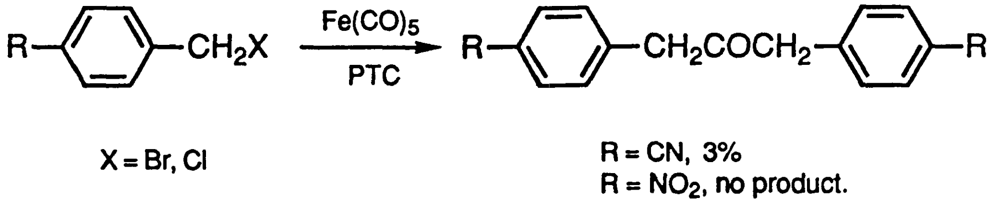
In order to explore the extent of this reaction it was decided to prepare some suitably substituted 1,3-diphenylpropan-2-ones. The effect of the substituent groups on the acidity of the methylene groups would be particularly interesting as this may support our postulated mechanism. With this in mind it was decided to prepare 1,3-bis(4-methoxyphenyl)propan-2-one and 1,3-bis(4-nitrophenyl)propan-2-one. The former was prepared as colourless needles using the method of Coan et al.[84] When treated with sulphur dichloride under the same conditions as used for (**81**) the corresponding dithiolium-4-olate was obtained but in a very poor yield (4%).

There were only three references in the literature to 1,3-bis(4-nitrophenyl)propan-2-one, which had been synthesized by nitration of 1,3-diphenylpropan-2-one.[85] A mixture of three isomers was obtained. When repeated the desired compound was obtained in very poor yield (5%) and this was not pure. Hence a different method was desirable. The method used for the methoxy analogue i.e. treatment of ethyl 4-nitrophenylacetate with base followed by hydrolysis and decarboxylation failed at the first stage when a black tar was obtained (Scheme 2.9).



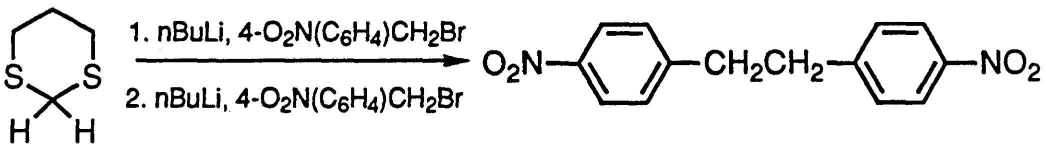
Scheme 2.9

Another method devised to synthesize symmetrical ketones was using the relevant benzyl halide and treating this with iron pentacarbonyl in the presence of a phase transfer agent (Scheme 2.10).[86] However with 4-nitrobenzylbromide none of the desired product was obtained; with 4-cyanobenzylchloride the symmetrical ketone was obtained but in very low yield (3%).



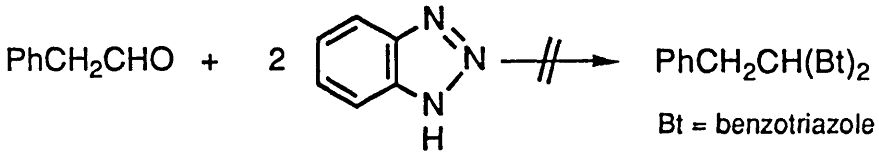
Scheme 2.10

As an alternative approach it was decided to try masking the ketone functionality using 1,3 dithiane.[87] Formation of the anion of 1,3-dithiane and reacting this with 4-nitrobenzyl bromide should give the corresponding substituted dithiane. Repeating this procedure followed by treatment of the dithiane ring with mercury (II) chloride should give the ketone functionality. The product actually obtained from this procedure was 1,2-bis(4-nitrophenyl)ethane (Scheme 2.11):



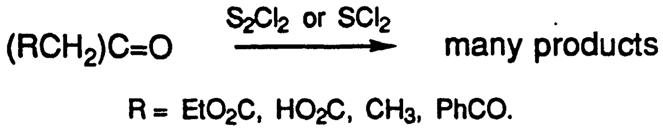
Scheme 2.11

Another method which also involved protection of the carbonyl function was Katritzky's method using benzotriazole and its reaction with aldehydes.[88] The proton on the carbon bearing the two benzotriazole groups can be removed using n -butyllithium and the carbanion formed can act as a nucleophile; it is stabilized by the benzotriazole groups. Although the reaction had been investigated extensively there was no mention in the literature of the reaction between phenylacetaldehyde and benzotriazole so this was tried as a model before trying 4-nitrophenylacetaldehyde. Unfortunately no reaction occurred between phenylacetaldehyde and benzotriazole (Scheme 2.12):



Scheme 2.12

Some other ketones with various functionality were reacted with disulphur dichloride and sulphur dichloride in order to try and synthesize the 1,2-dithiolium-4-olates. These included diethyl acetone-1,3-dicarboxylate, acetone-1,3-dicarboxylic acid, pentan-3-one, and 1,5-diphenylpentan-1,3,5-trione. In each case under various conditions the reactions were messy and no products could be isolated cleanly (Scheme 2.13)



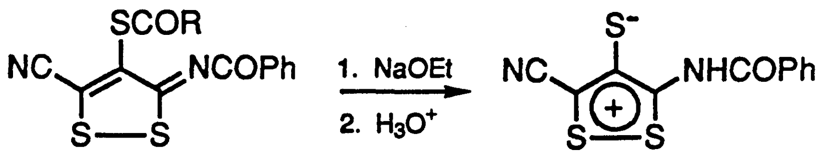
$$(RCH_2)C{=}O \xrightarrow{S_2Cl_2 \text{ or } SCl_2} \text{many products}$$

$$R = EtO_2C,\ HO_2C,\ CH_3,\ PhCO.$$

Scheme 2.13

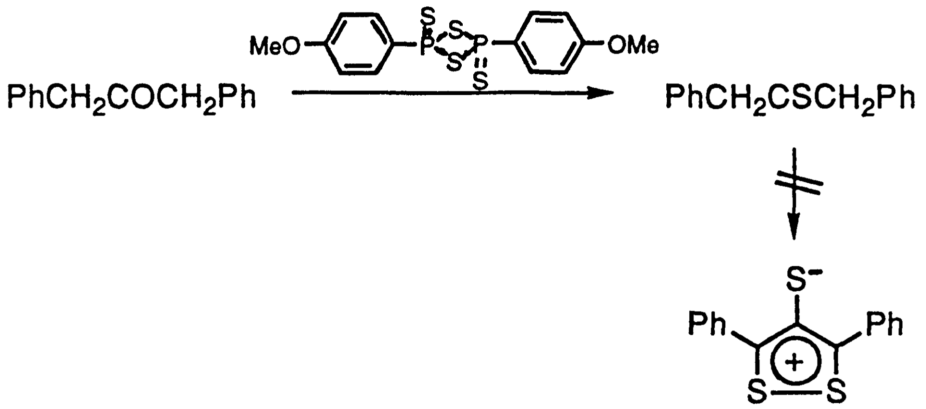
2.3 Attempts to synthesize 1,2-dithiolium-4-thiolates

There is only one example of this type B mesoionic (**84**) in the literature.[89] Compound (**83**) was prepared by treatment of sodium cyanothioformate with two equivalents of an appropriate benzoyl halide. Subsequent treatment of this compound with sodium ethoxide cleaved the sulphur-carbon bond with loss of the ester (RCO_2Et). An acid wash of the sodium thiolate gave the mesoionic.



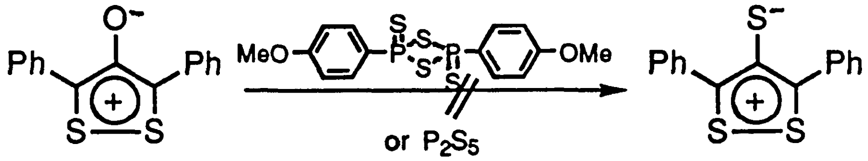
83 **84**

It would be very attractive if this type of compound could be made using the disulphur dichloride/ sulphur dichloride methodology. Hence 1,3-diphenylpropan-2-thione was prepared from 1,3-diphenylpropan-2-one with Lawesson's reagent in good yield (70%).[90] Treatment of this with disulphur dichloride and with sulphur dichloride under various conditions did not give the corresponding 1,2-dithiolium-4-thiolate (Scheme 2.14).



Scheme 2.14

An alternative approach to this type of compound would be to treat 3,5-diphenyl-1,2-dithiolium-4-olate with some sulphurizing agent such as phosphorus pentasulphide or Lawesson's reagent. Both these reagents were tried using the usual conditions of refluxing toluene, but no reaction occurred (Scheme 2.15).

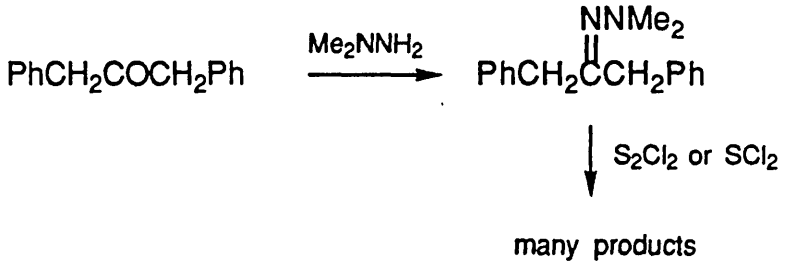


Scheme 2.15

The compound (79) was also treated with Lawesson's reagent; in this case at room temperature no reaction occurred but after refluxing for one hour TLC showed many products which could not be isolated cleanly.

Other groups to replace oxygen:

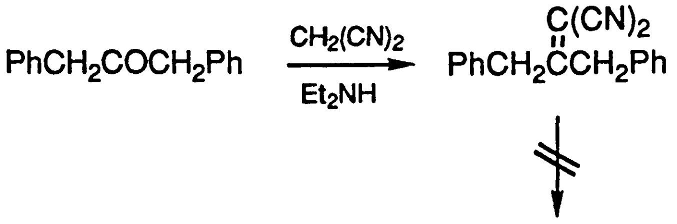
It would be interesting to obtain the 1,2-dithiolium ring system with a group containing nitrogen in the 4- position, and also with carbon in the 4-position. The former was introduced into 1,3-diphenylpropan-2-one using 1,1-dimethylhydrazine,[91] however all subsequent reactions with disulphur dichloride or sulphur dichloride gave many products on TLC even when carried out at -78 °C (Scheme 2.16).



$$PhCH_2COCH_2Ph \xrightarrow{Me_2NNH_2} PhCH_2\overset{NNMe_2}{\overset{\|}{C}}CH_2Ph \xrightarrow{S_2Cl_2 \text{ or } SCl_2} \text{many products}$$

Scheme 2.16

1,3-Diphenylpropan-2-one was condensed with malononitrile using the method of Ferrier and Campbell.[92] This group was chosen as it was postulated that the two cyano groups would help stabilize a negative charge on the adjacent carbon. When taken with disulphur dichloride or sulphur dichloride no reaction occurred even after prolonged refluxing in toluene (Scheme 2.17).



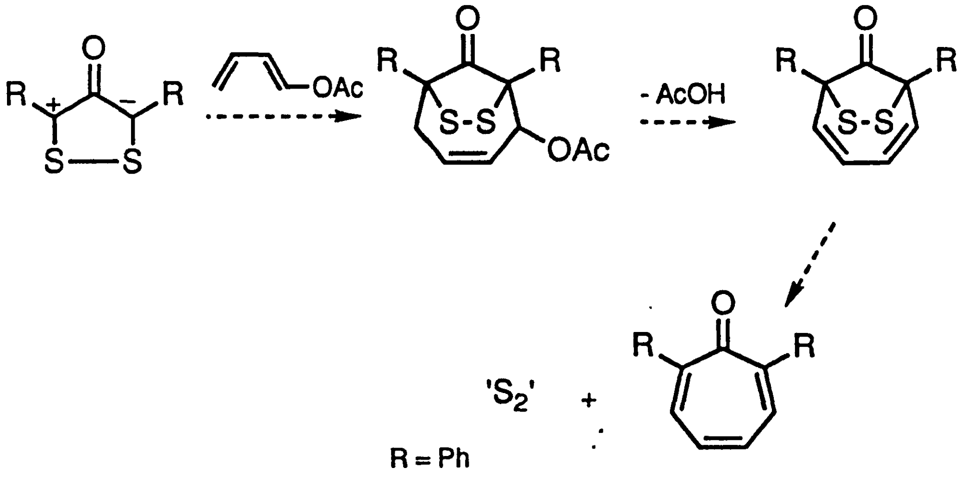
$$\mathrm{PhCH_2COCH_2Ph} \xrightarrow[\mathrm{Et_2NH}]{\mathrm{CH_2(CN)_2}} \mathrm{PhCH_2\overset{C(CN)_2}{\overset{\|}{C}}CH_2Ph}$$

Scheme 2.17

2.4 Reactions of 1,2-dithiolium-4-olates.

A paper was published in 1984 by Hantke and Gotthardt concerning cycloaddition reactions of 1,2-dithiolium-4-olates with 1,3-dienes.[93] The diene added across the 3- and 5- carbons to give a seven-membered ring with a disulphide bridge. Although type B mesoionics do not usually act as 1,3-dipoles, a paper published by Barillier on dipole moment measurements of 1,2-dithiolium-4-olates showed there was a significant contribution from the canonical form with the charges residing on the carbon atoms in the ring.[94]

This was of interest as we wanted to see if we could set up a system where "S_2" might be eliminated readily. Thus if the cycloaddition of 3,5-diphenyl-1,2-dithiolium-4-olate with acetoxy-1,3-butadiene was carried out followed by elimination of acetic acid, then the system would be set up to eliminate "S_2" (Scheme 2.18).



Scheme 2.18

When the reaction was carried out in refluxing toluene a product was obtained. Its mass spectrum showed an M^+ for the compound desired but ^1H

NMR showed it to be impure. Furthermore only a small amount was obtained. Other cycloaddition reactions were tried with tetraphenylcyclopentadienone, 2,5-dimethyl-3,4-diphenylcyclopentadienone, and diphenylcyclopropenone, but in each case no reaction occurred after prolonged refluxing in xylene.

2.5 Summary

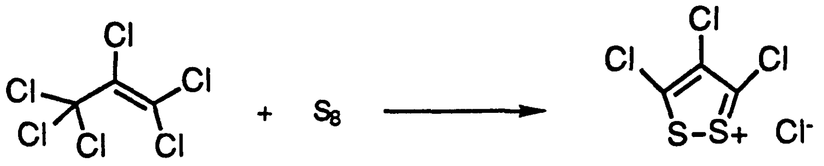
Certain 1,2-dithiolium-4-olates can be synthesized from the reaction of disulphur dichloride with active methylene compounds. Sulphur dichloride and dibenzyl ketone give the corresponding 3,5-diphenyl-1,2-dithiolium-4-olate in good yield; however this reaction is not general and attempts to make other 1,2-dithiolium ring systems using this methodology failed.

Chapter Three

Chemistry of 3,4,5-Trichloro-1,2-dithiolium chloride and related compounds

3.1 Introduction

In 1964 a paper was published by Boberg and his co-workers[95] concerning the reactions of perchloropropenes and fluorochloropropenes with sulphur, disulphur dichloride and chloromethane sulphenyl chlorides. One of the reactions investigated was that between hexachloropropene and sulphur, which when heated together in the absence of solvent gave as its major products disulphur dichloride (78%) and 3,4,5-trichloro-1,2-dithiolium chloride (**85**) (65% conversion).

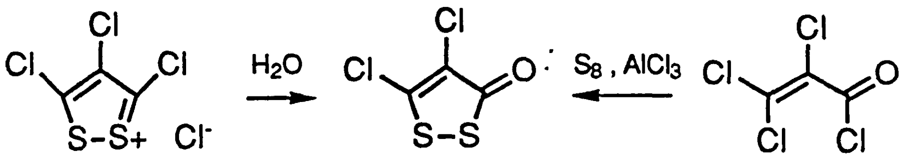


85

The reaction occurs above 160 °C when the sulphur ring ruptures to form a polymeric chain with radical ends. It appears that the presence of disulphur dichloride is important, since removal of this by distillation during the reaction leads to much poorer yields of the trichloro salt (**85**).

Boberg originally assigned the structure as 3,3,4,5-tetrachloro-1,2-dithiacyclopentene on the basis of its formation and hydrolysis to 4,5-dichloro-1,2-dithiol-3-one (**86**). Having considered the UV spectra and its insolubility in common organic solvents he acknowledged the more probable salt-like structure.

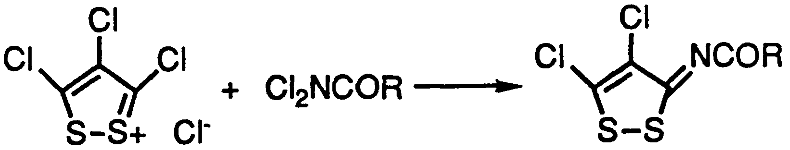
Some chemistry of the trichloro salt (**85**) has been studied; the ready hydrolysis to 4,5-dichloro-1,2-dithiol-3-one (**86**) was noted.[96] This can also be obtained directly from the reaction of trichloroacryloyl chloride, sulphur and aluminium



86

chloride.[95] Attempts to obtain the trichloro salt (**85**) from the corresponding 1,2-dithiol-3-one using oxalyl chloride failed.[52] No other reports on the trichloro salt

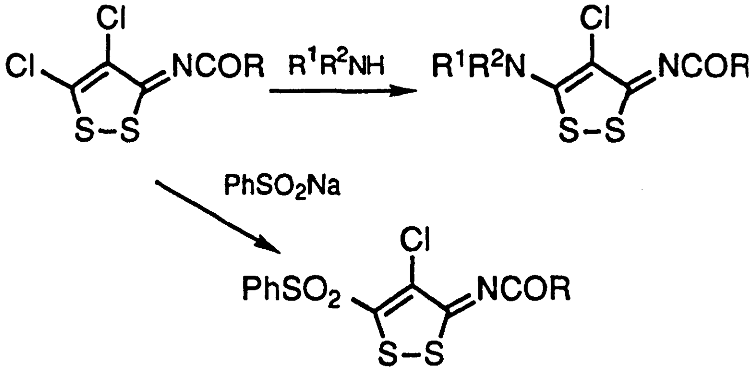
(**85**) were seen in the literature until 1973 when the reaction between 3-chloro-1,2-dithiolium chlorides and *N,N*-dichloronitrobenzamides was published.[97]



87

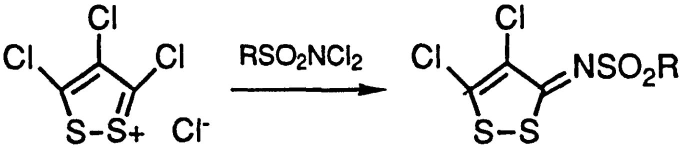
R = $2\text{-}NO_2C_6H_4$; $2,4\text{-}(NO_2)_2C_6H_3$

The products (**87**) of this reaction were shown to react with nucleophiles (specifically secondary and primary amines, and sodium benzene sulphinate) to give displacement of the chloro group in the 5- position (Scheme 3.1).



Scheme 3.1

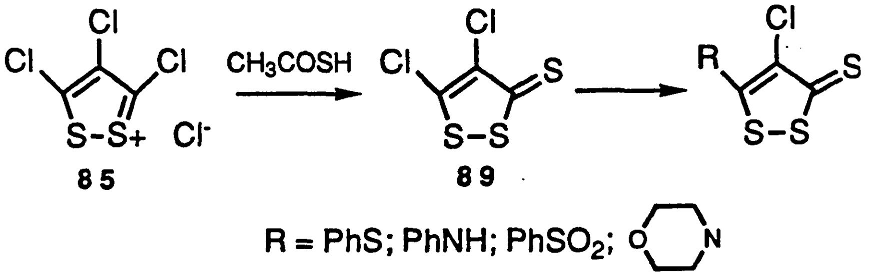
In an analogous manner, reaction between the trichloro salt (**85**) and *N,N*-dichlorosulphonamides gave the corresponding iminodithioles (**88**):[98]



88

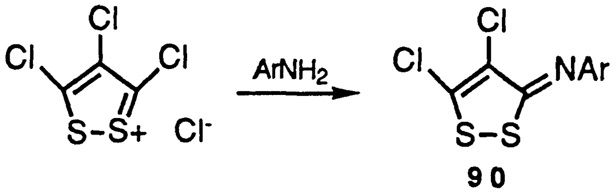
R = Ph; $N(CH_3)_2$

Treatment of the trichloro salt (**85**) with thioacetic acid was shown to give 4,5-dichloro-1,2-dithiol-3-thione (**89**) in 35% yield. Furthermore, the 5-chloro group was shown to be displaceable by various nucleophiles (Scheme 3.2).[99]



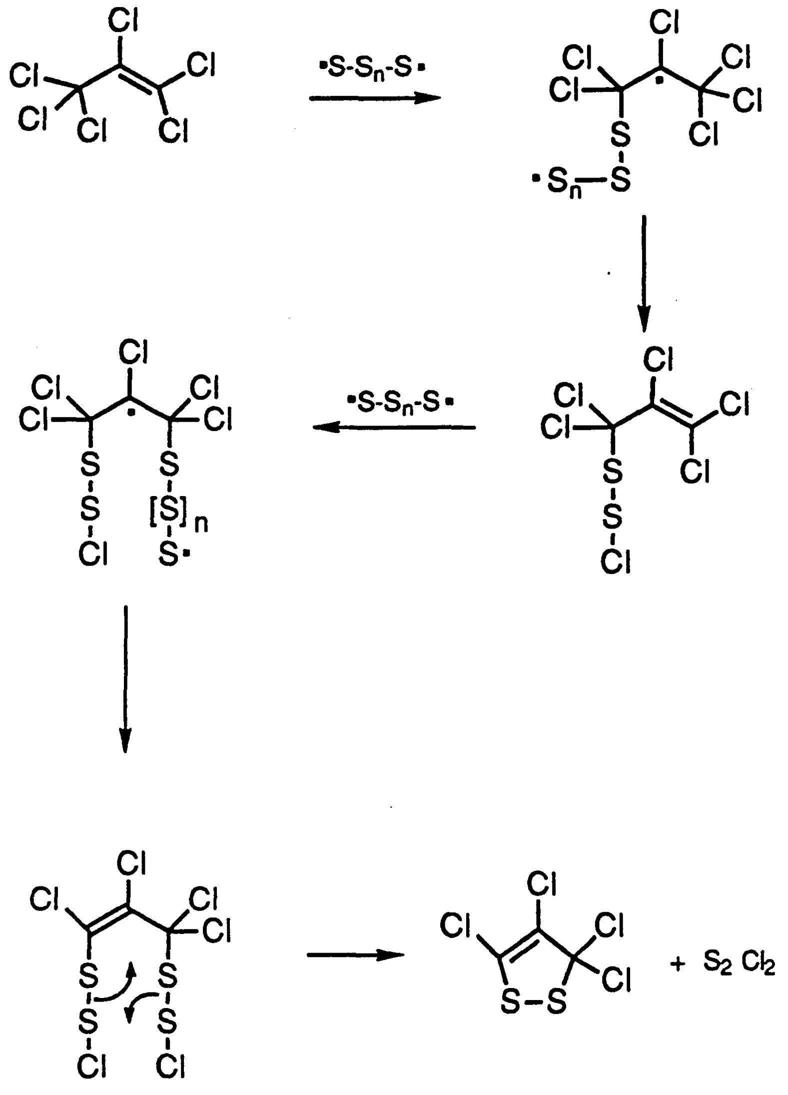
Scheme 3.2

Two patents were published concerning the arylimines (**90**) formed from the reaction of arylamines and the trichloro salt. These were found to be potent pesticides; the most active compounds having a chloro or methoxy substituent on the aryl ring.[100]



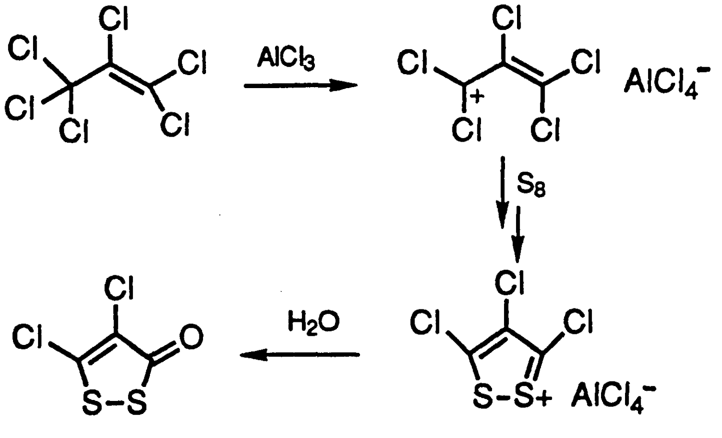
3.1.1 *Preparation of the trichloro salt* (85)

The trichloro salt (85) was prepared using Boberg's method.[95] The mechanism of the reaction between hexachloropropene and sulphur is not known; however it has been reported that above 160 °C the eight membered sulphur ring ruptures to give a diradical chain[101] - hence a radical mechanism seems likely. This is supported by some preliminary investigations made in our laboratory. Addition of a catalytic amount of potassium thiocyanate had no effect on either yield or temperature of the reaction. Addition of benzoquinone, a radical inhibitor, gave a black insoluble product which has not been characterized, but there was no trace of the trichloro salt (85) or 4,5-dichloro-1,2-dithiol-3-one (86). The mechanism proposed (Scheme 3.3) accounts for the above facts, as well as the formation of disulphur dichloride in such high yield.



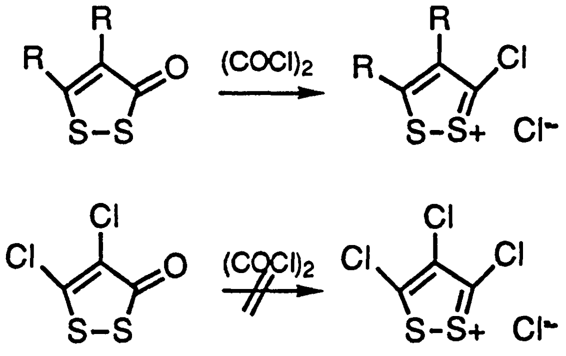
Scheme 3.3

It was also reported in the original paper, that in the presence of anhydrous aluminium chloride, hexachloropropene reacts with sulphur at 80 °C.[95] This reaction is so rapid that excess of hexachloropropene is necessary as a diluent. However, the product is very moisture sensitive, and is not isolated but hydrolyzed to the dithiolone (**86**). It seems likely in this case that the role of the aluminium chloride is to form a complex with the hexachloropropene such that a positive charge is present on carbon hence facilitating nucleophilic attack by the sulphur (Scheme 3.4).



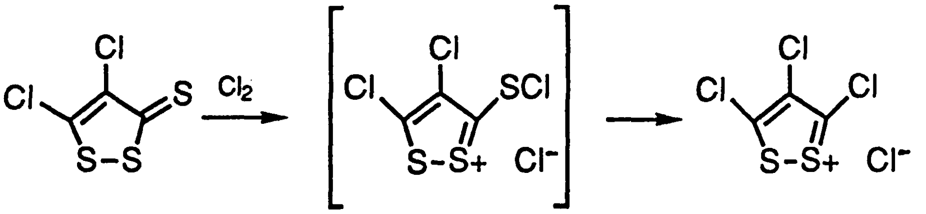
Scheme 3.4

3,4,5-Trichloro-1,2-dithiolium chloride (**85**) is formed as a brown solid which may be purified by vacuum sublimation when it is obtained as yellow crystals, though some decomposition also occurs. It was reported that treatment of 1,2-dithiol-3-ones with oxalyl chloride gave 1,2-dithiolium chlorides;[97] however treatment of 4,5-dichloro-1,2-dithiol-3-one (**86**) with oxalyl chloride under a variety of conditions did not give the trichloro salt (**85**) (Scheme 3.5).



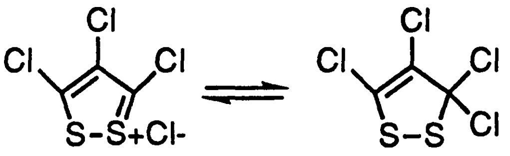
Scheme 3.5

When a solution of 4,5-dichloro-1,2-dithiol-3-thione (**89**) in DCM was treated with chlorine gas, a yellow precipitate was formed, which proved to be the pure trichloro salt (**85**) (37%). The intermediate sulphenyl chloride (**91**) was not isolated.



89 **91** **85**

The trichloro salt (**85**) is insoluble in all common organic solvents, and it is postulated that the aromatic, *i.e.* salt-like, form is favoured over the covalent form. However the mass spectrum of the trichloro salt (**85**) shows a molecular ion corresponding to the covalent form with an *m/z* value of 242. The UV spectra point to (**85**) having a salt-like character.[95]

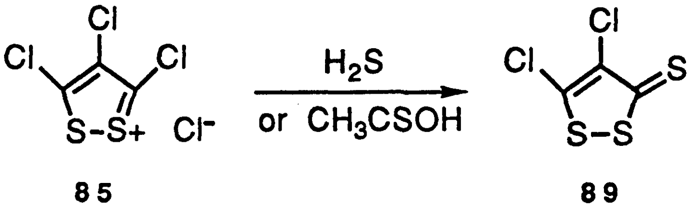


3,4,5-Trichloro-1,2-dithiolium chloride (**85**) reacts with water to give 4,5-dichloro-1,2-dithiol-3-one (**86**) in quantitative yield.[96] The salt is stable if stored under vacuum; if left open to the atmosphere it slowly converts to the dithiolone (**86**).

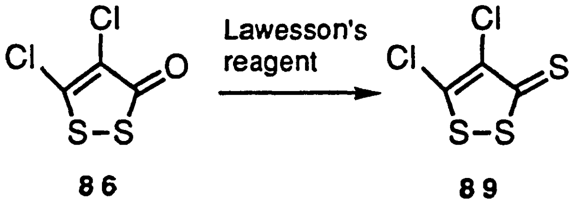
3.2 Chemistry of 3,4,5-trichloro-1,2-dithiolium chloride

3.2.1 *Reactions with water, hydrogen sulphide, and ammonia*

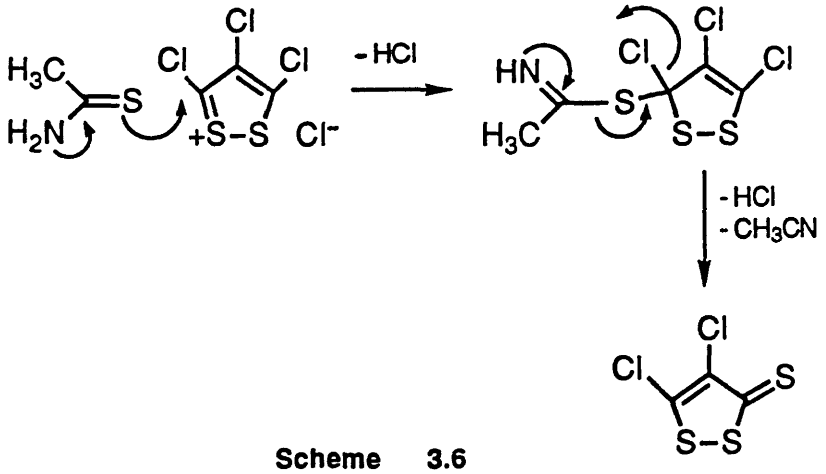
As mentioned previously, treatment of (85) with water gives 4,5-dichloro-1,2-dithiol-3-one (86) in quantitative yield. This product is commercially available (Fluka) and has been patented extensively as an anti-fouling agent.[102] Some of its chemistry will be discussed later in this chapter. In an analogous manner, treatment of (85) with hydrogen sulphide gives 4,5-dichloro-1,2-dithiol-3-thione (89) in 75-90% yield. As mentioned previously the dithiolthione (89) had been prepared by reaction of the trichloro salt (85) with thioacetic acid in 35% yield.[99]



The dithiolthione (89) is an orange crystalline compound which melts at 76 °C. Reaction of the dithiolone (86) with Lawesson's reagent (0.5 equivalents) also gives the dithiolthione (89) in 74% yield. However when

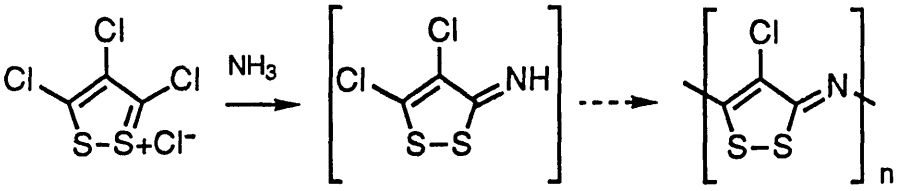


this method is used the ketone has to be isolated and purified otherwise the yield of dithiolthione is very poor due to purification problems. The best method for preparing the dithiolthione (89) is using thioacetamide in DCM as a sulphurating agent with the trichloro salt (85). The reaction occurs through the sulphur rather than the nitrogen atom of thioacetamide and acetonitrile is probably formed as a by-product. The yield of this reaction is at least 90%; it eliminates the need to use hydrogen sulphide and is in only one step from the salt (Scheme 3.6).



Scheme 3.6

No products were isolated from the reaction of the trichloro salt (**85**) and ammonia gas. The expected product would be the unsubstituted imine (**92**), assuming that the reaction between the salt and ammonia followed the same pattern as that for water and hydrogen sulphide, but this would probably be unstable and react further. There was no dithiolone (**86**) present and therefore hydrolysis had not occurred; polymerization is a possibility:

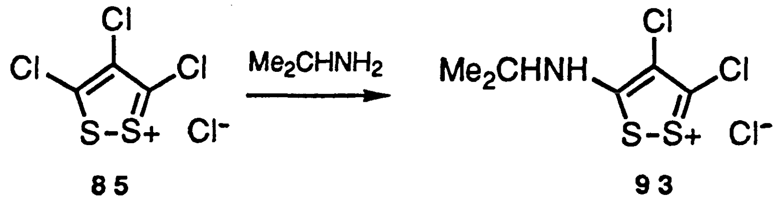


92

3.2.2 *Reactions of the trichloro salt with amines*

a) Aliphatic amines: The reaction of the trichloro salt (**85**) with *n*-butylamine, isopropylamine, *t*-butylamine and benzylamine were investigated. In the case of *n*-butylamine, two compounds were observed on TLC, one of which corresponded to the dithiolone (**86**). On work-up (treatment with pyridine followed by chromatography using silica gel or alumina) only the dithiolone (**86**) was obtained; hence if any imine was formed it was hydrolyzed during work-up.

With isopropylamine, the imine was formed as the hydrochloride salt (**93**) which was stable enough to be characterized.Treatment with base did not give the desired imine which was very sensitive to hydrolysis.



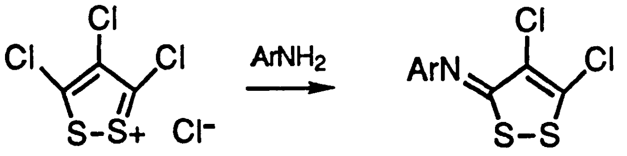
85 **93**

Reaction of the trichloro salt (**85**) with *t*-butylamine gave the dithiolthione (**89**) in 55% yield based on two equivalents of the trichloro salt for every dithiolthione (**89**). Hence it appears that *t*-butylamine attacks the sulphur in the ring preferentially to carbon and the opened ring reacts with another molecule of the trichloro salt (**85**) at the carbon to give the dithiolthione (**89**).

Benzylamine gave only dithiolone (**86**), and even heptamethyldisilazane gave only dithiolone (**86**), although this reacted with the analogous 4,5-dichloro-1,2,3-dithiazolium chloride (**94**) to give the corresponding methylimine (**95**).[103]

94 **95**

b) Aromatic amines: The reaction of the trichloro salt with aromatic amines gave the *N*-arylimines (**90**) after treatment with a suitable base.



90

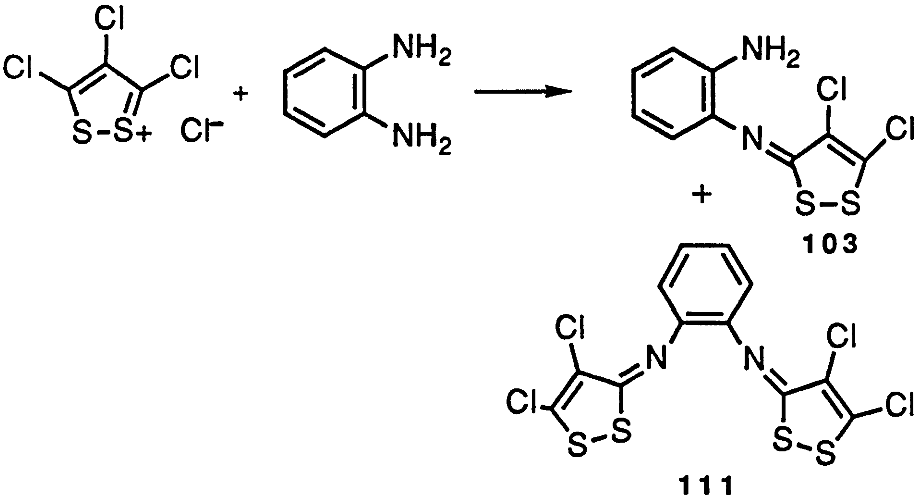
Ar	product	yield (%)	m.p. (°C)
C_6H_5	**(96)**	82	73
4-MeC_6H_4	**(97)**	77	102
4-$NO_2C_6H_4$	**(98)**	81	167
4-$MeOC_6H_4$	**(99)**	84	77
2-pyridyl	**(100)**	40	199
2,6-$Me_2C_6H_3$	**(101)**	65	oil
2-$NO_2C_6H_4$	**(102)**	72	118
2-$NH_2C_6H_4$	**(103)**	22	150
2-HOC_6H_4	**(104)**	80	80
3,5-diMe-2-HOC_6H_2	**(105)**	76	134
2-$N_3C_6H_4$	**(106)**	56	105
3-$NO_2C_6H_4$	**(107)**	63	128
4-ClC_6H_4	**(108)**	90	92
4-$EtO_2CC_6H_4$	**(109)**	93	122
4-$Et_2NC_6H_4$	**(110)**	29	oil

These imines have been extensively covered by patents as they have been found to be potent herbicides.[100] However their chemistry has not been investigated and so we made the compounds shown in Table 1. In general they were synthesized by addition of the trichloro salt (**85**) portionwise to a solution of the amine in DCM; subsequent treatment of the hydrochloride salt with two equivalents of pyridine and purification by column chromatography gave the required imine (**90**) in good yield, as shown in Table 1, in almost all cases. No decrease in either rate of reaction or yield of imine was observed for those anilines with electron withdrawing groups on the phenyl ring, except for 2,6-dinitroaniline which did not react at all under these conditions. This indicates the high reactivity of the trichloro salt (**85**).

The *N* -aryl imines (**90**) were obtained as yellow orange crystals from DCM and light petroleum and are stable to air and moisture for extended periods of time. The mass spectral fragmentation often shows loss of chlorine as well as fragmentation of any functional groups present on the phenyl ring. The IR spectra usually show peaks due to the carbon-nitrogen double bond in the range 1590-1620 cm^{-1} and a peak at *ca.* 850 cm^{-1} which is thought to be due to the dithiole ring as it is also observed in other compounds containing the dithiole ring.

A poor yield was obtained for the reaction between the trichloro salt and *p* -diethylaminoaniline, no other products being observed by TLC, except for baseline material. This may be due to easy oxidation of the aniline although the reaction was carried out under argon.

Reaction of the trichlorosalt (**85**) with *o* -phenylenediamine gave the desired product (**103**) in 11% yield when one equivalent of amine was used. The major product in this case was the di-imine (**111**), which was obtained in 58% based on (**85**). The yield of (**111**) was improved to 85% by having two equivalents of salt per amine. Compound (**103**) was obtained in 22% yield when a 10-fold excess of the amine was used. Slow addition of (**85**) to the solution of the amine was complicated by its insoluble nature. This was attempted by thorough mixing of finely ground trichloro salt (**85**) with silica gel (20x in terms of weight) but a yield of only 20% of (**103**) was obtained

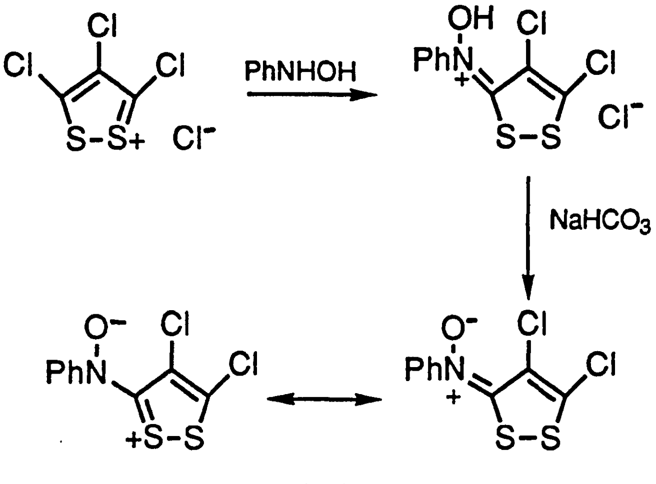


103

111

3.2.3 *Reaction of the trichloro salt with other nitrogen nucleophiles*

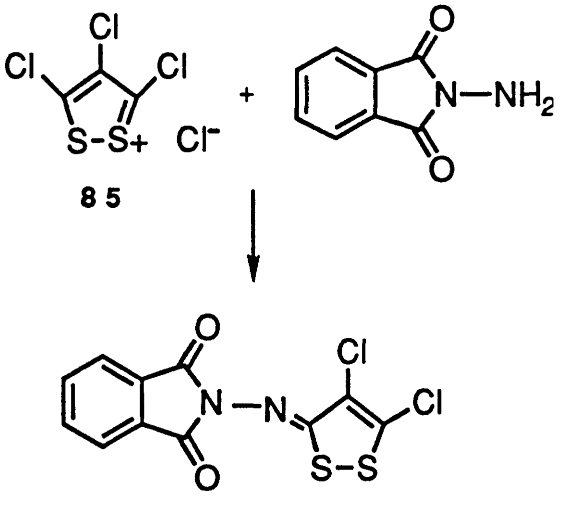
a) With *N* -phenylhydroxylamine: *N* -Phenylhydroxylamine reacted with the trichloro salt (**85**) to give a yellow coloured product. When treated in the usual way with one equivalent of pyridine, only the *N* -phenylimine (**96**) was obtained. However when the product in DCM was washed with sodium bicarbonate solution, followed by column chromatography, a yellow brown oil was isolated which proved to be the *N* -oxide of (**96**). This product, (**112**), was rather unstable reverting rapidly to the imine (**96**) *i.e.* deoxygenation occurred readily.



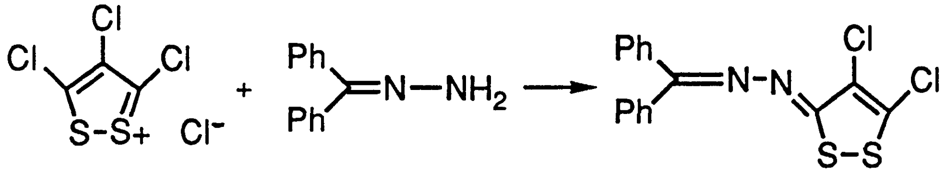
112

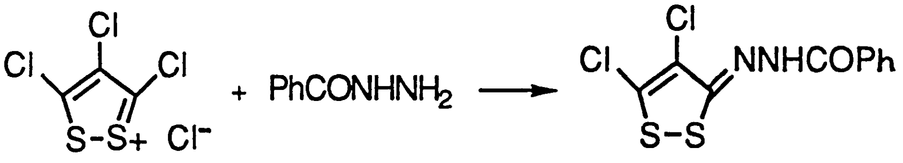
The ease with which oxygen was lost was interesting and warranted further investigation. It was thought that the oxygen might oxidize the dithiol ring. A sample of the sulphoxide of the imine was prepared from oxidation of the imine with mCPBA, but there was no sign of this on the TLC of the decomposed *N* -oxide.

b) With hydrazines and hydrazones: Reaction of the trichloro salt (**85**) with *N* -aminophthalimide gave the expected hydrazone (**113**) as a stable yellow solid but in only 13% yield. No other products were isolated, but baseline material was observed.


85
113

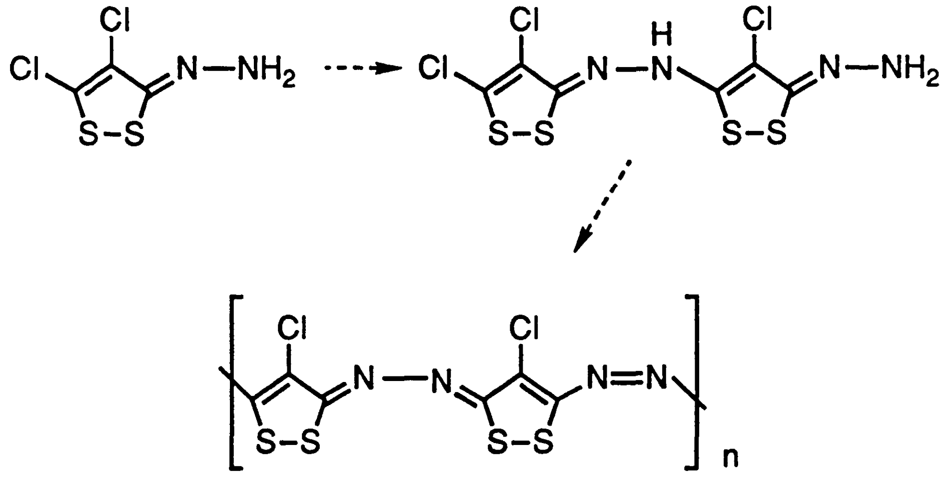
Benzophenone hydrazone with the trichloro salt (**85**) gave the expected hydrazide (**114**) in 82% yield and similarly benzoylhydrazine gave the corresponding hydrazide (**115**) in 52% yield. Both of these compounds were obtained as stable, crystalline yellow solids.


85
114


85
115

Phenylhydrazine, 4-nitrophenylhydrazine and tosylhydrazine all gave several products by TLC which were impossible to isolate cleanly. 1,1-Diphenylhydrazine with the trichloro salt (**85**) gave a product which had an M^+ corresponding to the expected product, but a pure sample of this product was not obtained.

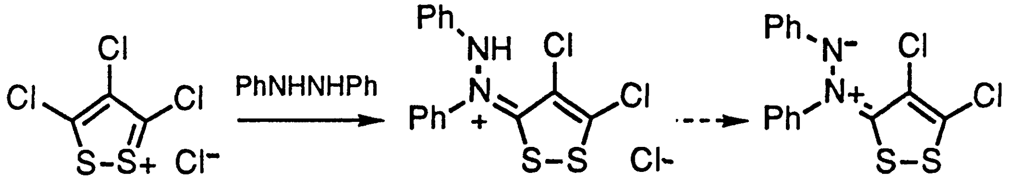
When the trichloro salt (**85**) was treated with anhydrous hydrazine the only isolable product was the dithiolthione (**89**); this was disappointing as the resultant compound could have been a precursor to a polymer, oxidation of which could have resulted in the fully conjugated polymer shown (Scheme 3.7).



Scheme 3.7

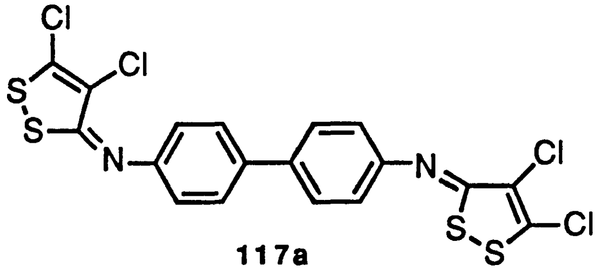
1,1-Dimethylhydrazine was also reacted with the salt; however the product obtained was susceptible to hydrolysis and only dithiolone (**86**) was obtained after attempted purification.

c) With 1,2-diphenylhydrazine: Reaction of the trichloro salt (**85**) with 1,2-diphenylhydrazine gave a yellow solid which was shown by FAB mass spectrometry to have an M^+ corresponding to that expected for the product (**116**) obtained as the hydrochloride salt.

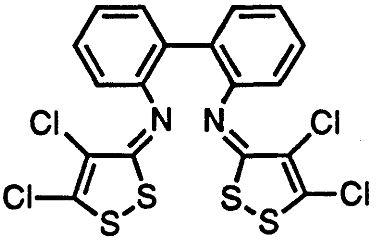


116

When this product was treated with pyridine the expected ylide was not obtained, the product was shown by the isotope pattern in the mass spectrum to contain four chlorines and coupled with the ^1H NMR spectrum was deduced to be a mixture of the two products shown (**117a** and **117b**)(22%). These two products were not separable by chromatography but the ^1H NMR showed them to be in a ratio of approximately 1:1.



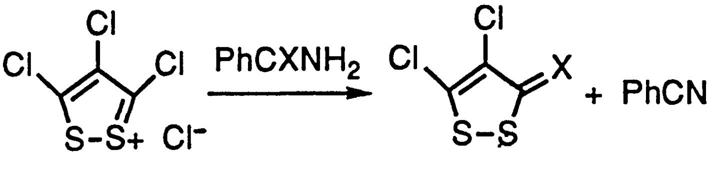
117a



117b

Thus a benzidine rearrangement had occurred; these are usually acid catalyzed and carried out using aqueous hydrochloric or sulphuric acid, the solvent being ethanol.[104] It is possible that here, in the initial reaction of hydrazobenzene with the trichloro salt (**85**), the hydrogen chloride released has caused the benzidine rearrangement of the hydrazobenzene to a mixture of 2,2'-diaminobiphenyl and 4,4'-diaminobiphenyl which reacts with the trichloro salt (**85**) present. This is shown by the presence of the products (**117a** and **117b**) on the TLC plate of the mixture.

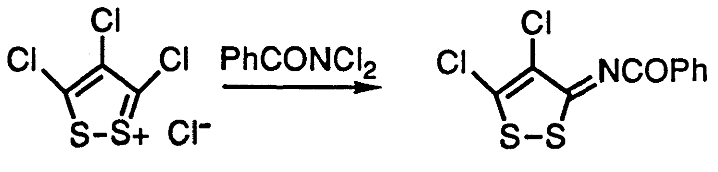
d) With benzamide, thiobenzamide and benzamidine: With benzamide, the trichloro salt (**85**) gave the dithiolone (**86**) in good yield (76%) and also benzonitrile, hence nucleophilic attack was occurring *via* oxygen. Thiobenzamide reacted analogously through the sulphur; the reaction mechanism probably being the same as for the reaction between thioacetamide and the trichloro salt (**85**)(see Sec. 3.2.1).



85

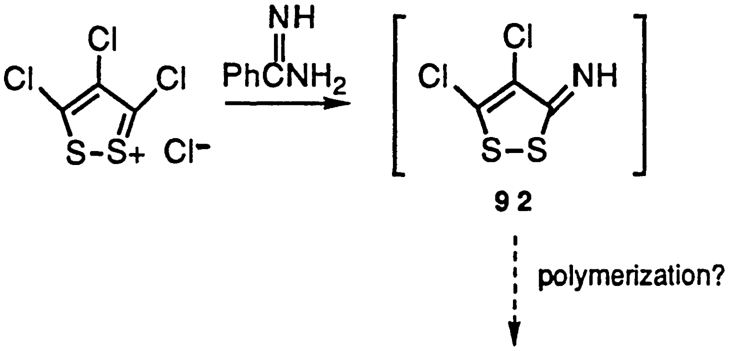
86 X = O
89 X = S

However *N,N*-dichlorobenzamide and the trichloro salt did give the amide (**118**), as a dark yellow solid (77%), in a similar reaction to those already reported.[97]



85 **118**

Benzamidine when reacted with the salt gave only baseline material. If the reaction was analogous to that of benzamide and thiobenzamide, then we would expect the reactive intermediate (**92**) (discussed in Sec. 3.2.1) to be formed, and probably to polymerize.

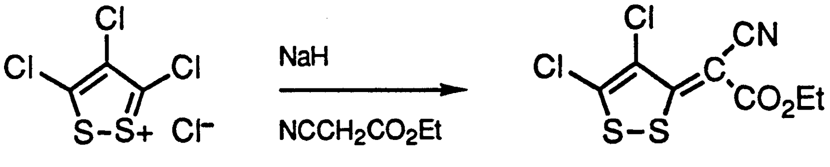


92

An attempt was made to trap this intermediate imine. One idea was to try to use benzoyl chloride, as the amide which would be formed had already been synthesized and characterized. However benzoyl chloride also reacted immediately with benzamidine, and addition of benzoyl chloride immediately after addition of the salt gave only baseline material.

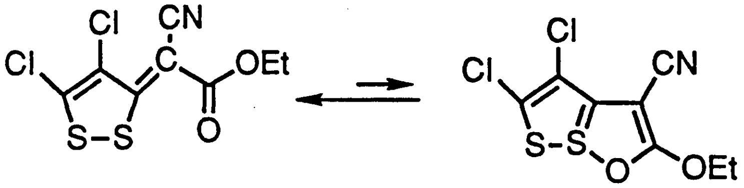
3.2.4 *Reactions of the trichloro salt with active methylene compounds*

There has been no report in the literature on the reaction of the trichloro salt (**85**) with active methylene compounds. When the trichloro salt (**85**) was taken with ethyl cyanoacetate in DCM at room temperature no reaction occurred. However when the anion of ethyl cyanoacetate was preformed using sodium hydride the expected product (**119**) was obtained in very low yield (9%);the major product isolated was the dithiolone (**86**) in 54% yield, indicating incomplete reaction of the trichlorosalt (**85**) with the anion. Using *n* -BuLi to preform the carbanion, or carrying out the reaction at low temperatures, did not improve the yield of (**119**).



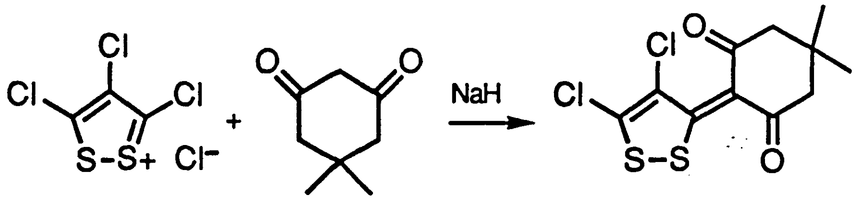
119

The product (**119**) was obtained as yellow crystals. The stereochemistry of the exocyclic double bond was not determined; written as in the structure above there could be some interaction between the sulphur of the dithiol ring and the carbonyl oxygen (Scheme 3.8). This type of interaction between a sulphur and an oxygen atom five atoms away was demonstrated by Appel[103] and in this case the carbonyl stretch in the IR spectrum is not particularly strong.



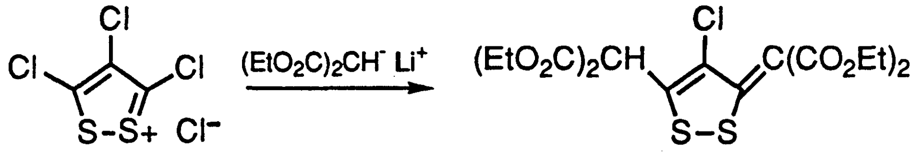
Scheme 3.8

The reaction between dimedone and the trichloro salt (**85**) also gave the expected compound (**120**), when the carbanion was preformed using *n* -BuLi, (18%). Again the dithiolone (**86**) was the major product (45%). The product was obtained as dark yellow crystals, both (**119**) and (**120**) were stable over extended periods of time.



120

When the trichloro salt (**85**) was reacted with the carbanion of diethyl malonate a product was obtained which had an M^+ in the mass spectrum corresponding to the disubstituted product shown.



121

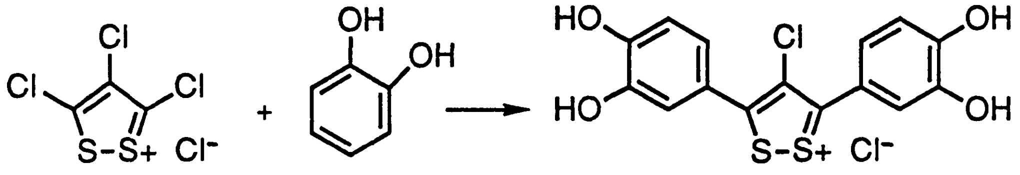
Other preformed carbanions were also tried including the carbanions of penta-2,4-dione and malononitrile. In the case of pentan-2,4-dione a product was obtained, the mass spectrum of which showed a parent ion for the desired compound i.e. 3-(4,5-dichloro-5*H* -1,2-dithiol-5-ylidene)pentan-2,4-dione; but it proved impossible to obtain a pure sample. Malononitrile did not react at all with the trichloro salt, either as the neutral compound or the preformed anion.

3.2.5 *Reactions of the trichloro salt with phenols and naphthols*

There has been no report in the literature on the reaction between the trichloro salt (**85**) and phenols although other 1,2-dithiolium salts have been shown to react with phenols both through the *para* carbon atom and through oxygen. In each case the product is still a salt.[105]

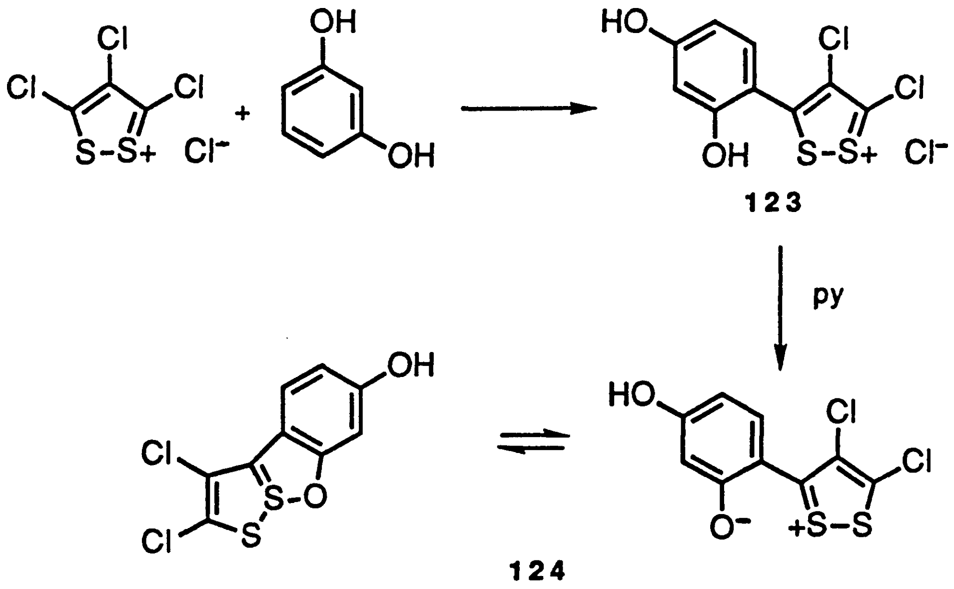
Phenol itself, when taken with the trichloro salt (**85**), gives the dithiolone (**86**). This is most probably due to the highly hygroscopic nature of phenol so that the water present reacts with the trichloro salt (**85**). Some substituted phenols were tried, namely *p* -nitrophenol, which did not react at all; *m* -methoxyphenol and *p* -*t* -butylphenol both reacted but no products were isolable.

However when 1,2-dihydroxybenzene was treated with the trichloro salt (**85**) a brown precipitate was formed. The base peak of *m/z* 36 in the mass spectrum showed this to be a hydrochloride salt and the very weak M^+ showed that two moles of 1,2-dihydroxybenzene had reacted with one of the trichloro salt (**85**) to give (**122**), the FAB mass spectrum showed the M^+ more clearly; ^{1}H NMR showed substitution to have occurred through the 4-carbon of the aromatic ring. The yield was good (65%).



122

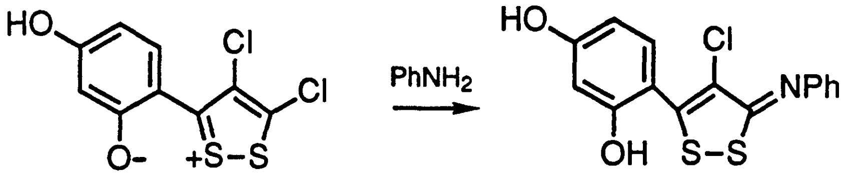
1,3-Dihydroxybenzene reacted in an analogous manner with the trichloro salt (**85**) also through the 4-carbon but in a 1:1 ratio to give the salt (**123**); when this was treated with a suitable base, *e.g.* pyridine, the betaine structure (**124**) was formed which was obtained as orange crystals. Disappointingly 1,4-dihydroxybenzene did not react with the salt, and only the dithiolone (**86**) was obtained. Also 1,3,5-trihydroxybenzene gave no reaction with the trichloro salt (**85**). It is possible that the major ketonic form is not nucleophilic enough to react with the trichloro salt (**85**).



123

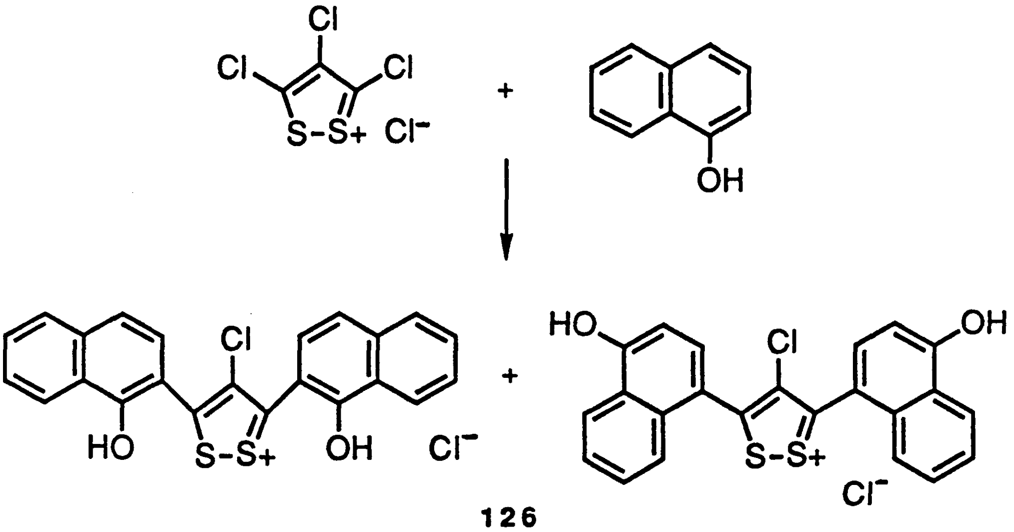
124

In the above structure (**124**) there is still a displaceable chlorine, this was demonstrated by reacting (**124**) with aniline to give a yellow solid which was shown by the mass spectrum and ^{1}H NMR to have the structure (**125**).



125

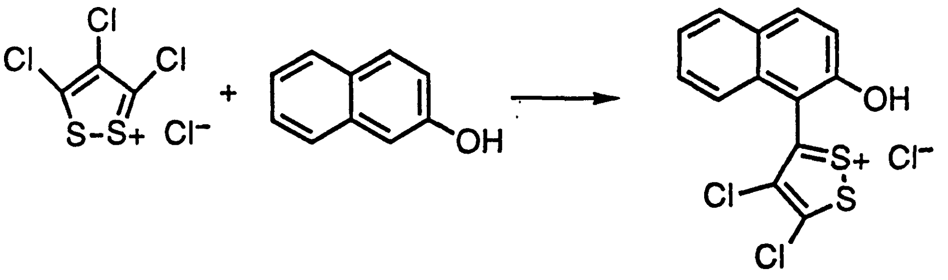
Two moles of 1-naphthol reacted with the trichloro salt (**85**) to displace two molecules of hydrogen chloride to give a red solid which was shown by ^{1}H NMR to be a mixture of the two symmetrical structures (**126**), in an approximate ratio of 3:1. An n.O.e experiment was attempted to try to differentiate between the two isomers and see which was the major product; however no n.O.e. was observed; this is probably due to some association of the molecules in solution .



126

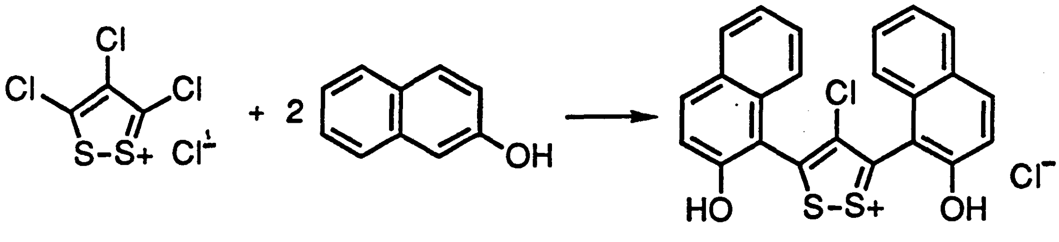
If a solution of this mixture of isomers was treated with a suitable base *e.g.* pyridine or aqueous ammonia the solution went blue with a shift in $\lambda_{max.}$ from 529 to 622 nm. A blue, very polar solid was isolated in low yield (10%) and was difficult to purify. The mass spectrum showed an M^+ corresponding to the betaine structure and the ^{1}H NMR showed it to be one isomer only.

When the trichloro salt was treated with one equivalent of 2-naphthol, two products were obtained. The first was a red fairly non-polar compound, the mass spectrum of this had a strong peak at *m/z* 36 indicating a hydrochloride salt, and the molecular ion corresponded to the monosubstituted salt (**128**).



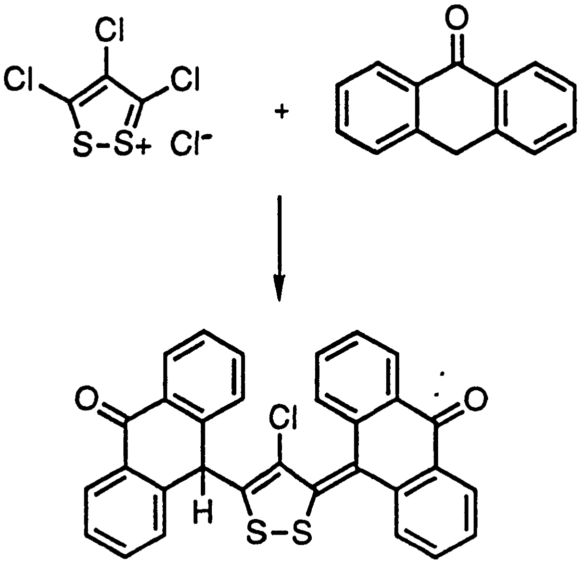
128

It was very surprising that this salt should be so non-polar. However from a study of models, it could be seen that in the covalent form the naphthol and dithiole rings lie in the same plane with the chloride ion sitting directly underneath. The second, purple, very polar product was shown by the FAB mass spectrum to have an M^+ corresponding to the product (**129**) where two moles of 2-naphthol react with one mole of the trichloro salt (**85**). 'Bond fixation' in 2-naphthol suggests that only one product would be expected and the ^{1}H NMR supported this; however the ^{1}H NMR were far simpler than expected but for both products (**128** and **129**) it followed the same pattern. Product (**129**) was obtained in good yield (72%) when two moles of 2-naphthol were taken for each mole of trichloro salt (**85**), but treatment with pyridine had no effect *i.e.* the betaine structure was not formed. There must be some adverse interactions between the covalent chlorine and the hydrogens in position 8 of the naphthol ring which probably means that the naphthol rings are twisted out of the plane of the dithiole ring. This would explain why the deprotonated form is not readily formed.



129

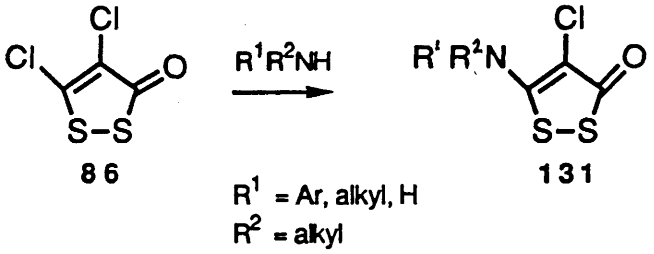
When the trichloro salt was reacted with anthrone a green precipitate was formed which is tentatively assigned the structure (**130**), based on the mass spectral data which showed an M^+ at 520 and an accurate mass measurement on this peak was consistent with that expected for the formula (**130**). It was very difficult to purify as it decomposed on silica gel and was only soluble in methanol. ^{1}H NMR showed that impurities were present and it was very difficult to analyze the spectrum accurately. Treatment with base also led to total decomposition of the compound.



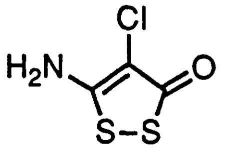
130

3.3 Reactions of 4,5-dichloro-1,2-dithiol-3-one

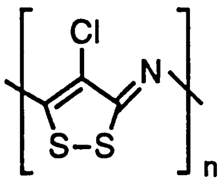
As previously mentioned 4,5-dichloro-1,2-dithiol-3-one (**86**) is well documented in the literature being used extensively as an anti-fouling agent.[103] However its chemistry has not been investigated so extensively. As with all 1,2-dithiole compounds it decomposes in basic solution. Nitrogen nucleophiles displace the 5-chloro group to give compounds (**131**):[96]



A compound which would have been of great interest to us is that where R_1 and R_2 are both hydrogen (**132**). This compound could be a monomer, which, by a condensation reaction, could give the polymer (**133**).

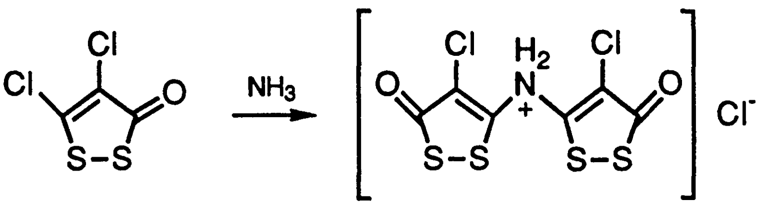


132



133

Several attempts were made to synthesize the precursor (**132**). When ammonia was passed through a solution of the dithiolone (**86**) in acetonitrile, an orange precipitate formed immediately. The mass spectrum shows a strong peak at *m/z* 36 indicating a hydrochloride salt and a molecular ion at *m/z* 317 which has an isotopic pattern indicative of two chlorines being present. There is also a peak at *m/z* 167 which corresponds to (**132**). The ^{13}C NMR shows three peaks, a weak signal at 209 ppm, the carbonyl carbon; the other two signals being at 31 and 24 ppm which are very low values for alkenic carbons. The IR spectrum has a pair of strong peaks *ca.* 3 000 cm^{-1} showing the presence of the secondary amine. Hence the structure is thought to be (**134**).

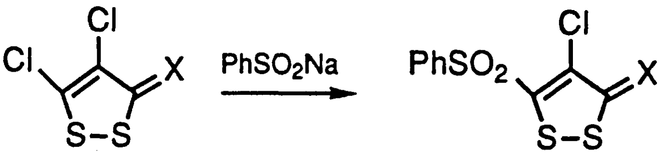


86 **134**

Treatment of this salt with pyridine, triethylamine, sodium bicarbonate solution or propylene oxide disappointingly failed to give the free amine.

Sodamide gave baseline material only when reacted with the dithiolone (**86**). Triphenylamine was tried as a form of protected ammonia, but did not react under various conditions; this was probably for steric reasons since we later found that it did not react with the trichloro salt (**85**); in fact the trichloro salt (**85**) was recovered. Hexamethyldisilazane also did not react with the dithiolone (**86**) when heated neat for 3 h, nor did potassium phthalimide under various conditions.

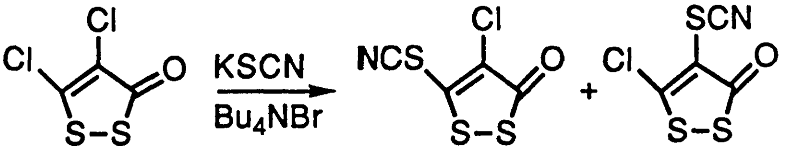
Sodium benzenesulphinate reacted with the dithiolone (**86**) to displace the chloro group in position 5 to give (**135**) as brown crystals in good yield (88%). The dithiolthione (**89**) had previously been shown to react similarly.[99]



135 X = O
136 X = S

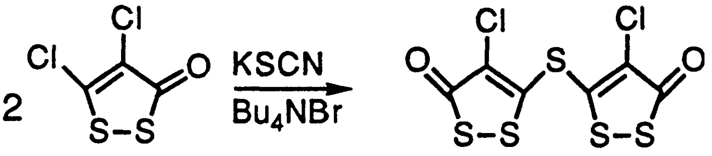
In compound (**135**) the chloro group in the 4- position could now be activated to displacement by the phenylsulphonyl group. Thus its reaction with lithium methanethiolate was attempted, but under all the conditions tried no reaction was observed. The phenylsulphonyl group could have been displaced in preference to the chloro group but this was not observed either. The same was found for the case where the oxygen is replaced by sulphur *i.e.* the dithiolthione (**136**).

A Japanese group reported that the reaction between the dithiolone and potassium thiocyanate in the presence of a phase transfer agent, *e.g.* tetrabutylammonium bromide, gave two products (**137a** and **137b**). However in the patent they only gave spectroscopic data for one of these compounds:[106]



86 **137a** **137b**

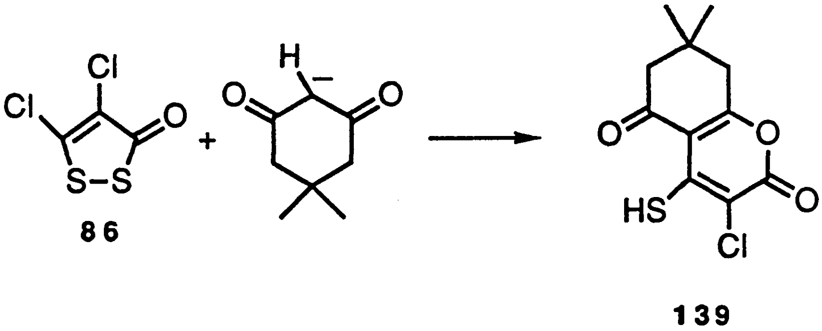
This is the only report in the literature that claims displacement of both chloro groups. When this reaction was repeated by us we isolated an entirely different product (**138**) in good yield (62%) as colourless crystals. The data obtained does not correspond at all to that given in the patent, except for the ^{13}C NMR which has three signals at very similar values; no signal was reported for the nitrile carbon:



86 **138**

The same product (**138**) was obtained (55%) if sodium sulphide was used under the same reaction conditions in place of potassium thiocyanate. When the same reaction was tried with the dithiolthione (**89**) a product was obtained which was analogous to (**138**) with the oxygens being replaced by sulphur, but in very poor yield (8%). The reaction was tried between the dithiolone (**86**) and potassium thiocyanate using different solvents and no phase transfer agent in order to get straightforward displacement of just one chloro group, but no reaction occurred.

The reaction between the dithiolone (**86**) and active methylene compounds was also investigated. When the preformed carbanion of dimedone was added to the dithiolone (**86**), yellow needle-shaped crystals were isolated. The ^{1}H NMR showed that the protons on the dimedone ring were in different environments. The mass spectrum gave a parent ion which was 32 mass units less than that expected for simple nucleophilic displacement by the carbanion of the 5-chloro group *i.e.* loss of sulphur had probably occurred. Two carbonyl absorptions were apparent in the IR, one at 1 723 cm^{-1} and the other at 1 657 cm^{-1}. The ^{13}C NMR showed that there were ten different carbons, seven of which were quaternary. This information led us to deduce the pyrone structure (**139**) for this product, which was formed in 5% yield.

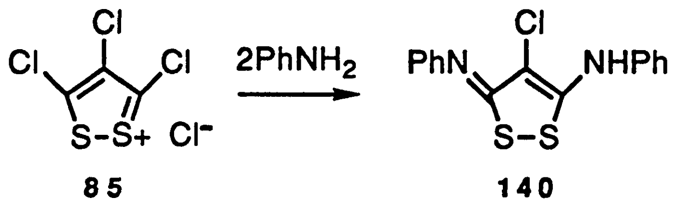


Hence it appears that the carbanion reacts with the dithiolone (**86**) to displace the 5-chloro group as we would expect. The hydroxy group of the enol form of this product could attack the δ+ carbon of the carbonyl group. Elimination of sulphur and a 1,5 proton shift would result in the observed product. However this is over-simplified as modelling shows the hydroxy group to be too far from the carbonyl group. Hence the dithiole ring must be opened prior to nucleophilic attack of the hydroxy group. This could be effected by another molecule of the preformed carbanion of dimedone, which would partially explain the poor yield obtained. Regrettably none of the other carbanions tried with the ketone *e.g.* *N,N'*-dimethylbarbituric acid and acetylacetone gave any identifiable products.

3.4 Reactions of the arylimines

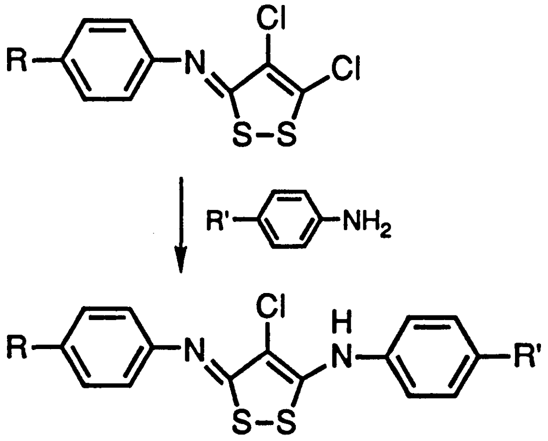
3.4.1 *Displacement of the 3-chloro group:*

When the trichloro salt **(85)** was taken with just one equivalent of aniline at room temperature, two products were obtained, albeit in poor yield. One was the monophenylimine **(96)** (12%), and a more polar compound which proved to be 3-anilino-*N* -(4-chloro-5*H* -1,2-dithiol-5-ylidene)aniline **(140)** (17%) *i.e.* the product of reaction of two moles of aniline with one mole of the trichloro salt **(85)**.



This compound **(140)** can be synthesized in 65% yield by using an excess of aniline and refluxing in acetonitrile. It is obtained as a yellow solid which is stable to air and moisture. Compound **(96)** was obtained in 82% yield by using four equivalents of aniline, but having a reaction time of 0.5 h and not adding pyridine. Carrying out the reaction at lower temperatures *e.g.* 0 °C; -20° C; -78 °C, gave only poor yields of **(96)**.

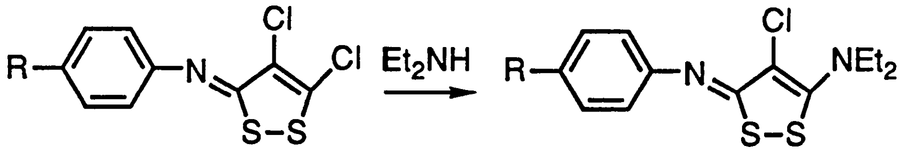
It was only in the case of aniline that more than one product was observed if the reaction was carried out at room temperature. When the imine **(99)**, from the trichloro salt **(85)** and *p* -methoxyaniline, was refluxed in acetonitrile with two equivalents of *p* -methoxyaniline the corresponding 3- substituted compound **(141)** was obtained, however it was very difficult to purify and therefore characterize fully. The 'mixed' compound **(142)** was prepared from the 4-nitrophenylimine **(98)** and *p* -methoxyaniline; using *p* -nitroaniline with the 4-methoxyphenylimine **(99)** gave no reaction under several conditions. This can be attributed to the poor nucleophilicity of *p* -nitroaniline as well as the lower reactivity to nucleophilic displacement of the 3-chloro group in the 4-methoxyphenylimine. No reaction occurred between *p* -nitroaniline and the 4-nitrophenylimine either.



141 R = R' = MeO
142 R = NO_2, R' = MeO

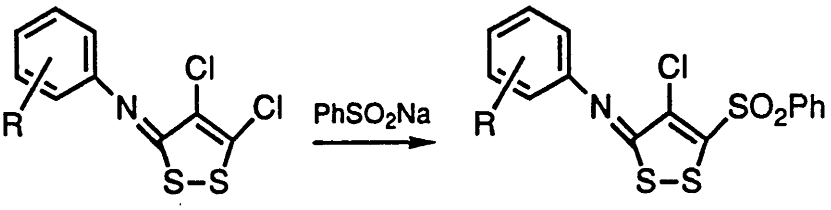
R = MeO, R' = NO_2 -no reaction
R = NO_2, R' = NO_2 -no reaction

The chloro group in position 5 can also be displaced by alkyl nitrogen nucleophiles as shown by reaction of diethylamine with selected imines. These were obtained as yellow oils or crystals (**143**, **144**, and **145**). In each of these compounds the mass spectrum shows ready loss of 99 mass units *i.e.* loss of ClS_2. The UV-visible spectra were recorded and a bathochromic shift was observed as the substituent on the aryl ring was changed from a methoxy group (*i.e.* electron-releasing) to a nitro group (*i.e.* electron-withdrawing).



143 R = MeO, λ = 329 nm
144 R = Me, λ = 330 nm
145 R = NO_2, λ = 387 nm

When the chloro group in position 3 was displaced using benzenesulphinate as the nucleophile with some of the arylimines this effect was again observed.

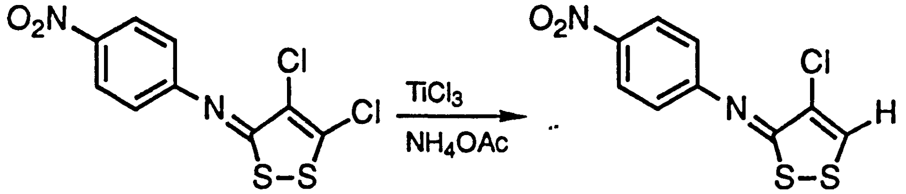


R = H, 2-NO_2, 4-NO_2, 2-NHBOC, 4-MeO, 2-NH_2, 4-NEt_2

R	Product	Yield (%)	m.p. (°C)	$\lambda_{max.}$ (nm)
H	**(146)**	8	184	220, 368
4-NO_2	**(147)**	40	84-86	272, 390
2-NO_2	**(148)**	80	165	258, 270
4-MeO	**(149)**	73	125	226, 408
2-NHBOC	**(150)**	71	199	224, 410
2-NH_2	**(151)**	18	138	451
4-Et_2N	**(152)**	40	165	262, 485

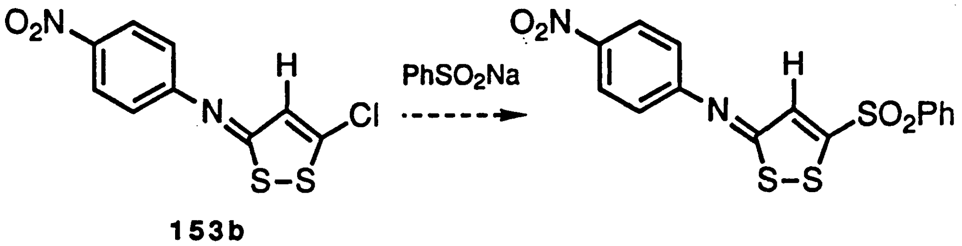
The electron-withdrawing effect of the phenylsulphonyl group had a pronounced effect on the colour of those arylimines which contained electron releasing groups, as demonstrated in the Table where the $\lambda_{max.}$ in the visible region is used as a measure of the push-pull effect.

Reduction of the nitro group in the 4-nitrophenylimine **(98)** was attempted as a model study for an alternative way to obtain **(103)** in good yield (see Sec. 3.2.2). The reducing agent needed to be such that it would leave the dithiole ring intact, so it was decided to try titanium (III) chloride with ammonium acetate as the buffer.^{107} However the product obtained **(153)** was not the expected amino compound, but instead one of the chloro groups had been reduced to hydrogen:



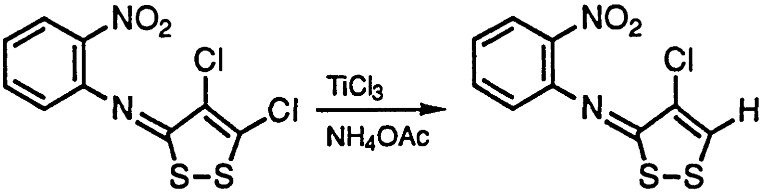
99 **153a**

There are two possible structural isomers (**153a** and **153b**) since either of the chlorines could be displaced. Apart from X-ray analysis, there is no spectroscopic method of differentiating between the two possibilities. However the structure could be supported by trying to react compound (**153**) with sodium benzenesulphinate; no reaction occurred which points to the structure being that shown above, since if the chloro group in the three position was still present it would be expected to be displaced by benzenesulphinate. Thus, not unexpectedly, the more reactive chloro group in the three position in the 4-nitrophenylimine (**98**) was reduced by titanium (III) chloride.



153b

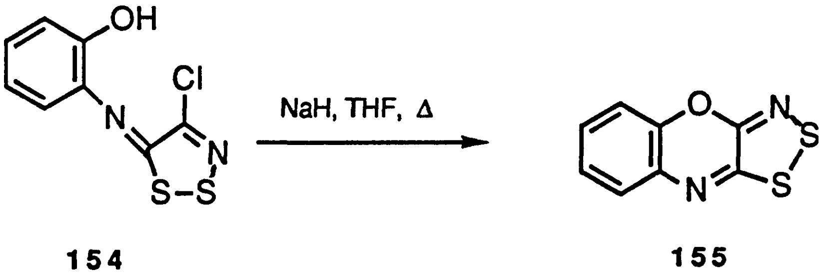
The scope of this titanium (III) chloride reduction was briefly explored, no reaction occurred with the phenylimine (**96**) where the aryl ring was unsubstituted even after prolonged reaction time (72 h). With a moderately electron-withdrawing group (*i.e.* EtO_2C, phenylimine **109**) no reaction occurred either again after 72 h. With a nitro group in the 2- position on the aryl ring, compound (**102**), reaction occurred albeit in poor yield and the mass spectrum showed it to be the isomer of compound (**153a**) where again the chloro group in the three position was reduced. However with the nitro group in the 3- position of the aryl ring in the phenylimine (**107**) no reaction occurred.



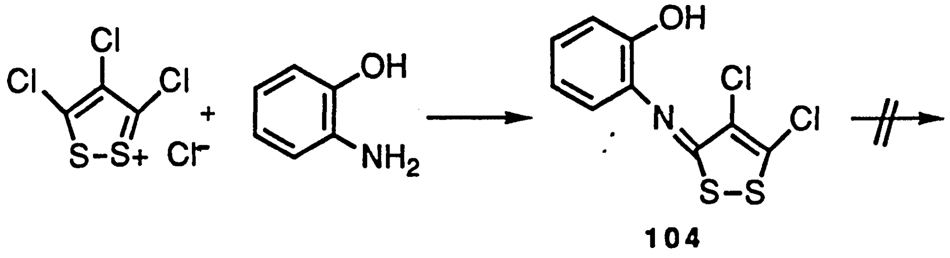
3.4.2 *Displacement of the 4-chloro group.*

In all the examples so far, only the chlorines in positions 3 and 5 have been displaced by various nucleophiles. Displacement of the less activated chlorine in position 4 was very attractive as this could be an alternative route into the mesoionic ring system described in Chapter 2.

In the analogous 4,5-dichloro-1,2,3-dithiazolium chloride the chlorine in the five position was readily displaced, but displacement of the chlorine in position four was only observed in one example. When *N* -(4-chloro-5*H* -1,2,3-dithiazolyl-5-ylidene)-2-hydroxyaniline (**154**) was treated with sodium hydride in THF at reflux for one hour, intramolecular displacement of the chloro group in position 4 by the phenoxide ion occurred to give [1,2,3]dithiazolo[4,5-*b*][1,4]benzoxazine (**155**).[108]

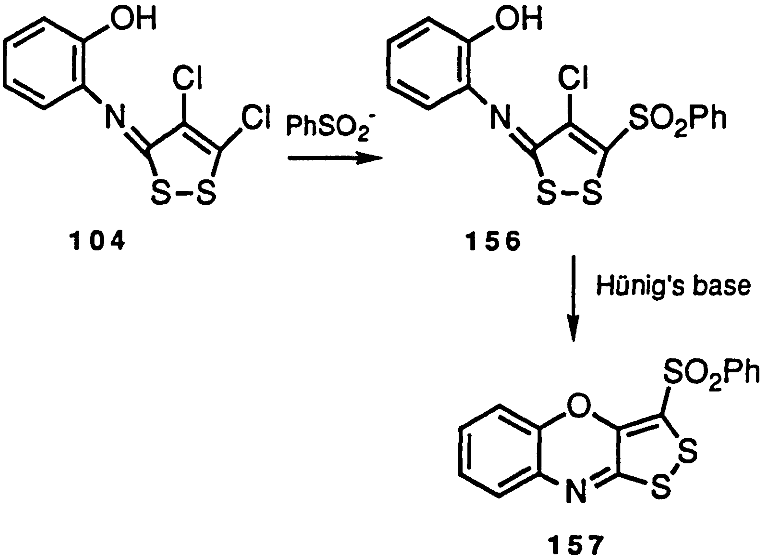


With this in view *N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-2-hydroxyaniline (**104**) was prepared from 2-hydroxyaniline and the trichloro salt (**85**) (80%). However under the same conditions as above no reaction occurred for compound (**104**). The reaction was repeated using more fierce conditions and longer reaction times (refluxing acetonitrile for 48 h, DMF at 120 °C for 1 h). In the first case no reaction occurred, in the second the starting material was completely destroyed by the DMF.

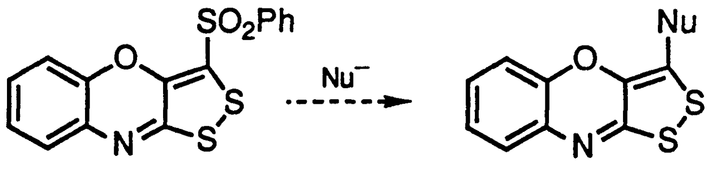


When compound (**104**) was thermolyzed at 180 °C for 2 min under nitrogen, the mass spectrum of the product obtained showed an M^+ of 482 and an isotopic pattern for two chlorine atoms present. This suggested a dimeric product which had lost two molecules of HCl. However it was very difficult to purify the compound in order to define the structure completely. Compound (**104**) was subjected to flash vacuum pyrolysis at 1.8 mbar and 400 °C but only starting material was recovered.

It was obvious that some activation to nucleophilic displacement of the chlorine in position 4 was required. This was provided by reacting compound (**104**) with sodium benzenesulphinate to give a phenylsulphonyl group in position 5 of the dithiol ring. When this compound (**156**) was treated with sodium hydride in refluxing THF overnight the desired cyclised product, 3-phenylsulphonyl[1,2]dithiol[4,5-*b*][1,4]benzoxazine (**157**) was obtained in 23% yield. It was felt that one reason for the low yield was the use of a strong nucleophilic base which could easily attack the sulphur atoms of the dithiol ring. Therefore a non-nucleophilic base was required which would be sufficient to remove the hydroxy proton. Hünig's base fulfilled these criteria and when used gave the tricyclic compound in yields of 40-45%.

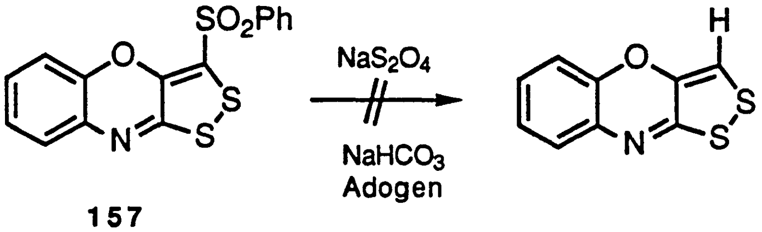


In this reaction of (**156**) with Hünig's base, the phenylsulphonyl group was chosen as the group to activate the vinylic chloro group in the 4-position towards displacement, for two reasons; firstly the ease of its introduction, and, secondly the possibility of displacement by other nucleophiles.[109]



157

A very attractive possibility would be to reduce out the phenylsulphonyl group in order to give the parent compound. The method tried was that developed by Julia using sodium dithionite as a mild reducing agent.[110] When (**157**) was taken under similar reaction conditions to those used in the literature *i.e.* sodium dithionite in cyclohexane at room temperature, only starting material was recovered. Sodium borohydride in propan-2-ol was also tried but TLC showed baseline material after only 5 minutes.

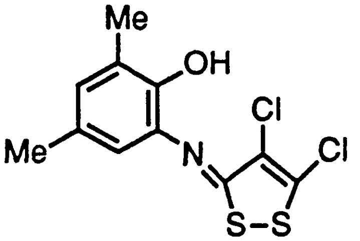


157

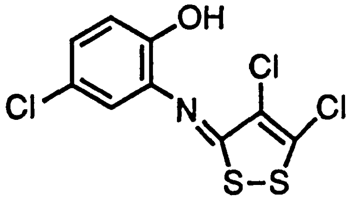
Other nucleophiles such as methanethiolate anion and cyanide ion were tried to displace the phenylsulphonyl group under various conditions , however no reaction occurred.

The synthesis of this ring system was also attempted using 2-hydroxy anilines which had other substituents on the aromatic ring. The anilines used were 3,5-dimethyl-2-hydroxyaniline, 2-amino-4-nitrophenol, 2-amino-4-chlorophenol and 2-amino-3-hydroxypyridine. In the cases of 2-amino-4-nitrophenol and 2-amino-3-hydroxypyridine the yields of the respective imines were very poor (11% and 17% respectively). This may be due to poor nucleophilicity of the amino group, but more likely because of the very poor solubility of the amines in either DCM or diethyl ether. No other products were isolated, but in view of the poor yield at the first stage these were abandoned.

3,5-Dimethyl-2-hydroxyaniline and 4-chloro-2-aminophenol gave good yields of the imines (**105**) and (**158**) with the trichloro salt (**85**).

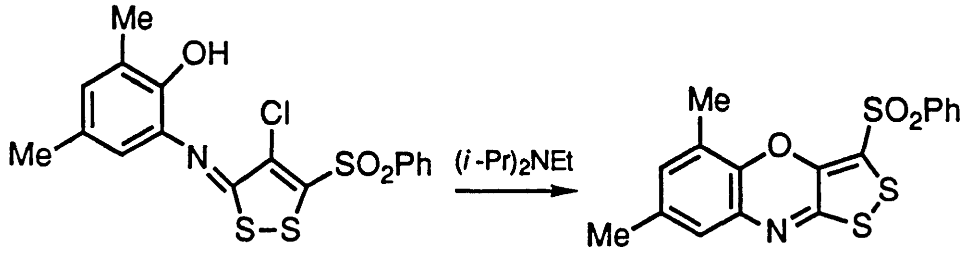


105



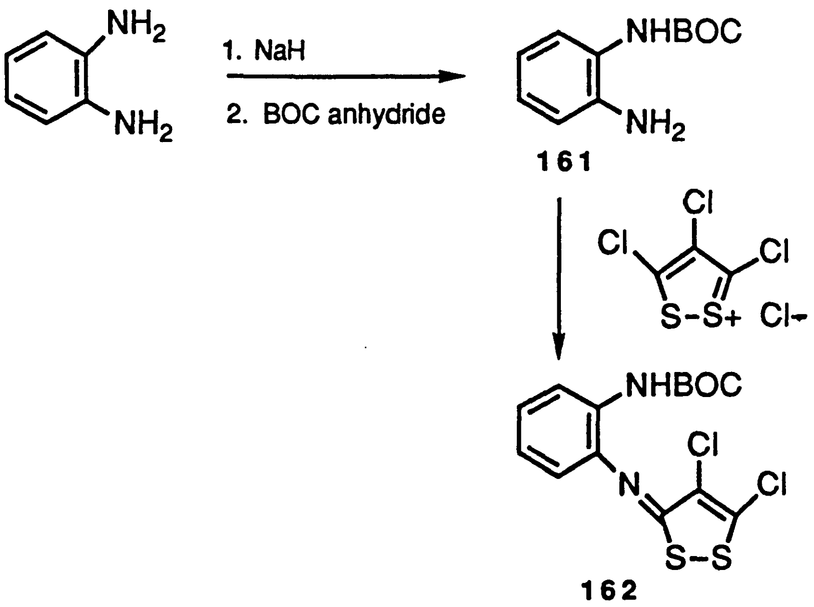
158

Treatment with sodium benzenesulphinate also went well in the case of (**105**) to give compound (**159**) and subsequent treatment with Hünig's base overnight in refluxing THF gave the tricyclic compound (**160**) in 35% yield. In the case of (**158**), the reaction with sodium benzenesulphinate was very messy and the corresponding 3-phenylsulphonyl substituted compound was isolated cleanly in a very low yield (10%) and so was abandoned at this stage.

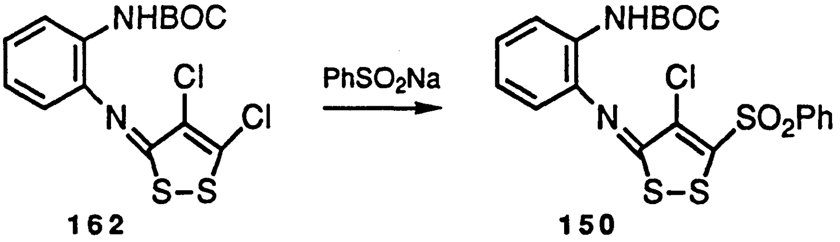


159 **160**

We also investigated the possibility of carrying out the same sequence of reactions using *o* -phenylenediamine with the trichloro salt (**85**) in order to have the 4-chloro group displaced by nitrogen rather than oxygen. However reaction between *o* -phenylenediamine and the trichloro salt (**85**) gave predominantly (**111**) (see Sec. 3.2.2) and hence protection of just one of the amino groups was required. It was decided to use the *t* -butoxycarbonyl group as this is well documented, both in introduction and removal of the group.[111] Using the standard method of treatment with di-*t* -butyldicarbonate and DMAP as the catalyst gave both mono- and di- protected *o* -phenylenediamine in equal amounts. Protection of just one of the amino groups was effected by treatment of *o* -phenylenediamine with an equivalent of sodium hydride followed by di-*t* -butyldicarbonate and gave the required compound (**161**) in good yield (90%). This in turn gave a good yield of the imine (**162**) (80%) when reacted with the trichloro salt (**85**).



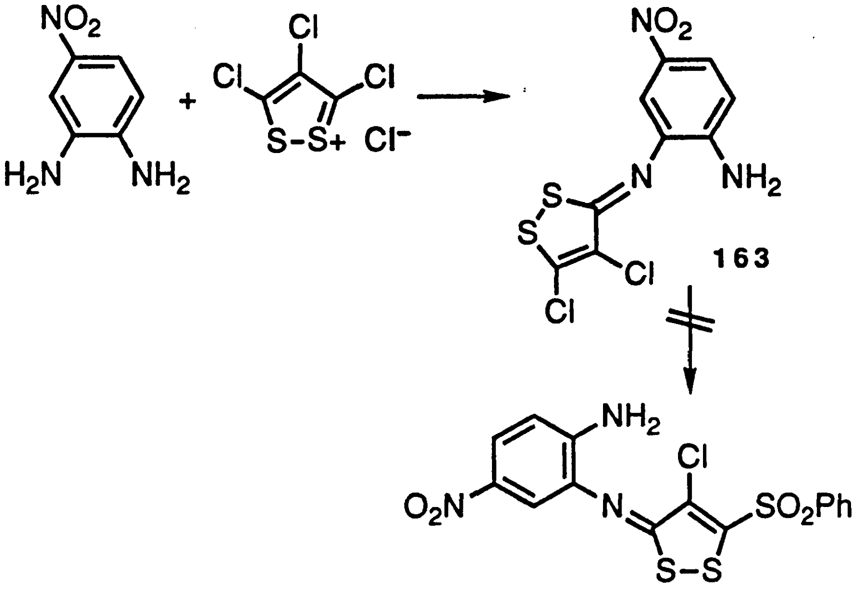
Deprotection of the BOC-protected amino group proved to be difficult. Several methods were tried, namely trifluoroacetic acid in DCM, at room temperature and at reflux, but no deprotection occurred. Thermolysis under nitrogen at 190 °C for 1.5 min had no effect and thermolysis at 280 °C for 0.5 min under nitrogen resulted in baseline material and sulphur only. 3M HCl in ethyl acetate gave the required deprotected compound in 22% yield and bubbling hydrogen chloride through a solution of **(162)** gave the deprotected amine **(103)** in 28% yield. It was then decided to try cyclizing without prior deprotection so **(162)** was reacted with sodium benzenesulphinate which gave the desired compound **(150)** in 70% yield.



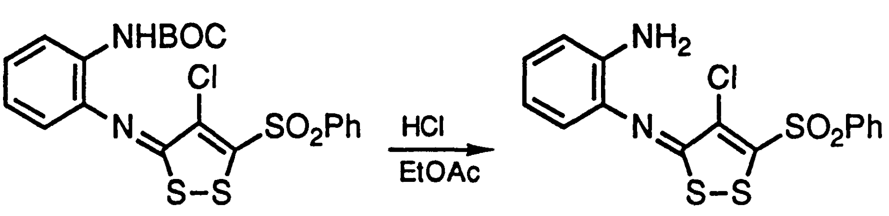
This was treated with sodium hydride as before; however no reaction occurred in refluxing THF overnight. Acetonitrile as the solvent led to total decomposition of **(150)** after just 2 h reflux.

A sample of 2-aminoarylimine **(103)** made directly from the trichloro salt (85) and *o* -phenylenediamine was reacted with sodium benzenesulphinate and gave the required compound **(151)** in low yield (8%).

1,2-Diamino-4-nitrobenzene was also reacted with the trichloro salt (**85**), giving the mono-imine (**163**) in 29% yield, as well as the di-imine. Hence the presence of the nitro group on the phenyl ring helped to deactivate one of the amino groups, but not to such an extent to make it synthetically advantageous. Also reaction of the mono-imine (**163**) with sodium benzene- sulphinate was messy and the expected product was not isolated.

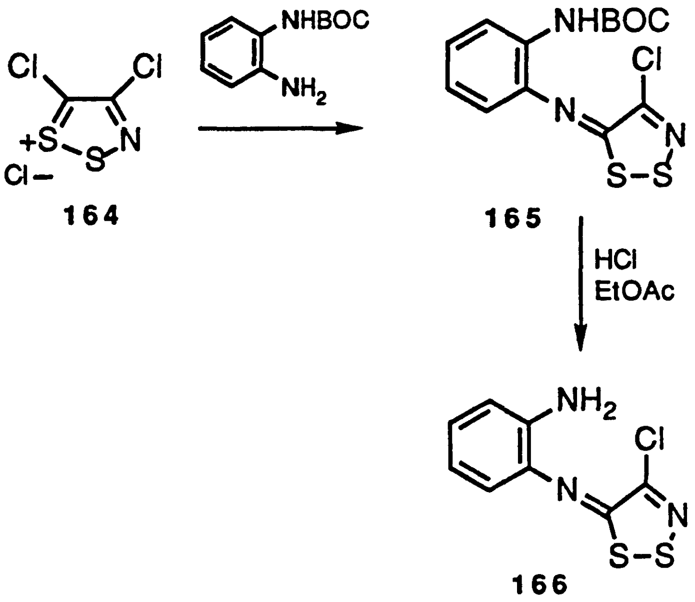


The method of deprotection for the BOC group using HCl in ethyl acetate which worked poorly in the case of compound (**162**) to give (**103**) (22%); worked very well in removal of the BOC group from compound (**150**) to give (**151**)(90%). This was formed in a yield of 45% overall from *o* - phenylenediamine.



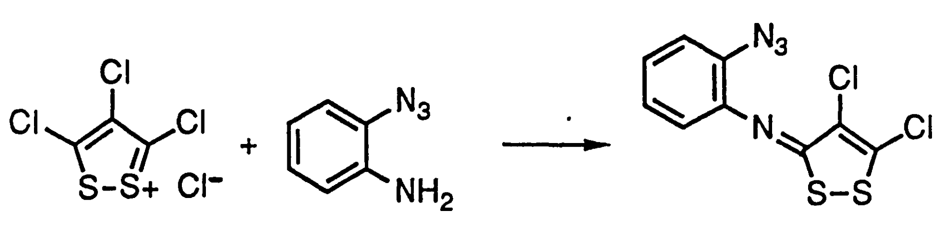
150 **151**

It was found previously that when the Appel salt (**164**) was reacted with *o* - phenylenediamine, it gave the di-imine only; use of lesser amounts of the Appel salt gave poorer yields of the di-imine but no mono-imine.[108] Use of a ten-fold excess of *o* -phenylenediamine still gave only the di-imine. However, we find that reaction with the BOC-protected *o* -phenylenediamine gave an excellent yield of the corresponding imine (**165**), and deprotection using HCl in ethyl acetate gave the mono-imine (**166**) in 69% overall yield.



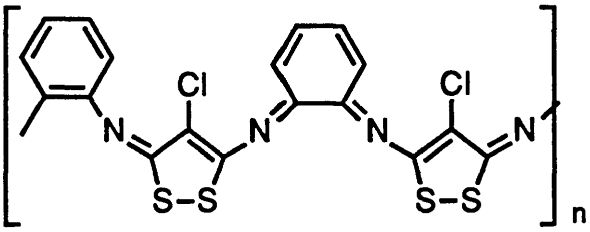
Cyclization of both of these compounds (**151** and **166**) was attempted using Hünig's base; however no reaction had occurred after 24 h reflux in THF. Use of DBU as the base resulted in baseline material only, after only 2 h reflux. This is probably because the nitrogen in DBU is less sterically hindered and hence acts as a nucleophile attacking sulphur of the dithiole ring. Sodium hydride as the base also had the same effect.

An alternative method to obtain the tricylic compound with two nitrogens in the central ring could be *via* decomposition of an *o* -azide group. The imine (**106**) with an azide group *ortho* to the imine nitrogen was synthesized in fair yield (56%), 2-azidoaniline being prepared by the method of Smith, Hall, and Kann.[112]



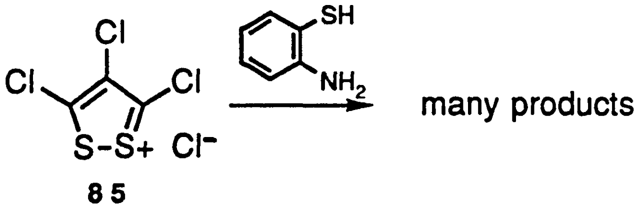
106

When this azido-imine (**106**) was thermolyzed at 175 °C under nitrogen an explosion occurred; TLC showed a trace of starting material and baseline material only. Photolysis of the azido-imine in a quartz tube in acetonitrile led to a bronze film being coated over the tube; this was soluble only in concentrated nitric acid which gave a dark brown solution. This could possibly be polymeric with the structure shown below (**167**):



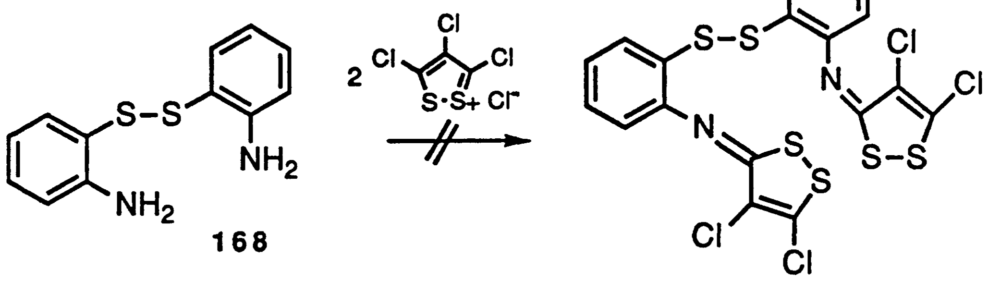
167

Another attractive possibility would be to obtain the imine with a thiol group *ortho* to the imine nitrogen. Due to the high nucleophilicity of sulphur it would be expected that the intramolecular displacement of the chloro group in the 4-position would be effected more easily than in the cases where the *ortho* group is oxygen or nitrogen. With this in view, the trichloro salt (**85**) was treated with *o*-aminothiophenol; however this gave many products which could not be isolated cleanly (Scheme 3.9).

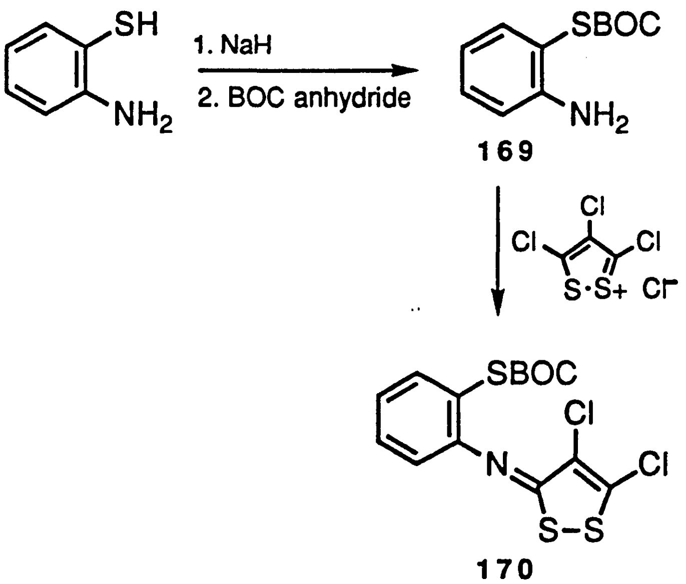


Scheme 3.9

As in the case with nitrogen, some protection of the sulphur group was necessary until the reactivity of the sulphur group was required. One possibility was use of the disulphide (**168**) which could be mildly reduced to give two moles of the required compound. This was prepared, but its reaction with the trichloro salt (**85**) was complex and did not proceed smoothly.

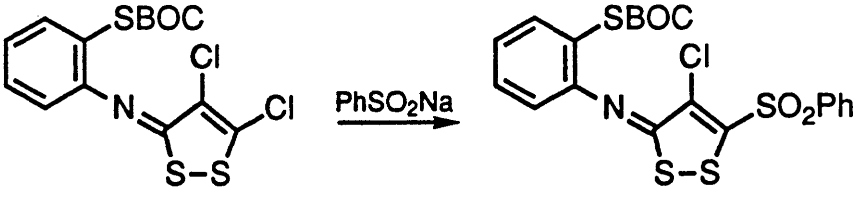


There have also been reports of using the *t* -butoxycarbonyl group to protect thiol groups,[113] and when the same procedure as used with *o* -phenylenediamine (i.e. sodium hydride followed by di-*t* -butyldicarbonate), when applied to *o* -aminothiophenol, the *S* -protected compound (**169**) was obtained in excellent yield. This in turn gave a good yield of the corresponding imine (**170**) when treated with the trichloro salt (**85**).



Several methods for deprotecting the *S* -protected group were tried; all were unsuccessful. Use of TFA in DCM, HCl in ethyl acetate, or thermolysis at 180 °C under nitrogen resulted in baseline material only. Refluxing in bromobenzene or treatment with TMS iodide had no effect and starting material only was recovered.

The imine (**170**) was then reacted with sodium benzenesulphinate which gave the corresponding compound (**171**) as yellow stable crystals in 74% yield.



170 **171**

Again, several methods of deprotection were attempted e.g. TFA in DCM, HCl in ethyl acetate, but only starting material was recovered.

3.5 Summary

The reaction of amines and certain carbanions with 3,4,5-trichloro-1,2-dithiolium chloride (**85**) leads to neutral 5-substituted *5H* -1,2-dithioles. The reaction of phenols and naphthols with 3,4,5-trichloro-1,2-dithiolium chloride (**85**) gives salts which are substituted through carbon rather than oxygen. Reaction of 3,4,5-trichloro-1,2-dithiolium chloride with thioacetamide gives 4,5-dichloro-1,2-dithiol-3-thione (**89**) in excellent yield.

Further reaction of the neutral 5-substituted *5H* -1,2-dithioles with nucleophiles leads to displacement of the chloro group in position 3. Displacement of the chlorine in position 4 could not be effected intermolecularly, but has been effected intramolecularly to give the new [1,2]dithiol[4,5-*b*][1,4]benzoxazine (**157** and **160**) ring system.

Reaction of 4,5-dichloro-1,2-dithiol-3-one (**86**) with various nucleophiles has also been investigated which usually results in displacement of the chlorine in position 5. With the carbanion of dimedone however a highly substituted pyrone is formed.

Chapter Four

Experimental

4.1 **Introduction**

4.1.1 *Solvents and reagents*

Commercially available solvents and reagents were used throughout without further purification except those shown below which were purified as described. Light petroleum refers to the fraction boiling between 40 °C and 60 °C and was distilled before use. Benzene, toluene and diethyl ether were dried by standing over sodium wire for several days. Tetrahydrofuran was dried by distillation from potassium metal under nitrogen. Dichloromethane was dried by distillation from phosphorus pentoxide and stored over 4 Å molecular sieves. Disulphur dichloride was distilled from elemental sulphur under reduced pressure and stored under nitrogen. Sulphur dichloride was distilled from phosphorus pentachloride at normal pressure immediately prior to use.

4.1.2 *Chromatography*

Flash Chromatography refers to the technique described by Still[114] using medium pressure (hand-bellows), and Dry-column Flash Chromatography to the technique described by Harwood.[115] The silica gel employed in both cases was Merck Kieselgel 60H and the sample mixture was applied to the column preadsorbed onto silica.

Commercial aluminium-backed thin-layer chromatography plates (Merck Kieselgel $60F_{254}$) were used throughout to check reactants and column eluants. After elution the plates were observed under UV light at 254 and 366 nm and/or developed in iodine vapour.

4.1.3 *Spectra*

Ultra-violet/visible spectra were recorded using a Philips PU 8740 scanning spectrophotometer.

Infra-red spectra were recorded on a Perkin-Elmer 1710 FT spectrometer.

^{1}H-Nuclear magnetic resonance spectra were recorded on the following machines: Jeol GSX 270 at 270 MHz; Bruker WM 250 at 250 MHz; Bruker WM 500 at 500 MHz.

Low resolution mass spectra and accurate mass measurements were recorded at Imperial College in the Organic Mass Spectrometry Laboratory, under the supervision of Dr. J. N. Bilton, on an AE1 MS12 mass spectrometer or a VG Micromass 7070B mass spectrometer using electron impact ionisation. Some accurate mass measurements were made by the Science and Engineering Research Council Mass Spectrometry Service Centre, University College, Swansea.

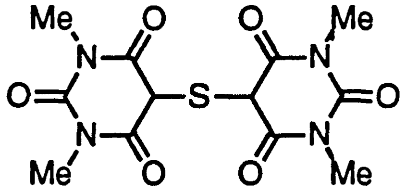
4.1.4 *Other data*

Melting points were recorded on a Reichert Kofler hot-stage microscope and are uncorrected.

Elemental microanalyses were carried out in the Department of Chemistry, Imperial College by the Organic Microanalytical Laboratory under the supervision of Mr. K. I. Jones.

4.2 Relating to Chapter Two

Bis(N,N'*-dimethylbarbituric acid)sulphide* (73)



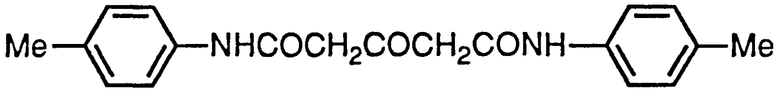
N,N' -Dimethylbarbituric acid (0.5 g, 3.2 mmol) was dissolved in benzene (5 ml) and disulphur dichloride (0.13 ml) was added dropwise with stirring. The mixture was refluxed for 2.5 h. After cooling the solvent was evaporated *in vacuo* and the resultant solid was dissolved in chloroform and reprecipitated using methanol, the title compound was obtained as a colourless solid (0.23 g, 42%), m.p. 210 °C (lit.,[75] 210 °C); $\nu_{max.}$ (nujol) 1 701s, 1 626, 1 500, 1 233, 1 197, 1 024, 775 and 751 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 3.4 (12H, s, C*H* $_3$) and 5.9 (2H, s, C*H*); *m/z* 342 (*M*$^+$, 31%), 310 (21), 222 (16), 187 (22), 156 (100), 99 (19), 72 (35), 58 (25), 42 (85), and 28 (32).

1,5-*bis(aniline)-penta-* 1,3,5-*trione* (77)

$$PhNHCOCH_2COCH_2CONHPh$$

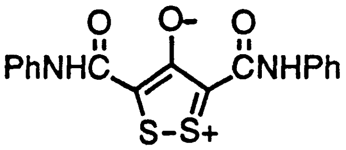
Diethyl acetone-1,3-dicarboxylate (6 g, 4.2 ml, 0.03 mol) and aniline (10 g, 6.4 ml, 0.1 mol) were heated together in a sealed tube at 100 °C for 24 h. After cooling the contents of the tube were poured into benzene (100 ml) and a colourless precipitate formed. This was filtered off and recrystallized from ethanol to give the title compound as colourless crystals (2.11 g, 24%), m.p. 156 °C (lit.,[78] 155 °C); $\nu_{max.}$ (nujol) 3 306, 1 711, 1 658, 1 603, 1 554, 1 447, 1 412, 1 301, 1 272, 1 178 and 1080 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 4.8 (4H, s, C*H* $_2$), 7.1 (2H, t, *J* = 6 Hz, 4'-H), 7.4 (4H, t, *J* = 8 Hz, 3'-H), and 7.6 (4H, d, *J* = 8 Hz, 2'-H).

1,5 -*bis(* 4-*methylaniline)-penta-* 1,3,5-*trione* (78)



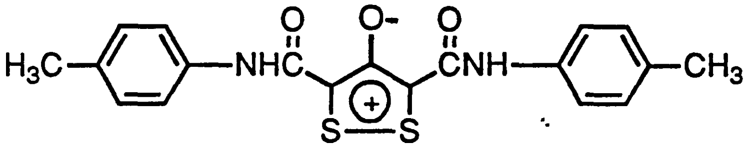
Diethyl acetone-1,3-dicarboxylate (4.9 g, 3.4 ml, 0.025 mol) and 4-methylaniline (8.9 g, 0.083 mol) were heated together in a sealed tube at 100 °C for 24 h. After cooling the contents of the tube were poured into benzene (100 ml) . The precipitate which formed was filtered off and recrystallized from ethanol to give colourless crystals (3.54 g, 45%), m.p. 172 °C (lit.,[77] 169 °C); $\nu_{max.}$ (nujol) 3 288, 3 131, 1 732, 1 716, 1 680s, 1 659s, 1 613s, 1 552, 1 514, 1 417, 1 407, 1 340, 1 291, 1 266 and 817 cm^{-1}; δ_H (270 MHz; CDCl$_3$) 2.2 (6H, s, C*H*$_3$), 3.7 (4H, s, C*H*$_2$), 7.1 (4H, d, *J* 8 Hz, 2'-H and 6'-H), and 7.4 (4H, d, *J* 8 Hz, 3'-H and 5'-H).

3,5-*bis(benzamido)*- 1,2-*dithiolium*- 4-*olate* (79)



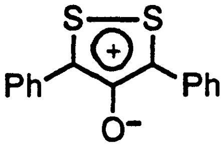
Disulphur dichloride (0.08 g, 50 µl, 0.6 mmol) was added dropwise with stirring to a solution of 1,5-(aniline)penta-1,3,5-trione (0.08 g, 0.3 mmol) in dry toluene (3 ml). The solution immediately went red and was refluxed for 2 h. On cooling a red preciptate formed which was filtered off. Dry column flash chromatography with 2% methanol in DCM gave a red solid (67 mg, 70%), m.p. 220 °C (decomp.)(Found C, 57.2; H, 3.5; N, 7.6. Calc. for $C_{17}H_{12}N_2O_3S_2$ C, 57.3; H, 3.4; N, 7.9%); $\lambda_{max.}$ (CH$_3$CN) 532 nm (log ε 4.07); $\nu_{max.}$ (nujol) 1 677, 1 649, 1 621, 1 601, 1 557, 1 495, 1 205 and 1 083 cm^{-1}; δ_H (270 MHz; CDCl$_3$) 7.2 (2H, t, *J* 8Hz, 4'-H), 7.4 (4H, t, *J* 8 Hz, 3'-H and 5'-H), and 7.8 (4H, d, *J* 8 Hz, 2'-H and 6'-H); *m*/*z* 356 (M^+ , 100%), 225 (14), 193 (31), 164 (PhNHCOCS, 53), 133 (75), 93 (94), 77 (55), and 65 (22).

3,5-*bis(4'-methylbenzamido)*- 1,2-*dithiolium*- 4-*olate* (80)



Disulphur dichloride (50 µl, 0.6 mmol) was added dropwise with stirring to a solution of 1,5-bis(4'-methylanilino)pentan-1,3,5-trione (0.1 g, 0.3 mmol) in dry toluene (3 ml). The mixture went red and was refluxed for 2 h. The mixture was adsorbed onto silica gel and dry column flash chromatography with ethyl acetate and petroleum ether (1:1) gave the title compound as a purple solid (58 mg, 49%), m.p. 230 °C; $\lambda_{max.}$ (CH_3CN) 482 nm (log ε 3.89); $\nu_{max.}$ (nujol) 3 564, 3 459, 1 660, 1 651, 1 663, 1 603, 1 556, 1 539, 1 514, 1 410, 1 315, 1 301, 1 259, 1 204s, 1 187, 1 125, 1 070, 821 and 784 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 2.3 (6H, s, CH_3), 7.2 (4H, d, *J* 8 Hz, 2'-H and 6'-H), and 7.8 (4H, d, *J* 8 Hz, 3'-H and 5'-H); *m/z* 384 (M^+, 100%), 207 (34), 178 (55), 147 (72), 133 (32), 107 (100), 91 (41), 77 (32), 65 (24), and 28 (28).

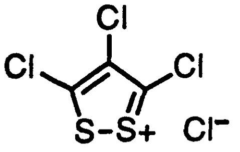
3,5-*diphenyl*- 1,2-*dithiolium*- 4-*olate* **(81)**



Sulphur dichloride (0.65 ml, 10 mmol) was added dropwise to a solution of dibenzylketone (1.0 g, 5 mmol) in THF (30 ml) and the mixture was refluxed for 1 h. The solvent was evaporated *in vacuo* and the yellow oil obtained was treated with pyridine (6 ml), fumes of HCl were observed with an exothermic reaction. The resultant mixture was poured into boiling water which was then cooled and left to stand overnight. The precipitate was filtered off and washed with ether. Dry column flash chromatography on this material with 2% methanolic ammonia in ethyl acetate gave the title compound as a purple solid (0.52 g, 40%), m.p. 235 °C (Found C, 66.45; H, 3.5; Calc. for $C_{15}H_{10}OS_2$ C, 66.6; H, 3.7); $\lambda_{max.}$ (DCM) 257 and 557 nm (log ε 4.10 and 4.08); $\nu_{max.}$ (nujol) 1 496, 1 437, 1 418, 1 338, 1 296, 1 162 and 763 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.4-7.6 (6H, m, ArH) and 8.3-8.5 (4H, m, ArH); *m/z* 270 (M^+, 16%), 192 (25), and 160 (20).

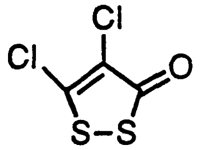
4.3 Relating to Chapter Three

3,4,5-*Trichloro*- 1,2-*dithiolium chloride* (**85**)



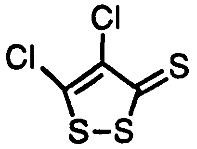
The method of Boberg *et al.* was modified as follows.[95] Hexachloropropene (7.5 g, 0.03 mol) and sulphur (2.58 g, 0.08 mol) were heated together in an RB flask fitted with an internal thermometer, reflux condenser and drying tube for 4 h at 180 °C. The reaction mixture was allowed to cool to ambient temperature and left to stand overnight. The dark brown precipitate was filtered off under a blanket of argon and washed with benzene (20 ml), and then stirred in carbon disulphide (40 ml) for 0.25 h, filtered off and and the solid washed again with benzene (20 ml) then dried and stored in a vacuum desiccator. The title compound (**85**) was obtained as a brown solid (3.1 g, 42%), m.p. 235 °C (lit.[95] 235 °C); *m/z* (100 °C) 246, 244, 242, 240 (M^+ 2, 8, 15, 11%), 209, 207, 205 (M^+ -Cl, 38, 100, 91), 137, 135 (C_3ClS_2, 9, 23), 100 (C_3S_2, 23), 81 (24), 79 (69), and 28 (23).

4,5-*Dichloro*- 1,2-*dithiol*- 3-*one* (**86**)



This compound was prepared using the method of Boberg *et al.* (*i.e.* treatment of 3,4,5-trichloro-1,2-dithiolium chloride (**85**) with water)[96] as yellow crystals (86)(100%) after chromatography on silica gel, m.p. 69 °C (lit.,[96], 69°C); $\nu_{max.}$ (nujol) 1 631s, 1 520s, 1 183, 968 and 848 cm^{-1}; δ_C (62.5 MHz; $CDCl_3$) 122 (5-C), 152 (4-C) and 183 (carbonyl); *m/z* (100 °C) 190, 188, 186 (M^+ 17, 75, 100%), 162, 160, 158 (M^+ -CO, 3, 12, 16), 149 (14), 81, 79 (CClS, 21, 56), and 64 (S_2, 19).

4,5-Dichloro- 1,2-dithiol- 3-thione (**89**)



Method 1: Hydrogen sulphide gas was passed through a stirred suspension of 3,4,5-trichloro-1,2-dithiolium chloride (**85**) (0.1 g, 0.4 mmol) in DCM (5 ml) for 2 min and an orange solution was formed. The mixture was adsorbed onto silica gel and purified by dry flash column chromatography (15 g silica gel, 10% ethyl acetate in light petroleum) to give the title compound as orange crystals (67 mg, 80%), m.p. 76 °C (lit.,[99], 76 °C); $\lambda_{max.}$ (EtOH) 232, 289, 324 and 423 nm (log ε 3.79, 3.67, 3.64 and 3.63); $\nu_{max.}$ (nujol) 1 700, 1 669, 1 524, 1 261s, 1 073, 955, 850s, and 753 cm^{-1}; δ_C (62.5 MHz; $CDCl_3$) 136 (5-C), 155 (4-C), and 203 (thiocarbonyl); *m/z* (100°C) 206, 204, 202 (M^+ 20, 81, 100%), 169, 167 (M^+ - Cl, 6, 13), 137, 135 (M^+ -SCl, 18, 46), 105, 103 (M^+ -ClS_2, 21, 59), 81, 79 (CClS, 9, 24), and 64 (S_2, 10).

Method 2: 4,5-Dichloro-1,2-dithiol-3-one (**89**) (72 mg, 0.4 mmol) and Lawesson's reagent (233 mg, 0.6 mmol) were dissolved in dry toluene (2 ml) and refluxed for 14 h. The excess of Lawesson's reagent was filtered off and the toluene evaporated *in vacuo*. Purification as described in Method 1 gave the title compound (**89**)(60 mg, 74%), m.p.76 °C.

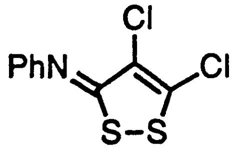
Method 3: 3,4,5-Trichloro-1,2-dithiolium chloride (**85**) (1.0 g, 4.2 mmol) was added to a solution of thioacetamide (0.31 g) in DCM (30 ml) and stirred at ambient temperature for 1 h. The solvent was evaporated *in vacuo* and the residue was purified by recrystallization from petroleum ether (b.p. 60-80 °C) to give the title compound (0.75 g,90%), m.p. 76 °C.

Reactions of the trichloro salt (**85***) with anilines*

General procedure.

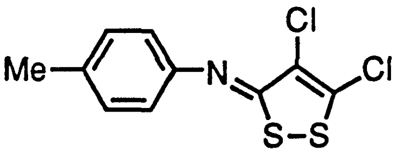
Except where noted the aniline (one equivalent) was dissolved in dry DCM and the trichloro salt (85) (one equivalent) was added portionwise. The reaction mixture was stirred at ambient temperature for 1 h and then pyridine (one equivalent) was added with stirring. After 0.5 h the mixture was adsorbed onto the minimum amount of silica gel and purified by dry flash column chromatography, the solvent system being 20% ethyl acetate in light petroleum.

N-(3,4-*Dichloro*- 5H- 1,2-*dithiol*- 5-*ylidene)aniline* **(96)**



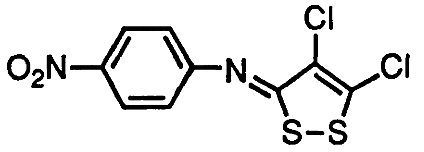
Aniline (0.3 ml, 3.3 mmol, 4 equivalents) was dissolved in DCM (10 ml) and the salt (**85**)(200 mg, 0.8 mmol) was added portionwise with stirring. The mixture was stirred at ambient temperature for 0.5 h, then adsorbed onto silica gel and purified by dry flash column chromatography, the solvent system being 20% ethyl acetate in light petroleum which gave the *title compound* (**96**) as brown crystals (178 mg, 82%), m.p. 73 °C (Found C, 41.0, H, 1.7, N, 5.2. $C_9H_5Cl_2NS_2$ requires C, 41.2, H, 1.9, N, 5.3%); $\lambda_{max.}$ (EtOH) 222 and 442 nm (log ε 4.10 and 3.64); $\nu_{max.}$ (nujol) 1 601s, 1 585s, 1 543s, 1 481s, 1 181, 1 071, 1 022, 975, 911, 848, 765 and 699 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 7.05-7.10 (2H, m, ArH), 7.37-7.43 (2H, m, ArH), and 7.16-7.23 (1H, m, ArH); *m/z* (130 °C) 265, 263, 261 (M^+, 6, 27, 38%), 228, 226 (M^+-Cl, 9, 23), 191 (M^+-2Cl, 4), 149 (100), 77 (Ph, 40), 57 (26), and 51 (25).

N-(3,4-*Dichloro*- 5H- 1,2-*dithiol*- 5-*ylidene)*- 4-*methylaniline* **(97)**



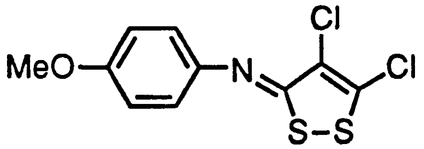
p -Toluidine gave the *title compound* (**97**) (77%) as yellow crystals, m.p. 102 °C (from DCM/petroleum ether) (Found C, 43.5, H, 2.4, N, 4.5. $C_{10}H_7Cl_2NS_2$ requires C, 43.5, H, 2.55, N, 5.1%); λ_{max} (EtOH) 226 and 344 nm (log ε 4.25 and 3.77); $\nu_{max.}$ (nujol) 1 699, 1 666, 1 607, 1 567s, 1 538s, 1 503s, 1 242, 1 183, 1 168, 1 111, 1 019, 978, 939, 867, 854s, 818, 790, 714 and 606 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 2.40(3H, s, C*H* 3), 6.90-7.10(2H, m, ArH), and 7.20-7.30(2H,m, ArH); *m/z* (160 °C) 279, 277, 275 (M^+, 17, 74, 100%), 264, 262, 260 (M^+ -Me, 8, 38, 51), 242, 240 (M^+ -Cl, 14, 34), 178, 176 (19, 57), 91 (60), and 65 (39%).

N-(*3,4-Dichloro-* 5H- *1,2-dithiol- 5-ylidene)- 4-nitroaniline* (98)



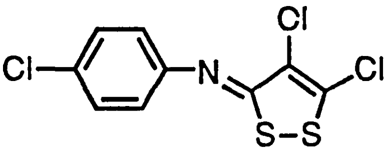
p -Nitroaniline gave the *title compound* (98) (81%) as yellow crystals, m.p. 165 °C (from DCM/petroleum ether) (Found: C, 35.4; H, 1.3; N, 9.2. $C_9H_4Cl_2N_2O_2S_2$ requires C, 35.2;H, 1.3; N, 9.1%); λ_{max} (EtOH) 304 and353 nm (log ε 3.87 and 3.83); $\nu_{max.}$ (nujol) 2 955s, 1 563, 1 527, 1 511, 1 339 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 7.10-7.20 (2H, m, ArH) and 8.25-8.35 (2H, m, ArH); *m/z* (130 °C) 310, 308, 306 (M^+ , 13, 60, 84%), 227, 225 (M^+ -NO_2, 8, 17), and 207 (M^+ -ClS_2, 27).

N-(*3,4-Dichloro-* 5H-1,2-*dithiol- 5-ylidene)- 4-methoxyaniline* (99)



p -Methoxyaniline gave the *title compound* (99) (84%) as yellow crystals, m.p. 105 °C (from DCM/petroleum ether) (Found: C, 41.4; H, 2.3; N, 4.6. $C_{10}H_7Cl_2NOS_2$ requires C, 41.1; H, 2.4; N, 4.8%); $\lambda_{max.}$ (EtOH) 227 and 360 nm (log ε 4.18 and 3.77); $\nu_{max.}$ (nujol) 1 614, 1 549, 1 502s, 1 295, 1 255s, 1 232, 1 189, 1 031, 976, 855s and 825 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 3.80 (3H, s, MeO), 6.90-6.95 (2H, m, Ar), and 7.00-7.05 (2H, m, Ar); *m/z* (130 °C) 295, 293, 291 (M^+, 16, 73, 100%), 280, 278, 276 (M^+ -CH_3,14, 65, 84), 194, 192 (M^+ -ClS_2, 10, 30), 124 (19), 92 (19), and 77 (20).

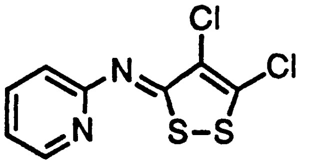
4-Chloro- N-(*3,4-dichloro-* 5H- *1,2-dithiol- 5-ylidene)aniline* (108)



p -Chloroaniline gave the title compound (**108**) as yellow crystals, (90%) m.p. 92 °C (from petroleum ether); $\lambda_{max.}$ (EtOH) 227 and 339 nm (log ε 4.22 and 3.82);

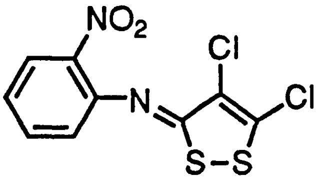
$\nu_{max.}$ (nujol) 1 566, 1 534s, 1 483, 1 096, 864, and 855 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 6.95-7.05 (2H, m, ArH) and 7.3-7.4 (2H, m, ArH); *m/z* (100 °C) 301, 299, 297, 295 (*M*$^+$, 6, 37, 100, 95%), 264, 262, 262 (*M*$^+$-Cl, 11, 50, 68), 200, 198, 196 (*M*$^+$- ClS_2, 6, 40, 61), 113, 111 (13, 41), 79 (12), and 75 (32).

2-[N-(*3,4-Dichloro-* 5H- *1,2-dithiol- 5-ylidene)amino]pyridine* **(100)**



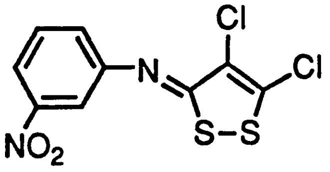
2-Aminopyridine gave the *title compound* **(100)** (40%) as pale yellow leaflets, m.p. 199 °C(from DCM/petroleum ether)(Found C, 36.6, H, 1.4, N, 10.55. $C_8H_4Cl_2N_2S_2$ requires C, 36.6, H, 1.5, N, 10.65%); $\lambda_{max.}$ (EtOH) 216, 389 and 408 nm (log ε 4.49, 4.07 and 4.05); $\nu_{max.}$(nujol) 1 602, 1 557, 1 493s, 1 149, 1 004, 987, 902 and 864s cm^{-1}; δ_H(270 MHz; $CDCl_3$) 7.1-7.3 (1H, m, ArH), 7.6-7.7 (1H, m, ArH), 7.8-7.9 (1H, m, ArH), and 8.4-8.5 (1H, m, ArH); *m/z* (150 °C) 266, 264, 262 (*M*$^+$, 7, 32, 43%), 231, 229, 227 (*M*$^+$- Cl, 4, 41, 100), and 78 (71).

N-(*3,4-Dichloro-* 5H- *1,2-dithiol- 5-ylidene)- 2-nitroaniline* **(102)**



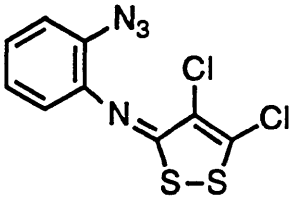
2-Nitroaniline gave the *title compound* **(102)** (72%) as yellow crystals, m.p. 118 °C (from DCM/petroleum ether)(Found C, 35.2, H, 1.1, N, 9.1. $C_9H_4Cl_2N_2O_2S_2$ requires C, 35.1, H, 1.3, N, 9.1%); $\lambda_{max.}$ (EtOH) 215 and 336 nm (log ε 4.39 and 3.93); $\nu_{max.}$(nujol) 1 615s, 1 599s, 1 572, 1 547s, 1 520s, 1 354s, 1 303, 1 264, 873, 853 and756 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.0-7.2 (1H, m, ArH), 7.3-7.5 (1H, m, ArH), 7.6-7.8 (1H, m, ArH), and 8.0-8.2 (1H, m, ArH); *m/z* (160 °C) 310, 308, 306 (*M*$^+$, 6, 27, 35%), 246, 244, 242 (*M*$^+$ - S_2, 3, 9, 11), 152 (45), 136 (33), 104 (28), and 79 (35).

N-(*3,4-Dichloro-* 5H- *1,2-dithiol- 5-ylidene)- 3-nitroaniline* **(107)**



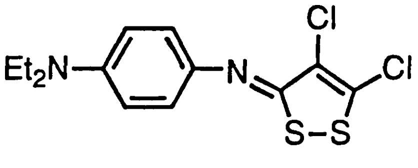
3-Nitroaniline gave the *title compound* **(107)** (63%) as yellow crystals, m.p. 128 °C (from petroleum ether/DCM)(Found C, 35.2; H, 1.2; N, 9.05; $C_9H_4Cl_2N_2O_2S_2$ requires C, 35.2; H 1.3; N, 9.1%); $\lambda_{max.}$ 214 and 336 nm (log ε 4.29 and 3.91); $\nu_{max.}$ 1 604, 1 546, 1 523s, 1 347, and 858 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.3-7.5 (1H, m, ArH), 7.5-7.7 (1H, m, ArH), 7.9-8.0 (1H, m, ArH), and 8.0-8.2 (1H, m, ArH); *m/z* (150 °C) 310, 308, 306 (*M*$^+$, 17, 75, 100%), 263, 261, 259 (3, 13, 15), 227, 225 (*M*$^+$-NO_2, Cl, 15, 32), 208, 206 (11, 32), and 76 (35).

2-Azido- N-(*3,4-dichloro-* 5H- *1,2-dithiol- 5-ylidene)aniline* **(106)**



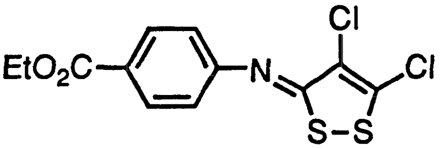
2-Azidoaniline was prepared by the method of Smith, Hall, and Kan[112] and gave the *title compound* **(106)** (56%) as pale yellow needles (from petroleum ether), m.p. 112 °C (Found *M*$^+$, 301.9254. $C_9H_4Cl_2N_4S_2$ requires 301.9255); $\lambda_{max.}$ (EtOH) 212 and 333 nm (log ε 4.32 and 3.77); $\nu_{max.}$ (nujol) 2 147, 2 108s, 1 699, 1 675, 1 597, 1 586, 1 541s, 1 528, 1 481, 1 445, 1 334, 1 097 and 981 cm^{-1}; δ_H (270MHz, $CDCl_3$) 7.0-7.1 (1H, m, ArH) and 7.1-7.3 (3H, m, ArH); δ_C (67.5 MHz; $CDCl_3$) 120, 121, 123, 126, 127, 131, 141, 144, 160, *m/z* (100 °C) 306, 304, 302 (*M*$^+$ 4, 16, 21%), 278, 276, 274 (*M*$^+$ -N_2, 4, 15, 20), 243, 241, 239 (*M*$^+$-N_2, -Cl, 5, 22, 51), 174, 172, 170 ($C_3Cl_2S_2$, 10, 47, 60), 137, 135 (C_3ClS_2, 42, 100), 100 (25), 85 (12), and 79 (29).

N-(*3,4-Dichloro-*5H- *1,2-dithiol- 5-ylidene)- 4-diethylaminoaniline* **(110)**



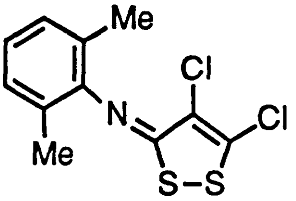
Freshly distilled 4-diethylaminoaniline was used and the reaction was carried out under argon to give the title compound (**110**) (29%) as orange crystals, m.p. 65 °C , no other products were observed by TLC; $\lambda_{max.}$ (EtOH) 267 and 409 nm (log ε 4.11 and 3.92); $\nu_{max.}$ 2 962s, 1 612s, 1 581, 1 540, 1 515s, 1 405, 1 352s, 1 272, 1 197, 1 147, 1 077, 1 014, 974, 840 and 813 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.2 (6H, t, C*H*$_3$), 3.4 (4H, q, C*H* $_2$), 6.6-6.7 (2H, m, ArH), and 7.0-7.1 (2H, m, ArH); *m/z* (120 °C) 336, 334, 332 (*M*$^+$ 8, 32, 43), 321, 319, 317 (*M*$^+$ -CH_3, 12, 50, 68), 258, 256 (*M*$^+$ -C_2H_5,- CCl, 35, 100), 204, 202 (17, 21), 192 (22), 160 (47), 128 (57), 79 (18), and 64 (67).

Ethyl 4-[N-*(3,4-dichloro-* 5H- *1,2-dithiolylidene)amino]benzoate* (**109**)



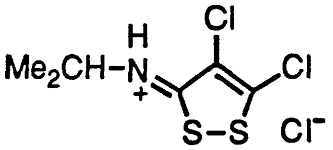
Ethyl 4-aminobenzoate gave the *title compound* (**109**) (93%) as yellow crystals (from DCM/petroleum ether), m.p. 128 °C (Found: C,43.3; H, 2.6; N, 4.0. $C_{12}H_9Cl_2NO_2S_2$ requires C, 43.1; H, 2.7; N, 4.2%); $\lambda_{max.}$ (EtOH) 245 and 345 nm (log ε 4.19 and 3.88); $\nu_{max.}$ (nujol) 1 703s, 1 584, 1 540, 1 311, 1 291s, 1 163, 1 127, 1 109, 1 026 and 864 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.3-1.5 (3H, t, C*H* $_3$), 4.3-4.5 (2H, q, C*H* $_2$), 7.0-7.2 (2H, m, ArH), and 8.0-8.2 (2H, m, ArH); *m/z* (160 °C) 337, 335, 333 (*M*$^+$ 17, 72, 100%), 292, 290, 288 (*M*$^+$ - EtO, 8, 36, 48), 264, 262, 260 (*M*$^+$ -EtOCO, 7, 29, 39), 236, 234 (7, 22), 227, 225 (11, 23), 205 (16), 103 (17), 76 (31), 65 (30), and 29 (90).

N-*(3,4-Dichloro-* 5H- *1,2-dithiol- 5-ylidene)- 2,6-dimethylaniline* (**101**)



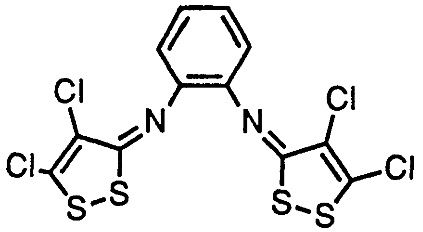
2,6-Dimethylaniline gave the title compound (**101**) (64%) as a yellow oil ; $\lambda_{max.}$ (EtOH) 323 nm (log ε 3.89); $\nu_{max.}$ (film) 2 917, 1 609, 1 587, 1 548, 1 439, 1 175, 1 093, 854, and 769 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 2.2 (6H, s, C*H* $_3$), 7.0 (1H, t, ArH), and 7.1 (2H, d, ArH); *m/z* (120 °C) 293, 291, 289 (*M*$^+$ 16, 75, 100%), 256, 254 (M^+ - Cl, 63, 97), 223, 221 (13, 33), 192, 190 (8, 25), 105 (26), and 77 (50).

N-(3,4-*Dichloro-* 5H- 1,2-*dithiol-* 5-*ylidene)-* 2-*aminopropane hydrochloride* **(93)**



3,4,5-Trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of 2-aminopropane (35 µl, 0.4 mmol) in DCM (2 ml). The mixture was stirred for 2 h and then the brown precipitate formed was filtered off and washed with DCM (10 ml) then dried *in vacuo* to give the *title compound* **(93)** (74 mg, 71%) as a brown powder , m.p. 155 °C (Found M^+, 226.9397. $C_6H_7Cl_2NS_2$ requires 226.9394); $\nu_{max.}$ (nujol) 3 402, 3 225, 2 819, 2 719, 1 612, 1 569, 1 511, 1 388, 1 169, 1 150, 857 and 804 cm^{-1}; δ_H (270 MHz; DMSO d^6) 1.6 (6H, d, C*H* $_3$) 3.7 (1H, m, C*H*); *m/z* (160 °C) 231, 229, 227 (M^+ -HCl, 7, 25, 30%), 189, 187, 185 (M^+ -C_3H_6, 15, 50, 64), 44 (100), and 38, 36 (HCl, 20, 64).

N,N'-*Bis-(* 3,4-*dichloro-* 5H- 1,2-*dithiol-* 5-*ylidene)-* 1,2-*diaminobenzene* **(111)**

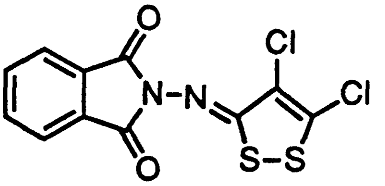


3,4,5-Trichloro-1,2-dithiolium chloride (0.2 g, 0.8 mmol) was added to a solution of *o* -phenylenediamine (0.045 g, 0.4 mmol) in DCM (10 ml). The mixture was stirred for 3 h at ambient temperature, then pyridine (0.13 ml, 1.6 mmol) was added dropwise with stirring. The mixture was stirred for a further 1 h and then the mixture was adsorbed onto silica gel. Dry column flash chromatography using 20% ethyl acetate in petroleum ether gave the *title compound* **(111)** (0.158 g, 85%) as pale yellow crystals, m.p. 130 °C (Found C, 32.45; H, 0.8; N, 6.1; $C_{12}H_4Cl_4N_2S_4$ requires C, 32.3; H, 0.9; N, 6.3); $\lambda_{max.}$ (EtOH) 336 nm (logε

4.06); $\nu_{max.}$ (nujol) 1 593, 1 576s, 1 537s, 1 177, 1 101, 1 032, 977, 937, and 876 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.1-7.2 (2H, m, ArH) 7.2-7.3 (2H, m, ArH); *m/z* (160 °C) 450, 448, 446, 444 (*M*$^+$,12, 43, 73, 48%), 413, 411, 409 (*M*$^+$ -Cl, 5, 10, 8), 349, 347, 345 (*M*$^+$ -S_2Cl, 37, 100, 93), 244, 242, 240 (36, 53, 20), 137, 135 (C_3S_2Cl, 14, 35), 79 (29), and 28 (35).

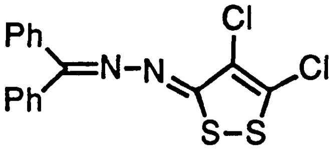
Reaction of the trichloro salt (85) with hydrazines, N*-phenylhydroxylamine, and* N,N*-dichlorobenzamide.*

N-*Amino-(* 3,4-*dichloro-* 5H- 1,2-*dithiol-* 5-*ylidene)phthalimide* **(113)**



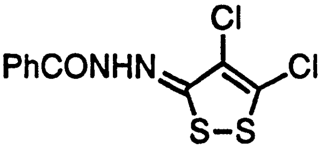
N -Aminophthalimide (0.134 g, 0.8 mmol) was dissolved in DCM (10 ml) and 3,4,5-trichloro-1,2-dithiolium chloride (0.2 g, 0.8 mmol) was added portionwise with stirring over 2 min. The mixture was stirred at ambient temperature for 3 h and then pyridine (0.13 ml) was added dropwise. After 0.5 h the mixture was adsorbed onto silica gel. Dry column flash chromatography with 20% ethyl acetate in petroleum ether gave the *title compound* **(113)** (0.036 g, 13%) as a yellow powder , m.p. 173 °C (Found: M^+, 329.9091. $C_{11}H_4Cl_2N_2O_2S_2$ requires 329.9091); $\lambda_{max.}$ (EtOH) 334 nm (log ε 3.97); $\nu_{max.}$ (nujol) 1 789, 1 743, 1 712s, 1 542, 1 108, 996, 886 and 707 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.70-7.85 (2H, m, phthalimide) and 7.80-7.95 (2H, m, phthalimide) *m*/*z* (180 °C) 334, 332, 330 (M^+ 0.3, 1, 2%), 297, 295 (M^+ -Cl, 0.3, 1), 147 (100), 104 (75), and 76 (68).

N-*(* 3,4-*Dichloro-* 5H- 1,2-*dithiol-* 5-*ylidene)benzophenonehydrazone* **(114)**



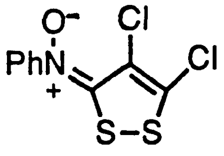
Benzophenonehydrazone (0.081 g, 0.4 mmol) was dissolved in DCM (15 ml) and 3,4,5-trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added with stirring. After 0.5 h pyridine (0.065 ml) was added dropwise and the mixture was adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* **(114)** (0.124 g, 82%) as small yellow crystals, m.p. 130 °C (from petroleum ether/DCM)(Found C, 52.4; H, 2.7; N, 7.6. $C_{16}H_{10}Cl_2N_2S_2$ requires C, 52.6; H, 2.8, N, 7.7%); $\lambda_{max.}$ (CH_3CN) 259, 273 and 403 nm (log ε 4.23, 4.22 and 4.06); $\nu_{max.}$ (nujol) 1 588, 1 569s, 1 533, 1 515, 1 301, 1 024, 993, 873s, 780 and 768 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.3-7.5 (6H, m, ArH) and 7.6-7.8 (4H, m, ArH); *m/z* (120 °C) 368, 366, 364 (M^+ 2, 15, 20%), 180 (Ph_2CN, 40), 165 (100), 137, 135 (C_3S_2Cl, 10, 25), 125 (28), 91 (95), and 77 (75).

N-(3,4-*Dichloro*-5H-1,2-*dithiol*-5-*ylidene)benzhydrazide* **(115)**



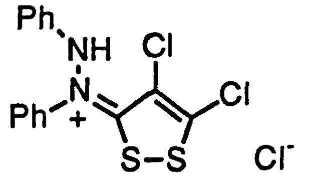
Benzhydrazide (0.056 g, 0.4 mmol) was dissolved in DCM (6 ml) and 3,4,5-trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added portionwise with stirring. After 0.5 h, pyridine (0.065 ml) was added dropwise and the mixture was adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* **(115)** (0.066 g, 52%) as yellow crystals, m.p. 144 °C (Found C, 39.3; H, 1.9; N, 9.2. $C_{10}H_6Cl_2N_2OS_2$ requires C, 39.35; H, 2.0; N, 9.2%); $\lambda_{max.}$ (CH_3CN) 230 and 346 nm (log ε 4.14 and 4.00); $\nu_{max.}$ (nujol) 1 626, 1 543s, 1 305, 987, 899, 853, and 796 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.4-7.6 (5H, m, ArH) 8.0 (1H, br, NH); *m/z* (120 °C) 308, 306, 304 (M^+ 4, 11, 14%), 273, 271 (M^+ -Cl, 2, 5), 207, 205 (M^+ -ClS_2, 3, 12), 105 (PhCO, 100), 77 (51), and 51 (24).

N-(3,4-*Dichloro*-5H-1,2-*dithiol*-5-*ylidene)aniline*-N-*oxide* **(112)**



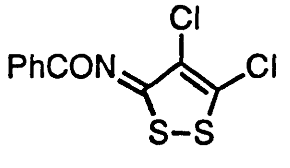
3,4,5-Trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of *N*-phenylhydroxylamine (0.045 g, 0.4 mmol) in DCM (5 ml). The mixture was stirred at ambient temperature for 16 h and was then was washed with sodium bicarbonate solution (5% solution, 20 ml), and then washed with water. The organic extract was dried ($MgSO_4$) and then adsorbed onto silica gel. Dry column flash chromatography with ether gave the *title compound* **(112)** (0.05 g, 43%) as a dark yellow oil (Found C, 38.9; H, 2.0; N, 4.7; $C_9H_5Cl_2NOS_2$ requires C, 38.9; H, 1.8; N, 5.0%); $\lambda_{max.}$ (CH_3CN) 222 and 308 nm (log ε 4.13 and 3.93); $\nu_{max.}$ ($CHCl_3$) 1 719, 1 293, 1 222, 1 219, 1 075, and 786 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.3-7.5 (5H, m, ArH); *m/z* (160 °C) 281, 279, 277 (M^+ 1, 3, 5%), 265, 263, 261 (M^+ -O, 15, 64, 88), 228, 226 (M^+ -OCl, 24, 56), 164, 162 (M^+-$OClS_2$, 20, 60), 77 (100), 51 (52), and 36 (54).

N- (*4,5-dichloro-* 5H-1,2-*dithiol* -5- *ylidene)* -N,N'-*diphenylhydrazine-chloride* **(116)**



3,4,5-Trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of 1,2-diphenylhydrazine (0.076 g, 0.4 mmol) in DCM (5 ml) and the mixture was stirred for 1.5 h at ambient temperature. The green solid formed was filtered off and washed with DCM (10 ml), then dried *in vacuo* giving the *title compound* (**116**) (0.067 g, 42%) as a yellow solid , m.p. 260 °C (decomp.)(Found M^+, 352.9741. $C_{15}H_{11}Cl_2N_2S_2$ requires 352.9471); $\nu_{max.}$ (nujol) 3 373, 1 602, 1 543s, 1 494s, 1 314, 1 242, 1 006, 818, and 764 cm^{-1}; δ_H (500 MHz; DMSO-d^6) 6.9-7.0 (1H, m, ArH) 7.0-7.1 (1H, m, ArH) 7.2-7.3 (1H, m, ArH) 7.3-7.4 (1H, m, ArH) 7.4-7.6 (4H, m, ArH) 7.7-7.8 (1H, m, ArH) 7.9-8.0 (1H, m, ArH); *m/z* (FAB) (NOBA) 357, 355, 353 (M^+, 10, 43, 57%), 265, 263, 261 (M^+ -PhNH, 3, 13, 16), 185 (21), 107 (33), 89 (41), and 77 (53).

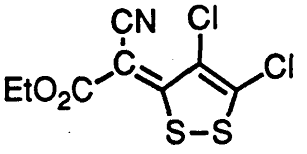
N-(*3,4-Dichloro-* 5H- *1,2-dithiol- 5-ylidene)benzamide* **(118)**



3,4,5-Trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of *N,N* -dichlorobenzamide (0.08 g, 0.4 mmol) in DCM (2 ml) with stirring. The mixture turned dark upon addition of the 3,4,5-trichloro-1,2-dithiolium chloride. After 2 h the mixture was adsorbed onto silica gel and dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* (**118**) (0.092 g, 77%) as a brown solid, m.p. 54 °C (Found *M*$^+$, 289.9268. $C_{10}H_6Cl_2NOS_2$ requires 289.9268); $\nu_{max.}$ (nujol) 1 695, 1 646, 1 521, 1 324, 1 290, 1 219, 1 183, 1 026, 968, 850, and 789 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.4-7.5 (2H, m, ArH), 7.5-7.6 (1H, m, ArH), and 8.1-8.2 (2H, m, ArH); *m/z* (160 °C) 293, 291, 289 (*M*$^+$, 13, 61, 82%), 105 (PhCO, 100), 77 (42), 51 (13), and 28 (10).

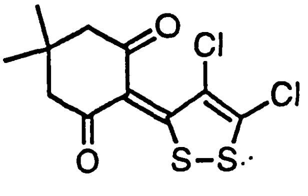
Reaction of the trichloro salt (**85** *) with active methylene compounds.*

Ethyl 2-cyano-2-(3,4-dichloro-1,2-dithiol-5-ylidene)acetate (**119**)



Ethyl cyanoacetate (52 mg, 0.45 mmol) was dissolved in THF (2 ml) and sodium hydride (18 mg, 0.45 mmol, 60% dispersion) was added. When effervescence had ceased the resultant milky suspension was added dropwise with stirring to a suspension of 3,4,5-trichloro-1,2-dithiolium chloride (100 mg, 0.4 mmol) at room temperature. After 2 h, the mixture was adsorbed onto silica gel; dry column flash chromatography (10% ethyl acetate in light petroleum) gave 4,5-dichloro-1,2-dithiol-3-one (42 mg, 54%) followed by the *title compound* (**119**) (11 mg, 9%) as yellow crystals, m.p. 180 °C (Found: M^+, 280.9139. $C_8H_5Cl_2NO_2S_2$ requires 280.9139); $\lambda_{max.}$ (EtOH) 220, 277, 407, and 427 nm (log ε 4.25, 3.71, 4.30, and 4.25); $\nu_{max.}$ (nujol) 2 206s (CN), 1 639s (C=O), 1 313s, 1 141, 1 032, 1 003, 870, and 765 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.2 (3H, t, CH_3) and 4.2 (2H, q, CH_2); δ_C (125 MHz; $CDCl_3$) 14 (CH_3) 63 (OCH_2) 87, 114, 122, 150, 168, and 169; *m/z* (100 °C) 285, 283, 281 (M^+ 13, 59, 82%), 257, 255, 253 (M^+ -C_2H_4, 3, 13, 18), 240, 238, 236 (M^+ -OC_2H_5, 4, 17, 23), 220, 218 (M^+ -C_2H_4,Cl, 41, 100), 186, 184, 182 (M^+-CO_2Et, CN, 5, 12, 15), 79 (24), and 64 (15).

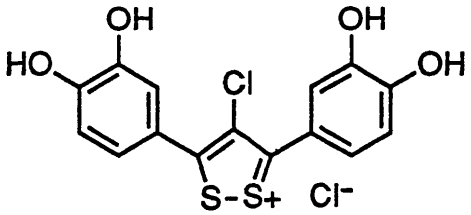
2-(3,4-*Dichloro*-1,2-*dithiol*-5-*ylidene*)-5,5-*dimethylcyclohexane*-1,3-*dione* (**120**)



Dimedone (84 mg, 0.6 mmol) was dissolved in THF (2 ml) and *n*-butyl lithium (0.5 ml, 1.6 M) was added dropwise with stirring. After 0.5 h the suspension was added dropwise with stirring to a suspension of 3,4,5-trichloro-1,2-dithiolium chloride (132 mg, 0.5 mmol) in THF (3 ml) with stirring. The mixture was stirred at room temperature for 3 h, then adsorbed onto silica gel. Wet flash column chromatography (10% ethyl acetate in light petrol) gave 3,4-dichloro-1,2-dithiol-3-one (46 mg, 45%) followed by the *title compound* **(120)** (30 mg, 18%) as brown crystals , m.p. 146 °C (Found *M*+, 307.9499. $C_{11}H_{10}Cl_2O_2S_2$ requires 307.9499); $\lambda_{max.}$ (EtOH) 219, 261, and 440 nm (log ε 4.01, 3.79, and 3.96); $\nu_{max.}$ (nujol) 1 651s, 1 547s, 1 333s, 1 277, 1 191, 1 113, 1 036, 1 011, 979, and 849 cm^{-1};δ_H (270 MHz; $CDCl_3$) 1.1 (6H, s, CH_3), 2.6 (2H, s, CH_2), and 2.7 (2H, s, CH_2); *m/z* (180 °C) 312, 310, 308 (M^+ 5, 22, 31%), 275, 273 (M^+ -Cl, 43, 100), 217 (39), 55 (38), and 41 (29).

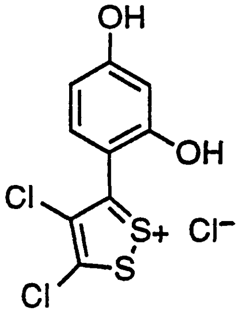
Reactions of the trichloro salt (85) with phenols and naphthols.

4-Chloro-bis -3,5-(3,4-dihydroxyphenyl) -1,2-dithiolium chloride (122)

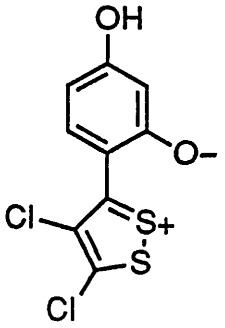


3,4,5-Trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of catechol (0.046 g, 0.4 mmol) in DCM (3 ml). The mixture was stirred at ambient temperature for 3 h, then the brown precipitate formed was filtered off, and washed with DCM (10 ml), followed by ether (10 ml). The solid was dried *in vacuo* giving the title compound (122) (0.052 g, 65%) as a brown solid , m.p. 220 °C; $\nu_{max.}$ (nujol) 3 250, 1 651, 1 600, 1 510, 1 298, 1 196, 843, and 817 cm^{-1}; δ_H (250 MHz; DMSO-d^6) 7.0 (2H, d, *J* 8.3 Hz, 5-H), 7.05 (2H, dd, *J* 8.3 and 2.1 Hz,6-H), and 7.15 (2H, d, *J* 2.1 Hz, 2-H); *m/z* (FAB) (NOBA) 355, 353 (M^+ , 10, 25%) 263, 261 (45, 100), 200 (5), 161 (5), and 110 (4).

3,4-Dichloro- 5-(2,4-dihydroxyphenyl)- 1,2-dithiolium chloride (123)



123

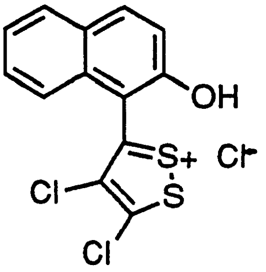


124

3,4,5-Trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of resorcinol (0.046 g, 0.4 mmol) in DCM (3 ml). The mixture was stirred for 5 h at ambient temperature. The brown precipitate formed was filtered off and washed with DCM (10 ml), followed by ether (10 ml) and dried *in vacuo* . This gave the *title compound* (123) (0.124 g, 95%) as a light brown solid , m.p. 200 °C (decomp.); $\lambda_{max.}$ (EtOH) 236 and 453 nm (log ε 4.50 and 4.36); $\nu_{max.}$ (nujol) 1 700, 1 609s, 1 400, 1 345s, 1 240s, 1 166, 1 150, 1 123, 960, 874, and

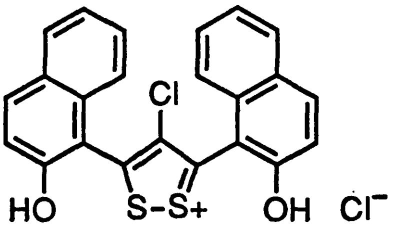
847 cm^{-1}; δ_H (250 MHz; DMSO-d^6) 6.5 (1H, d, *J* 2 Hz, 3-H), 6.8 (1H, dd, *J* 9.4 and 2.5 Hz, 5-H), and 8.8 (1H, d, *J* 9.4 Hz, 6-H); *m/z* (200 °C) 282, 280, 278 (*M*$^+$ -HCl, 10, 35, 50%), 245, 243 (*M*$^+$ -Cl, 42, 100), 208 (*M*$^+$ -2Cl, 12), 201, 199 (5, 15), 93 (14), and 69 (27). The title compound (123) was treated with one equivalent of pyridine and dry column flash chromatography on the resultant mixture with 2% methanol in DCM yielded 4-(*3,4-dichloro- 5H- 1,2-dithiol- 5-ylidene)cyclohex- 5-en- 1,3-dione* (124) (0.054 g, 47%) as orange crystals, m.p. 230 °C(decomp.) (Found C, 39.0; H, 1.7. $C_9H_4Cl_2O_2S_2$ requires C, 38.7; H, 1.4%); $\lambda_{max.}$ (EtOH) 225, 317, and 454 nm (log ε 4.32, 3.53, and 4.02); $\nu_{max.}$ (nujol) 3 468, 1 625, 1 559, 1 509, 1 286s, 1 190 and 856 cm^{-1}; δ_H (270 MHz; DMSO-d^6) 6.9 (1H, d, *J* 2.2 Hz) 7.1 (1H, dd, *J* 7.8 and 2 Hz) 9.2 (1H, d, *J* 7.8 Hz); *m/z* (200 °C) 282, 280, 278 (*M*$^+$ 8, 35, 46%), 245, 243 (*M*$^+$ -Cl, 42, 100), 149 (20), 125 (24), 79 (30), 43 (37), and 28 (61).

3,4-Dichloro -5-(2-hydroxynaphthalen -1-yl) -1,2-dithiolium chloride (128)



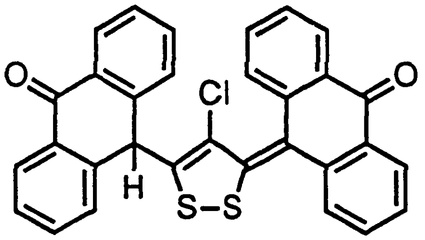
3,4,5-Trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of 2-naphthol (0.06g, 0.4mmol) in DCM (3 ml) and the mixture was stirred for 3 h at ambient temperature. The mixture was adsorbed onto silica gel and dry column flash chromatography using 5% ethyl acetate in petroleum ether gave the *title compound* (128) (34mg, 26%) as a red solid , m.p. 120 °C (Found *M*$^+$, 311.9237. $C_{13}H_6Cl_2OS_2$ requires 311.9237); $\lambda_{max.}$ (EtOH) 227 and 525 nm (log ε 4.76 and 3.72); $\nu_{max.}$ (nujol) 1 654, 1 623, 1 599, 1 581, 1 543, 1 512, 1 437, 1 350, 1 277, 1 213, 1 147, 855, and 819 cm^{-1}; δ_H (270 MHz; DMSO-d^6) 7.2-7.3 (1H, m, ArH), 7.4-7.5 (1H, m, ArH), 7.5-7.6 (2H, m, ArH), 7.8-7.9 (1H, m, ArH), and 8.0-8.1 (1H, m, ArH); *m/z* (170 °C) 316, 314, 312 (*M*$^+$, 1, 5, 7%), 279, 277 (*M*$^+$ -Cl, 13, 30), 85 (46), 79 (58), and 36 (100).

4-Chloro- 3,5-bis(2-hydroxynaphthalen- 1-yl)- 1,2-dithiolium chloride. **(129)**



3,4,5-Trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of 2-naphthol (0.12 g, 0.8 mmol) in DCM (10 ml) and the mixture was stirred for 24 h at ambient temperature. The purple precipitate formed was filtered off and washed with DCM (10 ml), followed by ether (10 ml); then dried *in vacuo* giving the *title compound* **(129)** (0.136 g, 72%) as a purple solid, m.p. 265 °C (decomp) (Found, M^+, 421.012. $C_{23}H_{14}ClO_2S_2$ requires 421.012); $\lambda_{max.}$ (EtOH) 335 and 523 nm (log ε 3.97 and 4.20); $\nu_{max.}$ (nujol) 3 060s, 1 620, 1 597, 1 577, 1 562, 1 518s, 1 436s, 1 403s, 1 349, 1 283, 1 249, 1 224, 1 191, 1 115, 893, 859, and 814 cm^{-1}; δ_H (500 MHz; DMSO-d^6) 7.3 (1H, d, *J* 8 Hz), 7.4 (1H, quin, *J* 4 Hz), 7.5 (2H, d, *J* 4 Hz), 7.9 (1H, d, *J* 8 Hz), and 8.1 (1H, d, *J* 10 Hz); δ_C (62.5 MHz; DMSO-d^6) 112, 118,123, 125, 127, 128, 129,130, 135, 160, 171; *m/z* (FAB) (NOBA) 423, 421 (M^+ -Cl, 30, 70%), 331 (25), 169 (23), 154 (24), 137 (100), and 109 (47).

Reaction of 3,4,5-trichloro-1,2-dithiolium chloride and anthrone:

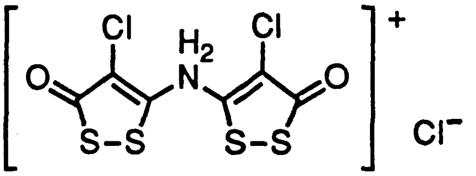


3,4,5-trichloro-1,2-dithiolium chloride (0.1 g, 0.4 mmol) was added to a solution of anthrone (0.16 g, 0.8 mmol) in ether (10 ml) and the mixture was stirred at ambient temperature for 72 h. The green precipitate formed was filtered off and washed with ether (20 ml) then dried *in vacuo* giving 10-[-3-(*anthron* -10-*yl*)-4-*chloro* -5H-1,2-*dithiol* -5-*ylidene*]*anthrone* (0.115 g, 54%), as a green solid m.p. 167 °C (Found M^+, 520.0359. $C_{31}H_{17}ClO_2S_2$ requires 520.0359); $\lambda_{max.}$ (MeOH) 237, 261, 369, and 390 nm (log ε 4.44, 4.51, 3.77, and 3.81); $\nu_{max.}$ (nujol) 1 556, 1 413, 1 363, 1 309, 1 274, 1 193, 1 169, and 1 148 cm^{-1}; δ_H

(500 MHz; CD_3OD) 7.4-7.8 (9H, m, ArH), 7.8-8.0 (3H, m, ArH), and 8.0-8.5 (4H, m, ArH); *m/z* (140 °C) 522, 520 (M^+, 3, 6%), 362, 360 (4, 8), 346, 344 (4, 9), 208 (54), 180 (38), 79 (71), 64 (53), and 36 (93).

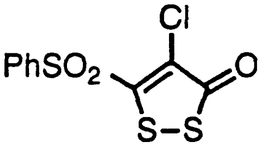
Reactions of 4,5-dichloro-1,2-dithiol-3-one (86) and 4,5-dichloro-1,2-dithiol-3-thione (89).

Bis-(4-chloro- 1,2-dithiol- 3-one)amine hydrochloride **(134)**



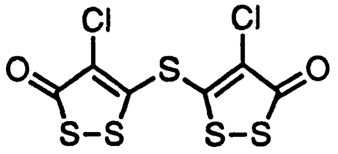
Ammonia gas was bubbled through a solution of 4,5-dichloro-1,2-dithiol-3-one (86) (0.25 g, 1.3 mmol) in acetonitrile (10 ml). An orange precipitate formed immediately; this was filtered off and washed well with acetonitrile and dried *in vacuo,* to give the *title compound* **(134)** (0.136 g, 57%) as an orange powder (Found M^+ -HCl, 316.8267. $C_6HCl_2NO_2S_4$ requires 316.8267); $\nu_{max.}$ (nujol) 3 138s, 3 049s (NH), 1 646, 1 515, 1 407s, 1 184, and 846 cm^{-1}; δ_C (62.9 MHz, CD_3OD) 24, 31 and 210; *m/z* (100 °C) 321, 319, 317 (M^+ 1, 3, 4%) 169, 167 ($C_3H_2ClNOS_2$, 3, 6) 121, 119 (C_3ClOS, 6, 15) 38, 36 (HCl, 33, 100).

4-Chloro- 5-phenylsulphonyl- 1,2-dithiol- 3-one **(135)**



To a solution of 4,5-dichloro-1,2-dithiol-3-one (0.187 g, 1 mmol) in THF (10 ml) a solution of sodium benzenesulphinate (0.246 g, 1.5 mmol) in methanol (2 ml) was added dropwise with stirring. The mixture was refluxed for 4 h, the white solid (excess sodium benzenesulphinate and sodium chloride) was filtered off and the mixture was adsorbed onto silica gel. Dry column flash chromatography with 25% ethyl acetate in petroleum ether gave the *title compound* **(135)** (0.25 g, 85%) as fawn crystals, m.p. 111 °C (Found C, 36.8; H, 1.5. $C_9H_5ClO_3S_3$ requires C, 36.9; H, 1.7%); $\lambda_{max.}$ (CH_3CN) 222 and 353 nm (log ε 3.71 and 3.68); $\nu_{max.}$ (nujol) 1 682s, 1 580, 1 447, 1 331s, 1 173, 1 149s, 1 080, 929, 861 and 754 cm^{-1}. δ_H (270MHz; $CDCl_3$) 7.6-7.7 (2H, m, Ar) 7.8-7.9 (1H, m, Ar) 8.0-8.1 (2H, m, Ar); *m/z* (80 °C) 294, 292 (M^+ 27, 56%), 153, 151 (M^+ - $PhSO_2$, 5, 11), 141 ($PhSO_2$, 14), 121, 119 (C_3ClOS, 9, 22), 105 (30), and 77 (100).

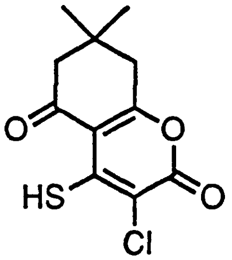
Bis- 3-(4-chloro- 1,2-dithiol- 3-one)sulphide **(138)**



a) From 4,5-dichloro-1,2-dithiol-3-one (**86**) and potassium thiocyanate:
Potassium thiocyanate (0.11 g, 1 mmol) was added to a mixture of 4,5-dichloro-1,2-dithiol-3-one (0.1 g, 0.5 mmol), tetrabutylammonium bromide (0.025 g), benzene (2 ml) and water (1 ml). This mixture was refluxed for 3 h, during which time it turned orange. The mixture was adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* (138) (0.043 g, 48%) as colourless needles, m.p. 120 °C (Found C, 21.7%. $C_6Cl_2O_2S_5$ requires C, 21.5%); $\nu_{max.}$ (nujol) 1 661s, 1 504s, 1 494s, 1 311, 1 163, 963, 932 and 845s cm^{-1}; δ_C (67.5 MHz, $CDCl_3$) 127 (4-C), 150 (5-C), and 186 (C=O); *m/z* (160 °C) 338, 336, 334 (M^+ 12, 40, 47%), 301, 299 (M^+ - Cl, 3, 5), 121, 119 (C_3ClOS, 37, 100), 91 (15), and 28 (18).

b) From 4,5-dichloro-1,2-dithiol-3-one and sodium sulphide:
A solution of sodium sulphide (0.085 g, 0.3 mmol) in water (1 ml) was added dropwise to a mixture of 4,5-dichloro-1,2-dithiol-3-one (0.1 g, 0.6 mmol), tetrabutylammonium bromide (0.005 g) and benzene (3 ml). the mixture was refluxed for 2 h and then adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* (138) (0.06 g, 66%), m.p. 120 °C identical with that described under a).

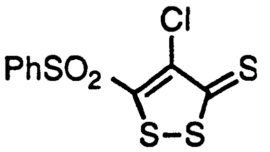
3-Chloro- 7,7-dimethyl- 4-mercaptocyclohexano [1,2-c] *pyran- 2,5-dione* **(139)**



Sodium hydride (0.022 g, 1.1 equivalents) was added to dimedone (0.07 g, 0.5 mmol) in THF (2 ml) under nitrogen. When the effervescence had completely ceased the milky white solution was added dropwise with stirring to 4,5-dichloro-

1,2-dithiol-3-one (**86**) (0.1 g, 0.5 mmol) in THF (3 ml). After stirring at ambient temperature for 2 h the mixture was adsorbed onto silica gel and dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* (**139**) (6 mg, 5%) as yellow crystals, m.p. 100-102 °C (Found C, 51.0; H, 4.1. $C_{11}H_{11}ClO_3S$ requires C, 51.1; H, 4.3%) $\nu_{max.}$ (nujol) 2 954s, 1 723, 1 657, 1 584, 1 500, 1 329, 1 300, 1 269, 1 059, 996, and 894 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.1 (6H, s, C*H* 3), 2.5 (2H, s, C*H* 2), and 2.8 (2H, s, C*H* 2); δ_C (125 MHz; $CDCl_3$) 28 (*C* H_3), 31 (7-C), 42 (8-C), 52 (6-C), 111 and 115 (4a-C and 8a-C), 152 (4-C), 154 (3-C), 170 (2-C), and 196 (5-C); *m/z* (100 °C) 260, 258 (M^+ , 38, 100), 232, 230 (M^+ -CO, 29, 79), 176, 174 (27, 72), 83 (17), 55 (15), and 41 (15).

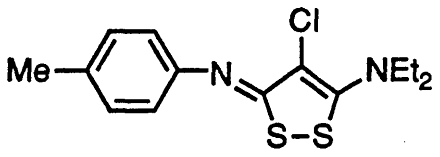
4-*Chloro*- 5-*phenylsulphonyl*- 1,2-*dithiol*- 3-*thione* (**136**)



Sodium benzenesulphinate (0.08g, 0.5mmol) in methanol (1 ml) was added dropwise to a solution of 4,5-dichloro-1,2-dithiol-3-thione (**89**) (0.1 g, 0.5 mmol) in THF (3 ml) and the mixture was refluxed for 2 h. The mixture was adsorbed onto silica gel; dry column flash chromatography with 25% ethyl acetate in petroleum ether gave the title compound (**136**) (0.1g, 65%) as a red solid, m.p. 138 °C (Found: C, 34.8; H, 1.5. Calc. for $C_9H_5ClO_2S_4$: C, 35.0; H, 1.6%); $\lambda_{max.}$ (EtOH) 237, 275, and 436 nm (log ε 4.10, 3.95, and 3.69); $\nu_{max.}$ (nujol) 1 640, 1 448, 1 338, 1 236, 1 181, 1 154s, 1 084, 1 056, 867, and 683 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.65 (2H, t, *J* 9Hz, 3-H and 5-H), 7.8 (1H, t, *J* 8Hz, 4-H), and 8.1 (2H, d, *J* 9Hz, 2-H and 6-H); *m/z* 310, 308 (M^+, 50, 100%), 169, 167 (C_3ClS_3, 33, 72), 100 (29), 91 (52), 77 (92), and 51 (44).

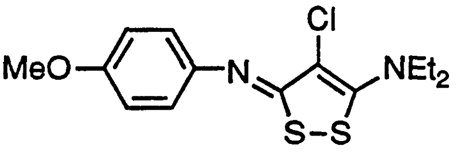
Reactions of N -phenylimines with nitrogen nucleophiles.

N-(*4-Chloro- 3-diethylamino-* 5H- *1,2-dithiol- 5-ylidene)- 4-methylaniline.* (143)



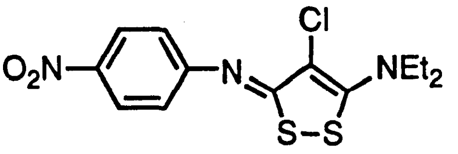
N -(3,4-Dichloro-5*H* -1,2-dithiol-5-ylidene)-4-methylaniline (0.1 g, 0.4 mmol) was dissolved in diethylamine (2 ml) and the mixture was refluxed for 2 h. The excess of diethylamine was evaporated *in vacuo* and wet flash column chromatography (10% ethyl acetate in petroleum ether) on the resultant oil gave the *title compound* (143) (0.06 g, 52%)as a yellow oil (Found M^+, 312.0522. $C_{14}H_{17}ClN_2S_2$ requires 312.0522); $\lambda_{max.}$ (EtOH) 214 and 330 nm (log ε 4.26 and 4.13); $\nu_{max.}$ (nujol) 1 594, 1 543, 1 503, 1 357, and 867 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.2 (6H, t, C*H* 3), 2.3 (3H, s, ArC*H* 3), 3.5 (4H, q, C*H* 2), 6.9 (2H, d, ArH), and 7.2 (2H, d, ArH); *m/z* (180 °C) 314, 312 (M^+ 32, 75%), 213 (M^+ -ClS_2, 100), 208 (64), 157 (18), and 91 (42).

N-(*4-Chloro- 3-diethylamino-* 5H- *1,2-dithiol- 5-ylidene)- 4-methoxyaniline* (144)



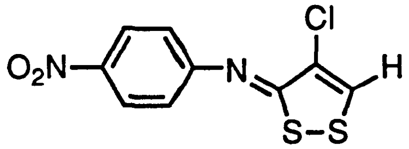
N -(3,4-Dichloro-5*H* -1,2-dithiol-5-ylidene)-4-methoxyaniline (0.1 g, 0.3 mmol) was dissolved in diethylamine (2 ml) and the resultant mixture was refluxed for 2 h. The excess of diethylamine was evaporated *in vacuo* and wet flash column chromatography (10% ethyl acetate in petroleum ether) on the resultant solid gave the *title compound* (144) (0.05 g, 44%) as a yellow oil (Found C, 51.0; H, 5.2; N, 8.6. $C_{14}H_{17}ClN_2OS_2$ requires C, 51.1; H, 5.2; N, 8.5%); $\lambda_{max.}$ (EtOH) 284 and 329 nm (log ε 4.07 and 4.06); $\nu_{max.}$ (film) 2 976, 1 737, 1 605, 1 548s, 1 501s, 1 464, 1 242, 868, and 840 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.2 (6H, t, C*H* 3), 3.5 (4H, q, C*H* 2), 3.8 (3H, s, OC*H* 3), and 6.8-7.1 (4H, m, ArH); *m/z* (150 °C) 330, 328 (M^+ 40, 94%), 315, 313 (M^+ - CH_3, 3, 13), 229 (M^+ -ClS_2, 100), 224 (59), and 36 (21).

N-(*4-Chloro- 3-diethylamino* - 5H- *1,2-dithiol- 5-ylidene)- 4-nitroaniline* **(145)**



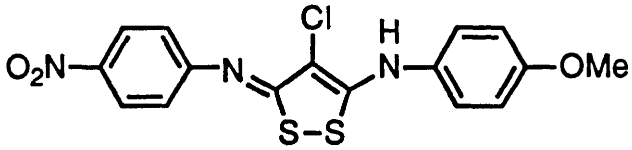
N -(4,5-Dichloro-5*H* -1,2-dithiol-5-ylidene)-4-nitroaniline (0.1 g, 0.3 mmol) was dissolved in diethylamine (2 ml) and the mixture was refluxed for 2 h. The excess of diethylamine was evaporated *in vacuo* and wet flash column chromatography (10% ethyl acetate in petroleum ether) on the resultant oil gave the *title compound* **(145)** (0.075 g, 67%) as yellow crystals, m.p. 138 °C (Found *M*+, 343.022. $C_{13}H_{14}ClN_3O_2S_2$ requires 343.022); $\lambda_{max.}$ (EtOH) 304 and 387 nm (log ε 4.15 and 4.09); $\nu_{max.}$ (nujol) 1 588, 1 520, 1 355, 1 331, 1 279,1 250, 1 201, 1 164, 1 107, 877 and 863 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.2-1.4 (6H, m, C*H* 3), 3.7 (2H, q, C*H* 2), 4.1 (2H, q, C*H* 2), 7.1-7.2 (2H, m, ArH), and 8.2-8.3 (2H, m, ArH); *m/z* (200 °C) 345, 343 (*M*+ 34, 75%), 244 (*M*+ $-ClS_2$, 100), 241, 239 (*M*+ $-NO_2$, $2C_2H_5$, 28, 71), 225,223 (28, 65), 116 (39), and 29 (61).

N-(*4-Chloro-* 5H- *1,2-dithiol- 5-ylidene)- 4-nitroaniline* **(153)**



N -(3,4-Dichloro-5*H* -1,2-dithiol-5-ylidene)-4-nitroaniline (0.1 g, 0.3 mmol) was dissolved in acetone (5 ml) ; ammonium acetate (8.8 ml, 4 M solution) was added followed by titanium (III) chloride solution (2.4 ml, 15% w/v) and the reaction mixture was shaken for 5 min. Ether (2x 20 ml) was used to extract the organics; the ether extract was washed with water (20 ml), brine (20 ml) and water (20 ml), dried ($MgSO_4$) and then adsorbed onto silica gel. Dry column flash chromatography with 20% ethyl acetate in petroleum ether gave the *title compound* **(153)** (0.052 g, 59%) as yellow crystals, m.p. 154 °C (Found C, 39.4; H, 1.7; N, 10.1. $C_9H_5ClN_2O_2S_2$ requires C, 39.6; H, 1.85; N, 10.3%); $\lambda_{max.}$ (EtOH) 306 and 370 nm (log ε 4.04 and 4.02); $\nu_{max.}$ (nujol) 1 593, 1 582s, 1 536, 1 497s, 1 343s, 863, and 763 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.2 (2H, d, ArH), 7.9 (1H, s, =C-*H*), and 8.3 (2H, d, ArH); *m/z* (120 °C) 274, 272 (*M*+ 43, 100%), 244, 242 (7, 16), 191 (*M*+ -Cl, NO_2, 17), 127 (9), 76 (15), and 28 (59).

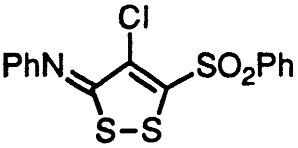
N-[4-*Chloro- 3-(* p-*methoxyanilino)-* 5H- 1,2-*dithiol- 5-ylidene*]-4-*nitroaniline* **(142)**



A mixture of *N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-4-nitroaniline (0.05 g, 0.2 mmol) with *p* -methoxyaniline (0.044 g, 0.4 mmol) in acetonitrile (2 ml) was refluxed for 4 h. The acetonitrile was evaporated *in vacuo* and the mixture was adsorbed onto silica gel. Dry column flash chromatography with 25% ethyl acetate in petroleum ether gave the *title compound* **(142)** (0.033 g, 51%) as a red-brown solid, m.p. 105 °C (Found M^+, 393.008. $C_{16}H_{12}ClN_3O_3S_2$ requires 393.008); $\lambda_{max.}$ (CH_3CN) 221, 365, and 369 nm (log ε 4.47, 4.38, and 4.38); $\nu_{max.}$ (nujol) 3 376, 1 598, 1 543s, 1 511s, 1 442, 1 340s, 1 284, 1 252, 1 182, 1 169, 1 110, 873, 861, and 834 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 3.9 (3H, s, C*H* $_3$O-), 6.95 (2H, d, *J* 8.3Hz, 3'-H and 5'-H), 7.2 (2H, d, *J* 8.3Hz, 2'-H and 6'-H), 7.3 (2H, d, *J* 9.3Hz, 2-H and 6-H), and 8.25 (2H, d, *J* 9.3Hz, 3-H and 5-H); *m/z* (160 °C) 395, 393 (M^+ , 5, 12%), 330, 328 (5, 15), 180 (21), 165 (27), 150 (24), 138 (38), 123 (37), 108 (62), 65 (40), and 36 (100).

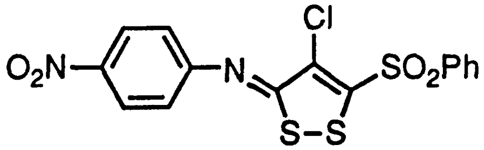
Reactions of N -phenylimines with sodium benzenesulphinate.

N-(*4-Chloro- 3-phenylsulphonyl-* 5H- *1,2-dithiol- 5-ylidene)aniline* **(146)**



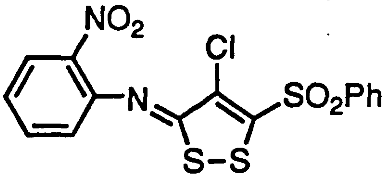
Sodium benzenesulphinate (0.125 g, 0.8 mmol) in methanol (1 ml) was added dropwise with stirring to a solution of *N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)aniline (0.1 g, 0.4 mmol) in THF (10 ml) and refluxed for 12 h. The mixture was adsorbed onto silica gel and dry column flash chromatography using 20% ethyl acetate in petroleum ether gave the *title compound* **(146)** (0.06g, 43%), m.p. 184 °C (Found C, 48.7; H, 2.8; N, 3.7; $C_{15}H_{10}ClNO_2S_3$ requires C, 48.9; H, 2.7; N, 3.8%); $\lambda_{max.}$ (EtOH) 220 and 367 nm (log ε 4.23 and 3.57); $\nu_{max.}$ (nujol) 1 574, 1 329, 1 151s, 1 083, 855, and 762 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.00 (2H, d, *J* 7.7Hz, 2-H and 6-H) 7.20 (1H, t, *J* 7.7Hz, 4-H) 7.40 (2H, t, *J* 7.7Hz, 3-H and 5-H) 7.65 (2H, t, *J* 7.7Hz, 3'-H and 5'-H) 7.80 (1H, t, *J* 7.7Hz, 4'-H) 8.15 (2H, d, *J* 7.7Hz, 2'-H and 6'-H); *m/z* (160 °) 369, 367 (M^+ 9, 19%), 275, 273 (11, 24), 261, 259 (16, 36), 250 (23), 228, 226 (M^+ -$PhSO_2$, 10, 22), 196, 194 (M^+ -$PhSO_2S$, 21, 55), 184, 182 (M^+ - $PhSO_2CS$, 5, 12), 174 (24), 125 (35), and 77(100).

N-(*4-Chloro- 3-phenylsulphonyl-* 5H- *1,2-dithiol- 5-ylidene)- 4-nitroaniline* (147)



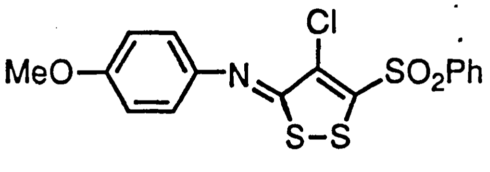
Sodium benzenesulphinate (0.03 g, 0.18 mmol) in methanol (0.5 ml) was added dropwise with stirring to a solution of *N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-4-nitroaniline (0.05 g, 0.16 mmol). The mixture was refluxed for 12 h the adsorbed onto silica gel. Dry column flash chromatography with 20% ethyl acetate in petroleum ether gave the *title compound* **(147)** (0.027 g, 40%)as yellow crystals , m.p. 85 °C (Found C, 43.65; H, 2.25; N, 6.9. $C_{15}H_9ClN_2O_4S_3$ requires C, 43.6; H, 2.2; N, 6.8%); $\lambda_{max.}$ (EtOH) 272 and 390 nm (log ε 4.26 and 4.01); $\nu_{max.}$ (nujol) 2 955s, 1 562, 1 511, 1 340s, 1 150, 1 110, 1 081, 955, 866, 841, 759, and 735 cm^{-1}; δ_H (270MHz; $CDCl_3$) 7.1-7.2 (2H, m, ArH), 7.6-7.7 (2H, m, ArH), 7.75-7.85 (1H, m, ArH), 8.1-8.2 (2H, m, ArH), and 8.25-8.35 (2H, m, ArH);*m/z* (250 °C) 414, 412 (M^+ 48, 100%), 384, 382 (11, 23), 273, 271 (M^+ -$PhSO_2$,12, 26), 237, 239 (M^+ -$PhSO_2S$, 30, 70), 229, 227 (M^+ -$PhSO_2CS$, 14, 41), and 79 (55).

N-(*4-Chloro-* 3-*phenylsulphonyl-* 5H- 1,2-*dithiol-* 5-*ylidene)-* 2-*nitroaniline* **(148)**



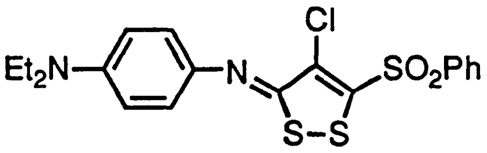
Sodium benzenesulphinate (0.214 g, 1.3 mmol) in methanol was added dropwise with stirring to a solution of *N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-2-nitroaniline (0.2 g, 0.65 mmol) in DCM (10 ml) and refluxed for 24 h. The mixture was adsorbed onto silica gel, dry column flash chromatography with 20% ethyl acetate in petroleum ether, gave N-(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-2-nitroaniline (0.1 g) and the *title compound* **(148)** (0.08 g, 30% overall, 60% conversion), m.p. 165 °C (Found C, 43.6; H, 2.1; N, 6.9. $C_{15}H_9ClN_2O_4S_3$ requires C, 43.6; H, 2.2; N, 6.8%); $\lambda_{max.}$ (EtOH) 258 and 370 nm (log ε 4.24 and 3.72); $\nu_{max.}$ (nujol) 1 592s, 1 519, 1 341s, 1 242, 1 156, 1 081, 953, 862, 841, 784, and 756 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.0-7.1 (1H, m, ArH), 7.2-7.4 (1H, m, ArH), 7.5-7.7 (3H, m, ArH), 7.8-7.9 (1H, m, ArH), 8.0-8.1 (1H, m, ArH), and 8.1-8.2 (2H, m, ArH); *m/z* (300 °C) 414, 412 (M^+ 49, 100%), 209, 207 (M^+- $PhSO_2S_2$, 13, 26), 152 (51), 141 (19), 138, 136 (28, 47), 125 (39) ,119 (66), and 77 (51).

N-(*4-Chloro-* 3-*phenylsulphonyl-* 5H- 1,2-*dithiol-* 5-*ylidene)-* 4-*methoxyaniline* **(149)**



Sodium benzenesulphinate (0.112 g, 0.7 mmol) in methanol (2 ml) was added dropwise, with stirring, to a solution of *N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-4-methoxyaniline (0.1 g, 0.3 mmol) in DCM (5 ml); the mixture was refluxed for 8 h then adsorbed onto silica gel. Dry column flash chromatography with 20% ethyl acetate in petroleum ether gave the *title compound* (**149**) (0.107 g, 73%) as orange crystals, m.p. 125 °C (Found: *M* $^+$, 396.9664; $C_{16}H_{12}ClNO_3S_3$ requires 396.9668); $\lambda_{max.}$ (EtOH) 226 and 408 nm (log ε 4.31 and 3.74); $\nu_{max.}$ (nujol) 1 607, 1 577, 1 563, 1 520, 1 504, 1 448, 1 337s, 1 307, 1 295, 1 249, 1 184, 1 158s, 1 146, 1 112, 1 085, 1 029, 953, 854, 833, 786, and 763 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 3.8 (3H, s, OC*H* $_3$), 6.8-7.0 (2H, m, ArH), 7.0-7.2 (2H, m, ArH), 7.6-7.7 (2H, m, ArH), 7.7-7.8 (1H, m, ArH), and 8.1-8.2 (2H, m, ArH); *m/z* (320 °C) 399, 397 (*M*$^+$ 47, 100%), 384, 382 (*M*$^+$-CH_2, 7, 15), 258, 256 (*M*$^+$- $PhSO_2$, 8, 19), 226, 224 (*M*$^+$-$PhSO_2S$, 13, 36), 182, 180 (20, 62), and 77 (47).

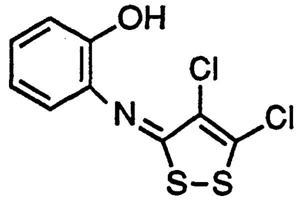
N-(*4-Chloro- 3-phenylsulphonyl-* 5H- *1,2-dithiol- 5-ylidene)- 4-diethylaminoaniline* (**152**)



Sodium benzenesulphinate (0.059 g, 0.4 mmol) in methanol (1 ml) was added dropwise with stirring to a solution of *N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-4-diethylaminoaniline (**110**) (0.057 g, 0.2 mmol). The mixture was refluxed with stirring for 16 h and then adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave first recovered (**110**) (0.029 g) and then the *title compound* (**152**) (0.03 g, 40% total, 81% conversion)as a red solid, m.p. 140 °C (Found *M*$^+$, 438.0927. $C_{19}H_{19}ClN_2O_2S_3$ requires 438.0927); $\lambda_{max.}$ (EtOH) 262 and 485 nm (log ε 4.31 and 4.05); $\nu_{max.}$ (nujol) 1 608, 1 520, 1 404, 1 359, 1 335, 1 269, 1 159, 1 140, 1 083, 949, and 840 cm^{-1}; $\delta_{max.}$ (270 MHz; $CDCl_3$) 1.2 (6H, t, C*H* $_3$), 3.4 (4H, q, C*H* $_2$), 6.7 (2H, d, ArH), 7.1 (2H, d, ArH), 7.6 (2H, m, ArH), 7.7 (1H, m, ArH), and 8.1 (2H, d, ArH); *m/z* (200 °C) 440, 438 (*M*$^+$ 38, 82%), 425, 423 (*M*$^+$ -CH_3, 48, 100), 191 (15), 177 (11), and 77 (31).

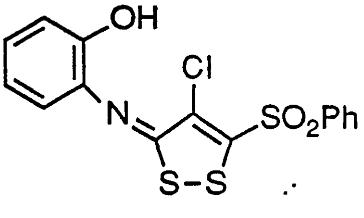
Displacement of the chloro group in position 4.

N-(3,4-*Dichloro*- 5H- 1,2 -*dithiol*- 5-*ylidene)*- 2-*hydroxyaniline* (**104**)



2-Aminophenol (225 mg, 2 mmol) was dissolved in ether (50 ml) and 3,4,5-trichloro-1,2-dithiolium chloride (500 mg, 2 mmol) was added portionwise with vigorous stirring. The mixture was stirred at ambient temperature for 2 h, then pyridine (0.35 ml) was added with stirring. The mixture was absorbed onto silica gel and purified by dry column flash chromatography, the solvent system being 20% ethyl acetate in petroleum ether, which gave the *title compound* (**104**) (460 mg, 80%) as dark yellow crystals, m.p. 80 °C (from petroleum ether/DCM)(Found C, 38.9; H, 1.7; N, 4.8. $C_9H_5Cl_2NOS_2$ requires C, 38.9; H, 1.8; N, 5.0%); $\lambda_{max.}$ (EtOH) 324 and 330nm (log ε 3.81 and 3.81); $\nu_{max.}$ (nujol) 3 328, 1 614, 1 588, 1 538s, 1 482s, 1 289, 1 244s, 1 167, 1 148, 1 033, 983, 857, and 814 cm^{-1}; δ_H (270MHz;$CDCl_3$) 6.75 (1H, s, O*H*), 6.90 (1H, dt, *J* 7.1 and 1.3 Hz, 3-H), 7.05 (1H, dd, *J* 8.4 and 1.3 Hz, 4-H), 7.15 (1H, dt, *J* 7.7 and 1.2 Hz, 2-H), and 7.30 (1H, dd, *J* 7.71 and 1.3 Hz, 1-H); *m/z* (130 °C) 281, 279, 277 (M^+ 6, 28, 39%), 180, 178 (M^+ -ClS_2, 32, 100), 149 (20), 65 (18), and 39 (19).

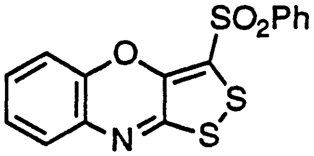
N-(4-*Chloro*- 3-*phenylsulphonyl*- 5H- 1,2-*dithiolylidene)*- 2-*hydroxyaniline* (156)



N -(4,5-Dichloro-5*H* -1,2-dithiol-5-ylidene)-2-hydroxyaniline (**104**) (0.5 g, 1.8 mmol) was dissolved in DCM (40 ml) and a solution of sodium benzenesulphinate (0.59 g, 3.6 mmol) in methanol (6 ml) was added dropwise with stirring. The mixture was refluxed for 5 h, adsorbed onto silica gel and purified by flash column chromatography using gradient elution (10% ethyl acetate in petroleum ether to 40%

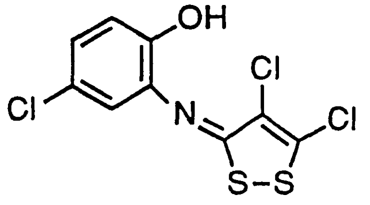
ethyl acetate in petroleum ether, steps of 10%), giving the *title compound* (156) (0.52 g, 76%) as orange crystals, m.p. 146 °C (from petroleum ether/DCM)(Found C, 46.8; H, 2.4; N, 3.5; $C_{15}H_{10}ClNO_3S_3$ requires C, 46.9; H, 2.6; N, 3.65%); $\lambda_{max.}$ (CH_3CN) 222 and 408nm (log ε 4.21 and 3.74); $\nu_{max.}$ (nujol) 3 374, 2 955s, 1 610, 1 582, 1 330, 1 292, 1 246, 1 152s, 1 082, 958, 862, 815, and 746 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.8 (1H, s, O*H*), 6.9 (1H, dt, *J* 7.7 and 1.2 Hz, 5-H), 7.0 (1H, dd, *J* 8.7 and 1.4 Hz, 6-H), 7.2 (1H, dt, *J* 7.7 and 1.2 Hz, 4-H), 7.3 (1H, dd, *J* 7.8 and 1.0 Hz, 3-H), 7.7 (2H, dt, *J* 8.8 and 0.5 Hz, 3'-H), 7.8 (1H, tt, *J* 6.8 and 0.5 Hz, 4'-H), and 8.1 (2H, dt, *J* 7.7 and 1.0 Hz, 2'-H); *m/z* (190 °C) 385, 383 (M^+ 5, 12%), 347 (M^+ - HCl, 47), 244, 242 (M^+ - $PhSO_2$, 28, 67), 212, 210 (36, 100) 200, 198 (M^+-$PhSO_2CS$, 32, 87), 162 (81), and 77 (76).

3-*(Phenylsulphonyl)* [1,2]*dithiol* [4,5-b][1,4]*benzoxazine* (157)



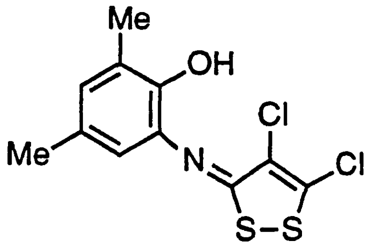
N -(4-Chloro-3-phenylsulphonyl-5*H* -1,2-dithiol-5-ylidene)-2-hydroxyaniline (156) (0.5 g, 1.3 mmol) was dissolved in THF (50 ml) and Hunig's base (0.185 g, 1.1 equivalents) was added dropwise with stirring. The mixture was refluxed for 16 h, then adsorbed onto silica gel. Flash column chromatography with 25% ethyl acetate in petroleum ether gave the *title compound* (157) (0.172 g, 38%)as a brown solid, m.p. 186 °C (Found C, 51.6; H, 2.4; N, 4.0; $C_{15}H_9NO_3S_3$ requires C, 51.85; H, 2.6; N, 4.0%); $\lambda_{max.}$ (CH_3CN) 228 and 424nm (log ε 4.39 and 4.08); $\nu_{max.}$ (nujol) 1 567, 1 328, 1 230, 1 153, 1 068, 980, 917 and 751 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 6.9-7.0 (1H, m, ArH), 7.0-7.1 (3H, m, ArH), 7.6-7.7 (2H, m, $PhSO_2$), 7.7-7.8 (1H, m, $PhSO_2$), and 8.0-8.1 (2H, m, $PhSO_2$); *m/z* (140 °C) 347 (M^+ 100%), 206 (M^+ -$PhSO_2$, 45), 162 (M^+ -$PhSO_2CS$, 58), 134 (PhNCS, 12), 102 (PhNC, 17), and 77 (11).

4-*Chloro-* N-(3,4 -*dichloro-* 5H- 1,2-*dithiol-* 5-*ylidene)-* 2-*hydroxyaniline* (158)



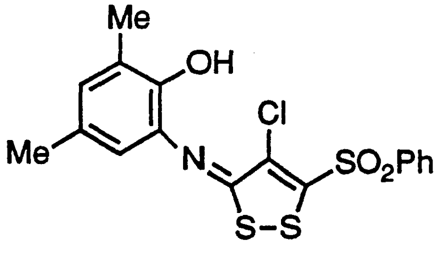
3,4,5-Trichloro-1,2-dithiolium chloride (0.2 g, 0.8 mmol) was added to a solution of 2-amino-4-chlorophenol (0.12 g, 0.8 mmol) in DCM (10 ml) and stirred at ambient temperature for 6 h. Pyridine (0.13 ml) was added and the mixture stirred for a further 0.5 h, then adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* (158) (0.23 g, 89%) as yellow crystals, m.p. 102 °C (petroleum ether/ DCM)(Found C, 34.7; H, 1.2; N, 4.3. $C_9H_4Cl_3NOS_2$ requires C, 34.6; H, 1.3; N, 4.5%) $\lambda_{max.}$ (CH_3CN) 222 and 334 nm (log ε 3.88 and 3.79); $\nu_{max.}$ (nujol) 3 297, 1 609, 1 591, 1 537, 1 245, 1 157, 988, 917, and 864 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.38 (1H, d, *J* 8.6 Hz, 3-H), 7.1 (1H, dd, *J* = 8.7 and 2.3 Hz, 4-H), and 7.3 (1H, d, *J* 2.4 Hz, 6-H); *m/z* (220 °C) 317, 315, 313, 311 (M^+, 3, 14, 37, 34%), 282, 280, 278, 276 (13, 37, 46, 16), 216, 214, 212 (M^+ -ClS_2, 10, 62 100), 63 (16), 36 (24), and 28 (29).

N-(3,4-*Dichloro*- 5H- 1,2-*dithiol*- 5-*ylidene)*- 2-*hydroxy* - 3,5-*dimethylaniline* (105)



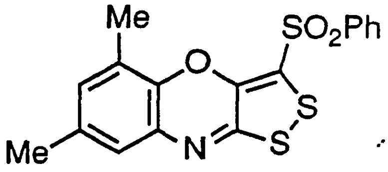
3,4,5-Trichloro-1,2-dithiolium chloride (0.5 g, 2 mmol) was added portionwise with stirring to a solution of 3,5-dimethyl-2-hydroxyaniline (0.285 g, 2 mmol) in DCM (50 ml). The mixture was stirred at ambient temperature for 1 h and then pyridine (0.35 ml, 4.4 mmol) was added dropwise and stirred for 0.5 h. The mixture was adsorbed onto silica gel and dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* (105) (0.48 g, 76%) as a dark yellow solid, m.p. 118 °C (Found C, 43.1; H, 2.8; N, 4.4. $C_{11}H_9Cl_2NOS_2$ requires C, 43.1; H, 3.0; N, 4.6%); $\lambda_{max.}$ (CH_3CN) 221 and 380 nm (log ε 4.37 and 3.98); $\nu_{max.}$ (nujol) 1 586, 1 564, 1 539, 1 493s, 1 307, 1 274, 1 237s, 1 035, 881, and 856 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 2.15 (6H, s, C*H* 3), 6.7br (1H, br, O*H*), 6.85 (1H, s, C-4), and 7.00 (1H, s, C-6); *m/z* (180 °C) 309, 307, 305 (M^+ 6, 25, 34%), 276, 274, 272 (M^+- 33, 4, 20, 34), 208, 206 (M^+ -ClS_2, 33, 100), 91 (20), 77 (16), and 65 (12).

N-(*4-Chloro- 5-phenylsulphonyl-* 5H- 1,2-*dithiol- 5-ylidene)- 2-hydroxy- 3,5-dimethyl aniline* (159)



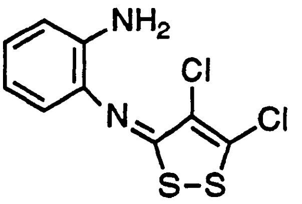
N -(3,4-Dichloro-5*H* -1,2-dithiol-5-ylidene)-3,5-dimethyl-2-hydroxyaniline (**105**) (0.2 g, 0.7 mmol) was dissolved in DCM (15 ml) and sodium benzenesulphinate (0.215 g, 1.4 mmol) in methanol (2 ml) was added dropwise with stirring. The mixture was refluxed for 5 h. The solvents were evaporated *in vacuo* and the resultant mixture was adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* (159) (0.128 g, 48%) as orange crystals, m.p. 154 °C (Found C, 49.6; H, 3.2; N, 3.2. $C_{17}H_{14}ClNO_3S_3$ requires C, 49.6; H, 3.4; N, 3.4%); $\lambda_{max.}$ (CH_3CN) 223 and 369 nm (log ε 4.62 and 4.11); $\nu_{max.}$ (nujol) 3 313, 1 576s, 1 520, 1 330s, 1 306, 1 277, 1 240s, 1 192, 1 153s, 1 085, 1 037, 862, and 793 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 2.2 (3H, s, C*H* 3), 2.3 (3H, s, C*H* 3), 6.7 (1H, s, O*H*), 6.9 (1H, s, ArH), 7.0 (1H, s, ArH), 7.6-7.7 (2H, m, $PhSO_2$), 7.7-7.8 (1H, m, $PHSO_2$), and 8.1-8.2 (2H, m, $PhSO_2$); *m/z* (320 °C) 413, 411 (M^+ 2, 5%), 375 (M^+ -HCl, 19), 272, 270 (M^+ -$PhSO_2$, 14, 32), 240, 238 (M^+ -$PhSO_2S$, 21, 57), 228, 226 (M^+-$PhSO_2CS$, 18, 48), 203 (M^+ -$PhSO_2SCl$, 43), 190 (40), 77 (100), and 51 (48).

5,7-*Dimethyl-* 3-*phenylsulphonyl* [1,2]*dithiol* [4,5-b][1,4]*benzoxazine* (160)



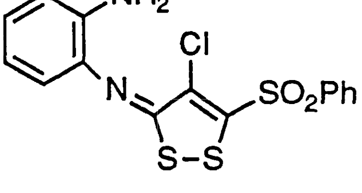
N -(4-Chloro-5-phenylsulphonyl-5*H* -1,2-dithiol-5-ylidene)-3,5-dimethyl-2-hydroxyaniline (159) (0.09 g, 0.2 mmol) was dissolved in THF (10 ml) and Hunigs base (0.05 ml) was added dropwise with stirring. The mixture was refluxed for 16 h. The solvent was evaporated *in vacuo* and the mixture adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* **(160)** (29 mg, 35%) as orange crystals, m.p. 195 °C (Found C, 54.2; H, 3.5; N, 3.8. $C_{17}H_{13}NO_3S_3$ requires C, 54.4; H, 3.5; N, 3.7%); $\lambda_{max.}$ (CH_3CN) 238 and 431 nm (log ε 4.27 and 4.07); $\nu_{max.}$ (nujol) 1 566s, 1 507, 1 331, 1 195, 1 151, 1 082, 970, 911, and 848 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 2.2 (3H, s, CH_3), 2.3 (3H, s, CH_3), 6.8 (2H, s, ArH), 7.6-7.7 (2H, m, $PhSO_2$), 7.7-7.8 (1H, m, $PhSO_2$), and 8.1-8.2 (2H, m, $PhSO_2$); *m/z* (280 °C) 375 (M^+ , 100%), 234 (M^+ -$PhSO_2$, 67), 190 (94), 110 (41), and 77 (46).

2-*Amino*- N-(3,4-*dichloro*- 5H- 1,2-*dithiol*- 5-*ylidene)aniline* **(103)**



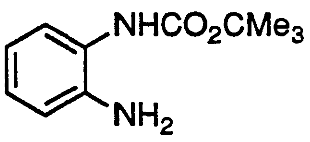
Finely ground 3,4,5-trichloro-1,2-dithiolium chloride (0.2 g, 0.8 mmol) was added slowly to a solution of *o* -phenylenediamine (0.89 g, 8 mmol) in DCM (50 ml). After stirring for 2 h at ambient temperature followed by addition of pyridine (0.065 ml), the mixture was adsorbed onto silica gel. Dry column flash chromatography using 5% ethyl acetate in petroleum ether gave **(111)** (0.046 g); 10% ethyl acetate in petroleum ether gave the *title compound* **(103)** (0.05 g, 22%) as a yellow, brown solid, m.p. 150 °C (decomp.)(Found M^+, 275.9349. $C_9H_6Cl_2N_2S_2$ requires 275.9349); $\lambda_{max.}$ (EtOH) 312 nm (log ε 3.79); $\nu_{max.}$ (nujol) 3 340, 3 334, 1 598, 1 562, 1 541, 1 486, 1 322, 1 300, 1 266, 1 144, 977, and 849 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 6.7-6.9 (2H, m, ArH) and 7.0-7.2 (2H, m, ArH); *m/z* (180 °C) 280, 278, 276 (M^+ 3, 15, 30%), 247, 245, 245 (4, 18, 30), 179, 177 (M^+ -ClS_2, 33, 100), 142 (30), and 36 (100).

2-*Amino*- N-(4-*chloro*- 3-*phenylsulphonyl*- 5H- 1,2-*dithiol*- 5-*ylidene)aniline* (151)



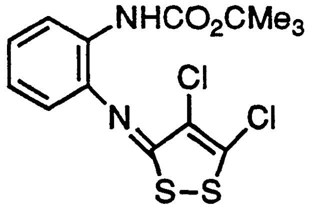
2-Amino-*N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)aniline (0.1 g, 0.4 mmol) was dissolved in DCM (4 ml) and sodium benzenesulphinate (0.12 g, 0.7 mmol) in methanol (1 ml) was added dropwise with stirring. The mixture was refluxed for 5 h and then adsorbed onto silica gel. Dry column flash chromatography with 20% ethyl acetate in petroleum ether gave the *title compound* **(151)** (0.025 mg, 18%) as a red solid, m.p. 138 °C (Found M^+ , 381.9671. $C_{15}H_{11}ClN_2O_2S_3$ requires 381.9671); $\lambda_{max.}$ (EtOH) 451 nm (log ε 3.70); $\nu_{max.}$ (nujol) 3 475, 3 369, 3 326, 1 604, 1 590, 1 557, 1 512, 1 484, 1 339, 1 325, 1 267, 1 154s, 1 083, 953, and 852 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 6.7-6.8 (2H, m, 3-H and 4-H), 7.05 (1H, dt, *J* 7.7 and 1.2 Hz, 5-H), 7.1 (1H, dd, *J* 7.9 and 1.3 Hz, 6-H), 7.65 (2H, dt, *J* 7.6 and 1.3 Hz, 3'-H),, 7.75 (1H, tt, *J* 7.4 and 2 Hz, 4'-H), and 8.1 (2H, dd, *J* 7.1 and 1.5 Hz, 2'-H); *m/z* (200 °C) 384, 382 (M^+ , 3, 6%), 330 (14), 250 (14), 209 (17), 141 (26), 125 (43), and 77 (100).

N-(*t-Butoxycarbonyl)- 1,2-diaminobenzene* (161)



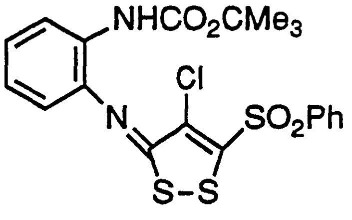
o -Phenylenediamine (1.0 g, 9 mmol) was dissolved in THF and sodium hydride (0.4 g, 1 mmol) was added portionwise with stirring over 5 min. When effervescence had ceased, di-*t* -butyldicarbonate (2.2 g, 10 mmol) was added dropwise with stirring over 5 min. The mixture was stirred overnight at ambient temperature and then adsorbed onto silica gel. Dry column flash chromatography using 10% ethyl acetate in petroleum ether gave a minor amount of *N,N'* -di(*t* -butoxycarbonyl)-1,2-diaminobenzene. 20% Ethyl acetate in petroleum ether gave the *title compound* **(161)** (1.7 g, 90%) as brown crystals, m.p. 108 °C (Found C, 63.6; H, 7.9; N, 13.5. $C_{11}H_{16}N_2O_2$ requires C, 63.4; H, 7.8; N, 13.45%); $\nu_{max.}$ (nujol) 3 414, 3 356, 1 681s, 1 595, 1 519s, 1 493s, 1 368, 1 307, 1 291, 1 257, 1 163s, 1 056, and 751 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.5 (9H, s, CH_3), 6.8-6.9 (2H, m, ArH), 7.0-7.1 (1H, m, ArH), and 7.2-7.3 (1H, m, ArH); *m/z* (140 °C) 208 (M^+ , 22%), 152 (M^+ -C_4H_8, 51), 108 ($C_6H_8N_2$, 100), 57 (83), 41 (23), and 28 (19).

N-(*t-Butoxycarbonyl)-* N'-(*3,4-dichloro-* 5H- *1,2-dithiol-* *5-ylidene)-* 1,2-*diaminobenzene* (162)



N -(*t* -Butoxycarbonyl)-*o* -phenylenediamine (**161**) (0.43 g, 2 mmol) was dissolved in DCM (50 ml) and 3,4,5-trichloro-1,2-dithiolium chloride (0.5 g, 2 mmol) was added portionwise with stirring. After 2 h, pyridine (0.32 g, 4 mmol) was added and the mixture stirred for a further 0.5 h. The mixture was adsorbed onto silica gel and dry column flash chromatography with 20% ethyl acetate in petroleum ether gave the title compound (**162**) (0.62 g, 80%) as a yellow, brown oil ; $\lambda_{max.}$ (EtOH) 358 nm (log ε 3.97); $\nu_{max.}$ (nujol) 3 386, 2 958, 2 927, 2 855, 1 733s, 1 588, 1 541, 1 444, 1 393, 1 369, 1 315, 1 241, 1 158, 1 049, 852, and 753 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.5 (9H, s, CH_3), 7.0-7.1 (2H, m, ArH), and 7.2-7.2 (2H, m, ArH); *m/z* (160 °C) 380, 378, 376 (M^+, 2, 8, 10%), 280, 278, 276 (M^+ -BOC, 3, 11, 15), 265, 263, 261 (5, 22, 30), 247, 245, 243 (4, 18, 30), 179, 177 (15, 44), 79 (49), and 57 (100).

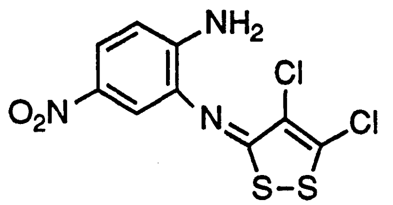
N-(*t-Butoxycarbonyl)-* N'-(*4-chloro-* *3-phenylsulphonyl-* 5H- *1,2-dithiol-* *5-ylidene)-* 1,2-*diaminobenzene* (150)

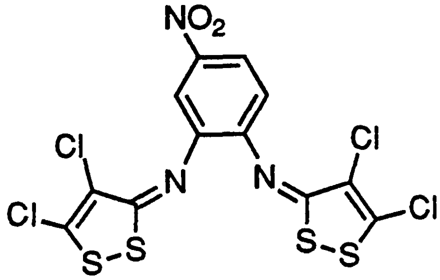


N -(*t* -Butoxycarbonyl)-*N'* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-1,2-diaminobenzene (**162**) (0.26 g, 0.7 mmol) was dissolved in DCM (10 ml) and sodium benzenesulphinate (0.69 g, 4.2 mmol) in methanol (5 ml) was added dropwise with stirring. The mixture was refluxed for 24 h, then adsorbed onto silica gel. Dry column flash chromatography with 20% ethyl acetate in petroleum ether gave the *title compound* (**150**) (0.24 g, 71%)as orange crystals, m.p. 199 °C (Found M^+, 482.0195. $C_{20}H_{19}ClN_2O_4S_3$ requires 482.0195); $\lambda_{max.}$ (CH_3CN) 224 and 410 nm (log ε 4.46 and 3.80); $\nu_{max.}$ (nujol) 3 375, 1 727, 1 587, 1 510s, 1 338, 1 313, 1 240, 1 154s, 1 083, 1 050, 856, and 827 cm^{-1}; δ_H

(270 MHz; $CDCl_3$) 1.5 (9H, s, C*H*$_3$), 7.0 (1H, dt, *J* 7.5 and 1.25 Hz, 4-H), 7.2 (1H, dt, *J* 6.25 and 1.25 Hz, 5-H), 7.25 (1H, d, *J* 15 Hz, 3-H), 7.65 (2H, dt, *J* 7.5 and 1 Hz, 3'-H), 7.8 (1H, tt, *J* 7.5 and 1 Hz, 4'-H), 8.15 (2H, td, *J* 7.5 and 1 Hz, 2'-H), and 8.25 (1H, d, *J* 8Hz, 6-H); *m/z* (150 °C) 484, 482 (M^+ 3, 8%), 382 (M^+ -BOC, 5), 243, 241 (M^+ -$PhSO_2$, BOC,10, 27), 211, 209 (M^+ -$PhSO_2$, S, BOC, 35, 100), 77 (65), 57 (88), and 41 (56).

2-*Amino*- N-(3,4-*dichloro*- 5H- 1,2-*dithiol*- 5-*ylidene)*- 5-*nitroaniline* (163)

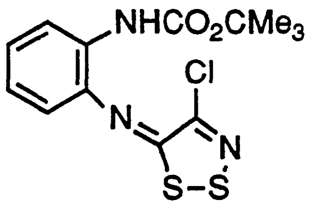




1,2-Diamino-4-nitrobenzene (0.26 g, 1.7 mmol) was dissolved in DCM (50 ml) and 3,4,5-trichloro-1,2-dithiolium chloride (0.2 g, 0.8 mmol) was added portionwise with stirring at ambient temperature. After 2 h, pyridine (0.13 ml) was added and the mixture stirred for a further 0.5 h. The mixture was adsorbed onto silica gel; dry column flash chromatography with 5% ethyl acetate in petroleum ether gave 1,2-*diamino*- N,N' -*bis-(* 3,4-*dichloro*- 5H-1,2-*dithiol*- 5-*ylidene)*- 4-*nitroaniline* (66 mg) as orange crystals, m.p. 148 °C (Found C, 29.5; H, 0.6; N, 8.3. $C_{12}H_3Cl_4N_3O_2S_4$ requires C, 29.3; H, 0.6; N, 8.55%); $\lambda_{max.}$ (CH_3CN) 222 and 342 nm (log ε 4.29 and 4.13); $\nu_{max.}$ (nujol) 1 604, 1 532, 1 504, 1 343, 1 084, and 861 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 7.2-7.3 (2H, m, ArH) and 8.1 (1H, s, ArH); *m/z* 495, 493, 491, 489 (M^+ , 4, 13, 22, 15%), 396, 394, 392, 390 (2, 10, 27, 25), 206, 204, 202 (20, 78, 100), 137, 135 (C_3ClS_2, 20, 51), 105, 103 (C_3ClS, 20, 54), 79 (27), 64 (18), 38, 36 (15, 48).

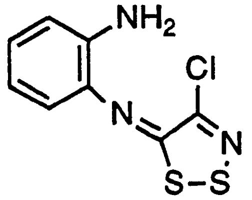
20% Ethyl acetate in petroleum ether gave the *title compound* (163) (77 mg, 29%), m.p.150 °C (decomp.)(Found C, 33.25; H, 1.3; N, 12.8. $C_9H_5Cl_2N_3O_2S_2$ requires C, 33.55; H, 1.6; N, 13.0%); $\lambda_{max.}$ (EtOH) 382 nm (log ε 4.29); $\nu_{max.}$ (nujol) 3 472, 3 348, 1 622s, 1 603, 1 542, 1 486, 1 433, 1 317s, 1 266s, 1 229, 1 158, 1 098, 856, and 825 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 4.8 (2H, s, N*H*$_2$), 6.8 (1H, d, *J* 9 Hz, 3-H), 8.0 (1H, dd, *J* 9 and 2 Hz, 4-H), and 8.1 (1H, d, *J* 2 Hz, 5-H); *m/z* (300 °C) 325, 323, 321 (M^+ 7, 30, 40%) 292, 290, 288 (7, 34, 55) 224, 222 (M^+ -ClS_2, 33, 100) 178, 176 (5, 16) 38, 36 (12, 38).

N-(*t-Butoxycarbonyl)-* N'-(*4-chloro-* 5H- 1,2,3-*dithiazol-* 5-*ylidene)-* o-*phenylenediamine* **(165)**



4,5-Dichloro-1,2,3-dithiazolium chloride (0.5 g, 2.4 mmol) was added to a solution of *N* -(*t* -butoxycarbonyl)-*o* -phenylenediamine (0.5 g, 2.4 mmol) in DCM (50 ml) and this mixture was stirred at ambient temperature for 2 h. Pyridine (0.4 ml, 8.4 mmol) was added dropwise and after 0.5 h the mixture was adsorbed onto silica gel. Dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the *title compound* **(165)** (0.688 g, 84%) as yellow crystals, m.p. 63 °C(Found C, 45.1; H, 4.1; N, 11.9. $C_{13}H_{14}ClN_3O_2S_2$ requires C, 45.4; H, 4.1; N, 12.2%); $\nu_{max.}$ (film) 3 389, 2 982, 1 734s, 1 589, 1 445, 1 393, 1 368, 1 315, 1 288, 1 235, 1 160, 1 050, 1 025, 869, 826, and 805 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.5 (9H, s, C*H* 3), 7.1 (1H, dt, *J* 8 and 1.5 Hz, 5-H), 7.3 (1H, dt, *J* 6 and 0.5 Hz, 4-H), 7.4 (1H, dd, *J* 7.6 and 1 Hz, 3-H), 7.7 (1H, s, N*H*), and 8.3 (1H, dd, *J* 8.6 and 1.2 Hz, 6-H); *m/z* (120 °C) 345, 343 (M^+ , 4, 8%), 245, 243 (M^+ -BOC, 3, 7), 144 (79), 71 (18), and 57 (100).

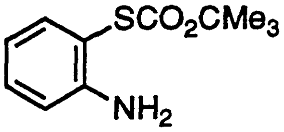
2-*Amino-* N-(*4-chloro-* 5H- 1,2,3-*dithiazolylidene)aniline* **(166)**



N -(*t* -Butoxycarbonyl)-*N'* -(4-chloro-5*H* -1,2,3-dithiazol-5-ylidene)-1,2-diaminobenzene (165) (0.688 g, 2 mmol) was added to HCl in ethyl acetate (10 ml). After 0.5 h a yellow precipitate formed, the mixture was washed with sodium bicarbonate solution (3x 10 ml). The organic extract was washed with brine (10 ml), dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give the title compound (166) (0.39 g, 80%) as orange crystals m.p. 129 °C; $\lambda_{max.}$ (CH_3CN) 223 and 433 nm (log ε 4.15 and 3.92); $\nu_{max.}$ (nujol) 3 419s, 3 303s, 1 608, 1 592s, 1 557, 1 532, 1 498, 1 480, 1 328, 1 301, 1 261s, 1 230, 1 150s, 1 134s, 853, and 766 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 5.4 (2H, s, N*H* 2), 7.0-7.1

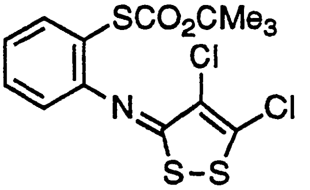
(1H, m, ArH), 7.2-7.3 (1H, m, ArH), 7.4-7.5 (1H, m, ArH), and 7.5-7.6 (1H, m, ArH); *m/z* (240 °C) 245, 243 (*M*+, 6, 15%), 150 (*M*+ -CClSN, 17), 144 (*M*+ -ClS$_2$, 100), 118 (30), 91 (15), and 65 (14).

2-*Amino*- S-(t-*butoxycarbonyl)thiophenol* **(169)**



2-Aminothiophenol (1.0 g, 8 mmol) was dissolved in THF (50 ml) and sodium hydride (0.35 g, 8.8 mmol) was added portionwise with stirring. When effervescence ceased, di-*t* -butyldicarbonate (1.9 g, 8.8 mmol) was added dropwise with stirring, and the mixture was stirred at ambient temperature for 16 h. The mixture was adsorbed onto silica gel and dry column flash chromatography with 10% ethyl acetate in petroleum ether gave the title compound (**169**) (1.65 g, 92%); $\nu_{max.}$ (nujol) 3 482, 3 387, 1 719, 1 602, 1 307, 1 199, 1 127s, 1 073, 835, and 757 cm^{-1}; δ_H (270 MHz; CDCl$_3$) 1.5 (9H, s, C*H* $_3$), 6.7-6.9 (2H, m, ArH), and 7.2-7.4 (2H, m, ArH); *m/z* (120 °C) 225 (*M*+ , 11%), 152 (*M*+ -(CH$_3$)$_3$CO, 8), 125 (*M*+ -BOC, 53), 57 (100).

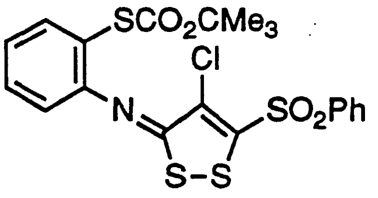
S-(t-*Butoxycarbonyl)*- N-(3,4-*dichloro*- 5H- 1,2-*dithiol*- 5-*ylidene)*- 2-*thioaniline* (170)



2-Amino-*S* -(*t* -butoxycarbonyl)thiophenol (0.3 g, 1.3 mmol) was dissolved in DCM (5 ml) and 3,4,5-trichloro-1,2-dithiolium chloride (0.3 g, 1.2 mmol) was added portionwise. After stirring for 0.5 h, pyridine (0.2 ml) was added and the mixture was stirred for a further 0.5 h. Adsorption of the mixture onto silica gel, followed by dry column flash chromatography with 20% ethyl acetate in petroleum ether gave the *title compound* (**170**) (0.43 g, 88%) as a yellow oil(Found M+ , 392.9486. $C_{14}H_{13}Cl_2NO_2S_3$ requires 392.9486); $\lambda_{max.}$ (CH$_3$CN) 228, 288, and 335 nm (log ε 4.27, 3.64, and 3.59); $\nu_{max.}$ (nujol) 3 059, 1 728s, 1 611, 1 581, 1 543, 1 244, 1 199, 1 182, 1 116s, 1 063, 1 046, and 851 cm^{-1}; δ_H (250

MHz; $CDCl_3$) 1.5 (9H, s, CH_3), 7.1 (1H, dd, *J* 7.5 and 1.25 Hz, 3-H), 7.2 (1H, dt, *J* 7.5 and 1.25 Hz, 5-H), 7.4 (1H, dt, *J* 7.5 and 1.25 Hz, 4-H), and 7.65 (1H, dd, *J* 7.5 and 1.25 Hz, 6-H); *m/z* (150 °C) 397, 395, 393 (M^+ 3, 8, 10%), 342, 340, 338 (3, 10, 12), 297, 295, 293 (M^+ -BOC, 5, 15, 18), 264, 262, 260 (10, 40, 60), 196, 194 (10, 22), and 57 (100).

S-(*t-Butoxycarbonyl)-* N-(*4-chloro- 3-phenylsulphonyl-* 5H- *1,2-dithiol- 5-ylidene)- 2-thioaniline* (171)



S -(*t* -Butoxycarbonyl)-*N* -(3,4-dichloro-5*H* -1,2-dithiol-5-ylidene)-2-thioaniline (0.26 g, 0.7 mmol) was dissolved in DCM (20 ml) and sodium benzenesulphinate (0.44 g, 2.7 mmol) in methanol (5 ml) was added dropwise with stirring. The mixture was refluxed with stirring for 48 h, then adsorbed onto silica gel. Dry column flash chromatography with 20% ethyl acetate in petroleum ether gave *S* -(*t* -butoxycarbonyl)-*N* -(3,4-dichloro-5H-1,2-dithiol-5-ylidene)-2-thioaniline (170) (0.05 g); 40% ethyl acetate in petroleum ether gave the *title compound* (171) (0.24 g, 74%) as yellow crystals, m.p. 165 °C (Found C, 47.7; H, 3.6; N, 2.7; $C_{20}H_{18}ClNO_4S_4$ requires C, 48.0; H, 3.6; N, 2.8%); $\lambda_{max.}$ (CH_3CN) 223 and 387 nm (log ε 4.46 and 3.88); $\nu_{max.}$ (nujol) 1 701s, 1 583, 1 572s, 1 329s, 1 311, 1 212s, 1 185, 1 154s, 1 140s, 1 122, 1 082, 873, and 858 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 3.4 (9H, s, CH_3), 7.1 (1H, dd, *J* 8 and 1.3 Hz, 6-H), 7.2 (1H, dt, *J* 8.3 and 1.3 Hz, 4-H), 7.4 (1H, dt, *J* 7.7 and 1.3 Hz, 5-H), 7.6-7.7 (3H, m, 2-H and 3'-H), 7.8 (1H, tt, *J* 7 and 1.6 Hz, 4'-H), and 8.1 (2H, td, *J* 8.3 and 1.3 Hz, 2'-H); *m/z* (140 °C) 501, 499 (M^+ 8, 14%), 401, 399 (M^+ -BOC, 11, 21), 260, 258 (M^+ -BOC, $PhSO_2$, 25, 54), 228, 226 (M^+ -BOC, $PhSO_2$, S, 27, 65), 191 (72), 110 (48), 77 (93), 57 (80), and 41 (100).

References

1. H.N. McCoy and W.C. Moore, *J. Am. Chem. Soc.,* 1911, **33**, 273
2. D. Bloor, *Chem. Br.,* 1983, **19**, 725.
3. M.R. Bryce, *Chem. Br.,* 1988, **24**, 781.
4. F. Wudl, *Acc. Chem. Res.,* 1984, **17**, 227.
5. J. Williams, M. Beno, H. Wang, P. Leung, T. Emge, U. Geiser, and K. Carlson, *Acc. Chem. Res.,* 1985, **18**, 261.
6. J. Ferraris, D.O. Cowan, V.V. Walakta, and J.H. Perlstein, *J. Am. Chem. Soc.,* 1973, **95**, 948.
7. F.P. Burt, *J. Chem. Soc.,* 1910, 1171.
8. M. Goehring, *Q. Rev. Chem. Soc.,* 1956, **10**, 437.
9. V.V. Walakta, Jr., M.M. Labes, and J.H. Perlstein, *Phys. Rev. Lett.,* 1973, **31**, 1139.
10. R.L. Greene, G.B. Street, and L.J. Suter, *Phys. Rev. Lett.,* 1975, **34**, 577.
11. M.M. Labes, P. Love, and L.F. Nichols, *Chem. Rev.,* 1979, **79**, 6.
12. M. Villena-Blanco and W.L. Jolly, *Inorg. Synth.,* 1967, **9**, 98.
13. G. Wolmershauser, J. Fuhrmann, R. Jotter, T. Wilhelm, and O. Scherer, *Mol. Cryst. Liq. Cryst.,* 1985, **118**, 435.
14. M. Goehring and D. Voight, *Z. Anorg. Chem.,* 1956, **285**, 181.
15. G. B. Street, H. Arnal, W. D. Gill, P.M. Grant, and R.L. Greene, *Mater. Res. Bull.,* 1975, **10**, 877.
16. C.M. Mikulski, P.J. Russo, M.S. Saran, A.G. Mac Diarmid, A.F. Garito, and A.J. Heeger, *J. Am. Chem. Soc.,* 1975, **97**, 6358.
17. M.M. Labes, P. Love, and L.F. Nichols, *Chem. Rev.,* 1979, **79**, 3.
18. G. B. Street, W. D. Gill, R.H. Geiss, R.L. Greene, and J.J. Mayerle, *J. Chem. Soc., Chem. Commun.,* 1977, 407.
19. J. Kuyper and K. Vrieze, *J. Organomet. Chem.,* 1975, **86**, 127.
20. F.P. Olsen and J.C. Barrick, *Inorg. Chem.,* 1973, **12**, 1353.
21. V. Busetti, G. Valle, and M. Mammi, *J. Chem. Soc. Chem. Commun.,* 1970, 413.
22. J. Kuyper and G.B. Street, *J. Am. Chem. Soc.,* 1977, **99**, 7848.
23. J. Weiss and H. Pierchaczek, *Z. Naturforsch., Teil B.,* 1963, **18**, 1139.
24. J.C. Chien and S. Ramakrishnan, *J. Polym. Sci., Polym. Chem. Ed.,* 1987, **25**, 1433.
25. J.J. Mayerle, J. Kuyper, and G.B. Street, *Inorg. Chem.,* 1978, **17**, 2610.
26. I. Ruppert, V. Bastian, and R. Appel, *Chem. Ber.,* 1975, **108**, 2329.

27. W. Lidy, W. Sundermeyer, and W. Verbeek, *Z. Anorg. Allg. Chem.,* 1974, **406**, 228.
28. H.W. Roesky, W. Shaper, O. Petersen, and T. Muller, *Chem. Ber.,* 1977, **110**, 2695.
29. R. Lux and G. Kresze, *Liebigs Ann. Chem.,* 1989, 605.
30. M. Witt, H.W. Roesky, M. Noltenmeyer, W. Clegg, M. Schmidt, and G.M. Sheldrick, *Angew. Chem. Int. Ed. Engl.,* 1981, **20**, 974.
31. O.J. Scherer, G. Wolmershauser, and R. Jotter, *Z. Naturforsch.,* 1982, **37b**, 432.
32. G. Wolmershauser, R. Jotter, and T. Wilhelm, *J. Phys. Coll. (Paris) C3,* 1983, **44**, 729.
33. F. Wudl, E.t. Zellers, and D. Nalewajek, *J. Org. Chem.,* 1980, **45**, 3211.
34. J.C.W. Chien and M.Y. Zhou, *J. Polym. Sci., Polym. Chem. Ed.,* 1986, **24**, 2947.
35. J.C.W. Chien and S. Ramakrishnan, *Macromolecules,* 1988, **21**, 2007.
36. F. Wudl, A. Kruger, and G. Thomas, *Ann. N.Y. Acad. Sci.,* 1978, **313**, 79.
37. O. Loew, *Z. Chem.,* 1868, **4**, 622.
38. M.T. Sidot, *C.R. Hebd. Seances Acad.,* 1872, **74**, 179.
39. J. Dewar and H.O. Jones, *Proc. R. Soc. London, Ser. A,* 1910, **83**, 408 and 526.
40. *Ibid.,* 1911, **85**, 574.
41. K.J. Klabunde, E. Moltzen, and K. Voska, *Phosphorus, Sulfur and Silica,* 1989, **43**, 47.
42. H. Beringer and E. Meinetsberger, *Tetrahedron Lett.,* 1975, 3473.
43. R. Mayer, 'Elemental Sulfur and its Reactions', in Organic Chemistry of Sulfur, edited by S. Oae (Plenum Press, New York and London, 1977) pp. 33-49.
44. A. Luttringhaus and W. Cleve, *Liebigs Ann. Chem.,* 1952, **575**, 112.
45. B.S. Pedersen and S.O. Lawesson, *Tetrahedron,* 1979, **35**, 2433.
46. R. Mayer, P. Wittig, J. Fabian, and R. Heitmuller, *Chem. Ber.,* 1964, **97**, 654.
47. F. Challenger, A.E. Mason, E.C. Holdsworth, and R. Emmott, *J. Chem. Soc.,* 1953, 292.
48. E. Baumann and E. Fromm, *Chem. Ber.,* 1897, **30**, 110.
49. P. Raoul and J.Vialle, *Bull. Soc. Chim. Fr.,* 1959, 1670.
50. B. Oude-Link and D. Redmore, *Chem. Abs.,* 1976, **85**, 94346.

51. H. Hartmann, K. Fabian, B. Bartho, and J. Faust, *J. Prakt Chem.*, 1970, **312**, 1197.
52. J. Faust and R. Mayer, *Liebigs Ann. Chem.*, 1965, **688**, 150.
53. H. Quinion and N. Lozach, *Bull. Soc. Chim. Fr.*, 1963, 1167.
54. C. Th. Pedersen and V. Parker, *Tetrahedron Lett.*, 1972, 771.
55. H. Hartmann and R. Mayer, *Chem. Ber.*, 1964, **97**, 1886.
56. E. Fanghanel, K.H. Kuhnemund, and A.M. Richter, *J. Prakt Chem.*, 1982, **324**, 669.
57. C. Th. Pedersen, *Sulfur Rep.*, 1980, **1**, 1.
58. H. Beringer and E. Meinetsberger, *Liebigs Ann. Chem.*, 1981, 1928.
59. G. Schukat, A.M. Richter, and E. Fanghanel, *Sulfur Rep.*, 1987, **7**, 155.
60. V.A. Bobylev, M.L. Petrov, and A.A. Petrov, *Zh. Org. Khim.*, 1982, **18**, 239.
61. L. Jakisch, H. Viola, and R. Mayer,*Chem. Abs.*, 1988, **109**, 22955m.
62. H. Prinzbach, E. Futterer, and A. Luttringhaus, *Angew. Chem.*, 1966, **78**, 492.
63. H. Shiawaka, E.J. Louis, A.G. Diarmid, C.K. Chiang, and A.J. Heeger, *J. Chem. Soc.*, 1977, 578.
64. E. Fanghanel, A.M. Richter, B. Kordts, and N. Beye, in 'Developements in the Organic Chemistry of Sulfur' ed. C. Th. Pedersen and J. Becher, Gordon and Breach Science Publishers, 1989.
65. N. Loayza and C. Th. Pedersen, *J. Chem. Soc., Chem. Commun.*, 1975, 496.
66. T. Tamamura, M. Yokoyama, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 442.
67. O. Simonsen, N. Loayza, and C. Th. Pedersen, *Acta Chem. Scand., Ser. B*, 1977, **31**, 281.
68. J.M. Catel and Y. Mollier, *C.R. Acad. Sci. Paris. Ser. C.*, 1975, **280**, 673.
69. G. Le Coustomer, J. Amzil, and Y. Mollier, *J. Chem. Soc., Chem. Commun.*, 1979, 353.
70. G.C. Papvassiliou, J.S. Zambouis, A.E. Underhill, B. Kaye, and H.P. Geserich, *Mol. Cryst. Liq. Cryst.*, 1986, **134**, 53.
71. K.G. Naik, D.I.C. thesis, Imperial College, 1921
72. K.G. Naik, *J. Chem. Soc.*, 1921, **119**, 379.
73. G. Kutney and I. Still, *Can. J. Chem.*, 1980, **58**, 1233.
74. K.G. Naik and Y.N. Byat, *Quart. J. Indian Chem. Soc.*, 1927, **4**, 525.

75. R. Gompper, H. Euchner, and H. Kast, *Justus Liebigs Ann. Chem.,* 1964, **675**, 151.
76. K.G. Naik, *J. Chem. Soc.,* 1921, **119**, 1166.
77. K.G. Naik, *J. Chem. Soc.,* 1921, **119**, 1231.
78. E. Besthorn and E. Garben, *Chem. Ber.,* 1900, **33**, 3443.
79. C.G. Newton and C.A. Ramsden, *Tetrahedron,* 1982, **38**, 2967.
80. D. Barillier, *Phosphorus and Sulfur,* 1978, **5**, 251.
81. D. Barillier, P. Rialt, and J. Vialle, *Bull. Soc. Chem. Fr.,* **1973**, 3031.
82. A. Schonberg and E. Frese, *Tetrahedron Lett.,* 1969, **46**, 4063.
83. V. Inouye, S. Sato, and M. Okta, *Bull. Chem. Soc. Japan,* 1970, **43**, 1911.
84. S. Coan, D. Trucker, and E. Becker, *J. Am. Chem. Soc.,* 1955, **77**, 60.
85. G. Settimj, R. Landi Vittory, F. Delle Monache, and S. Chiavarelli, *Gazz. Chim. Ital.,* 1966, **96**, 311.
86. Y. Kimura, Y. Tomita, S. Nakanishi, and Y. Otsuji, *Chem. Lett.,* **1979**, 321.
87. E. Corey and D. Seebach, *Angew. Chem. Int. Ed. Engl.,* 1965, **4**, 1075.
88. A.R. Katritzky, W. Kuzmierkiewicz, B. Rachwal, S. Rachwal, and J. Thomson, *J. Chem. Soc. Perkin Trans.,* **1987**, 811.
89. U. Kibbel, J. Teller, P Hanson, and A. Reiter, *J. Prakt. Chem.,* 1980, **322**, 769.
90. B.S. Pedersen, S. Scheibye, N. Nilsson, and S.O. Lawesson, *Bull. Soc. Chem. Belg.,* 1978, **87**, 223.
91. J. Buckingham, *Q. Rev. Chem. Soc.,* 1969, **23**, 37.
92. B. Ferrier and N. Campbell, *J. Chem. Soc.,* **1960**, 3513.
93. K. Hantke and H. Gotthardt, *J. Chem. Soc. Chem. Commun.,* **1984**, 1682.
94. J. Barillier, *Phosphorus and Sulfur,* 1980, **8**, 79.
95. F. Boberg, *Annalen,* 1964, **679**, 109.
96. F. Boberg, *Angew. Chem.,* 1960, **72**, 629.
97. F. Boberg and G.-J. Wentrup, *Liebigs Ann. Chem.,* **1973** 241.
98. F. Boberg, G.-J. Wentrup, and M. Koepke, *Synthesis,* 1975, **75**, 502.

99. F. Boberg, G.-J. Wentrup, and M. Koepke, *Synthesis,* 1975, **75**, 525.

100. Bayer AG, 5090 Leverkusen, P 27 07 227.1, 1978.
Bayer AG, 5090 Leverkusen, P 26 37 692.1, 1978.

101. M.G. Voronkov, N.S. Vyazankin, E.N. Deryagina, A.S. Nakhmanovich, and V.A. Usov, 'Reactions of sulphur with organic compounds'

102. O. Umekawa, Y. Sano, and S. Katauama, *Chem. Abs.* 1986, **104**, 104459p.

103. R. Appel, H. Janssen, M. Siray, and F. Knoch, *Chem. Ber.*, 1985, **118**, 1632.

104. H.J. Shine,'Aromatic Rearrangements,' Elsevier Publishing Company, 1967, p. 127

105. J. Faust, B. Bartho, and R. Mayer, *Z. Chem.,* 1975, **15**, 395.

106. Katayama Chemical Works Co. Ltd., *Chem. Abs.,* 1985, **103**, 37469f.

107. K.F. Rahimtoola, Ph. D. thesis, University of London, 1990.

108. R.F. English, Ph.D. thesis, University of London, 1989.

109. P.A. Wade, H.K. Yen, S.A. Hardinger, M.K. Pubay, N.V. Amin, P.D. Vail, and S.D. Warren, *J. Org. Chem.,* 1983, **48**, 1796.

110. M. Julia and J.P. Stacino, *Bull. Soc. Chim. Fr.,* 1985, 831.

111. T. Greene, 'Protective groups in organic synthesis', John Wiley and Sons, 1981, p. 232.

112. P.A.S. Smith, J. Hall, and R.O. Kan, *J. Amer. Chem. Soc.,* 1962, 485.

113. T. Greene, 'Protective groups in organic synthesis', John Wiley and Sons, 1981, p. 211.

114. W.C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.,* 1978, **43**, 2923.

115. L.M. Harwood, *Aldrichimica Acta,* 1985, **18**(1), 25.