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SOME METAL CARBONYL COMPLEXES OF THIOCARBONYL COMPOUNDS

BEING AN M.SC. THESIS PRESENTED TO THE UNIVERSITY OF ST. ANDREWS

The thesis deals with three main subjects. Firstly, the preparation of a new class of organosulphur-metal carbonyl compounds is described. Secondly, an attempted preparation of sulphines is described, and finally, a new method of preparing methylthioketones is described.

The metal carbonyl complexes were prepared from three types of thiocarbonyl compound. Pyran- and thiopyran-4-thiones were found to readily form complexes provided that the 3 and 5 positions on the nucleus were unsubstituted, or at the most, mono-substituted. Indolizine thioaldehydes were also found to form stable complexes with molybdenum hexacarbonyl, although in lower yields than with pyran- and thiopyranthiones. Also forming stable complexes, the pyrrolothiazole thioaldehydes. Some difficulty was experienced in assigning a molecular formula to these compounds as two possibilities remained after elementary analysis, namely the  $\pi$ -complex  $M(CO)_3L$  and the  $\sigma$ -complex  $M(CO)_5L$  where M is the metal, and L is the ligand. The obvious solution to the problem, X-Ray crystallography, was ruled out by not being able to obtain large enough crystals of the complex. Similarly mass spectra was unhelpful in assigning a correct formula, as no recognised molecular ion peaks were discernable. However one peak to be recognised was  $MOCOS$  indicating that bonding is through the thiocarbonyl sulphur, or in other words a  $\sigma$ -complex had been formed. Similarly, infra red studies indicated that the symmetry was  $C_{2v}$ , compatible once again with a  $\sigma$ -complex. N.m.r. studies were inconclusive but the degree of shielding at the positions closest to the thiocarbonyl group in the case of the pyran- and thiopyranthiones, and deshielding, in the case of the groups closest to the thioformyl group in the thioaldehydes indicated a  $\sigma$ -complex.

Because of the current interest in the sulphine system, an attempt was made to synthesise a sulphine from various indolizine thioaldehydes. All attempts

were unsuccessful, and it was concluded that the indolizine nucleus is unsuitable for the purpose.

Because of the low yields obtained in the synthesis of methylthioketones by the Vilsmeier-Haack method, a new synthesis was devised. The parent indolizine was heated in a solution of triethylamine and thioacetic acid. The resulting methylthioketone was extracted with benzene, and the benzene solution was washed with water and aqueous sodium bicarbonate. After chromatography, the methylthioketone was recrystallised from cyclohexane in high yield.

SOME METAL CARBONYL COMPLEXES OF  
THIOCARBONYL COMPOUNDS

being a Thesis presented by

RICHARD BUTLER MOORE

to the University of St. Andrews in  
application for the degree of M.Sc.



(i)

DECLARATION

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

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

June, 1970.

(11)

CERTIFICATE

I certify that Richard Butler Moore has spent four terms at research work under my direction, that he has fulfilled the conditions of Ordinance No. 51 (St. Andrews) and is qualified to submit the accompanying thesis in application for a degree of M.Sc.

June, 1970.

Director of Research.

UNIVERSITY CAREER

I first matriculated in the United College of St. Salvator and St. Leonard, St. Andrews University, in October, 1964, and subsequently graduated B.Sc. with Third Class Honours in Chemistry in June, 1968.

I was admitted as a Research Student in the Department of Chemistry, United College, St. Andrews University in September, 1968.

ACKNOWLEDGEMENTS

I am indebted to Dr. D. H. Reid of the Department of Chemistry, United College, St. Andrews University, for the advice and assistance given to me during the prosecution of the work described in this thesis.

Thanks are also due to members of teaching and technical staff whose advice I have sought.

I should like to express my gratitude to Professors J. I. G. Cadogan and Lord Tedder for permission to use the facilities of the Research Laboratories of the Department of Chemistry, United College, St. Andrews University, where this research was carried out.

Finally I would like to express my gratitude to the trustees for the award of a Drummond Studentship.

EXPLANATORY NOTE

This thesis is divided into three parts, numbered 1, 2 and 3.

The first part, the introduction, is subdivided into three main sections. The first section describes thioketone and thioaldehyde chemistry related to the research matter of this thesis. The second section describes relevant metal-organosulphur chemistry. The third section concludes Part 1 with a brief review of sulphine chemistry.

The second part, the discussion, is divided into two sections. The first section describes the aims of the research, and is a discussion of results achieved and the conclusions reached. The second section consists of tables of numerical results, and concludes Part 2.

Part 3 is devoted entirely to experimental details.

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

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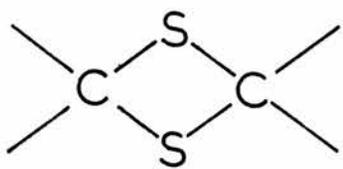
PART 1

## Introduction

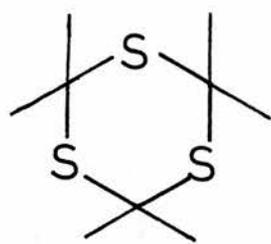
This thesis is concerned mainly with reactions and properties of thioaldehydes and thioketones. An attempt will be made, therefore, to give a brief summary of the chemistry of thioaldehydes and thioketones.

A separate summary will be devoted to the organometallic chemistry of sulphur-containing compounds. This will be divided into thiocarbonyl organometallics and other sulphur-containing ligands with metal carbonyls.

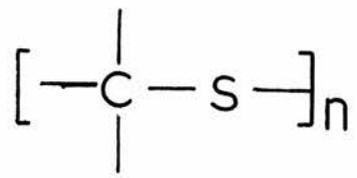
A brief review of sulphine chemistry will conclude the introduction.



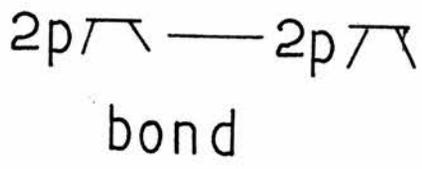
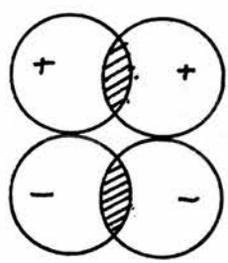
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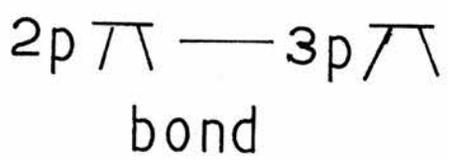
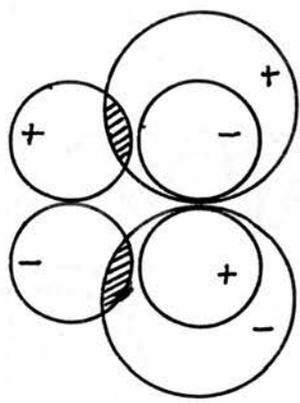
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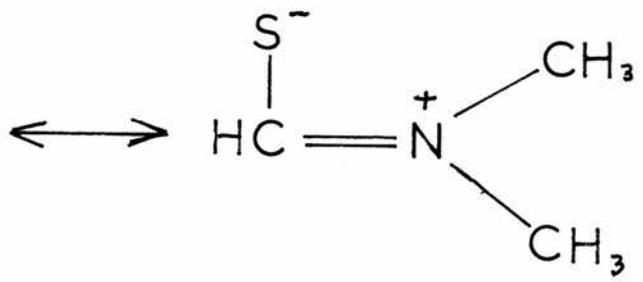
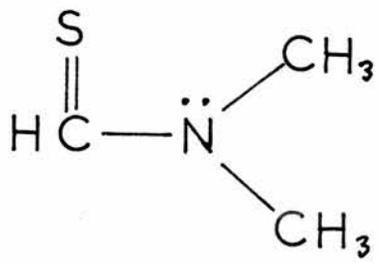
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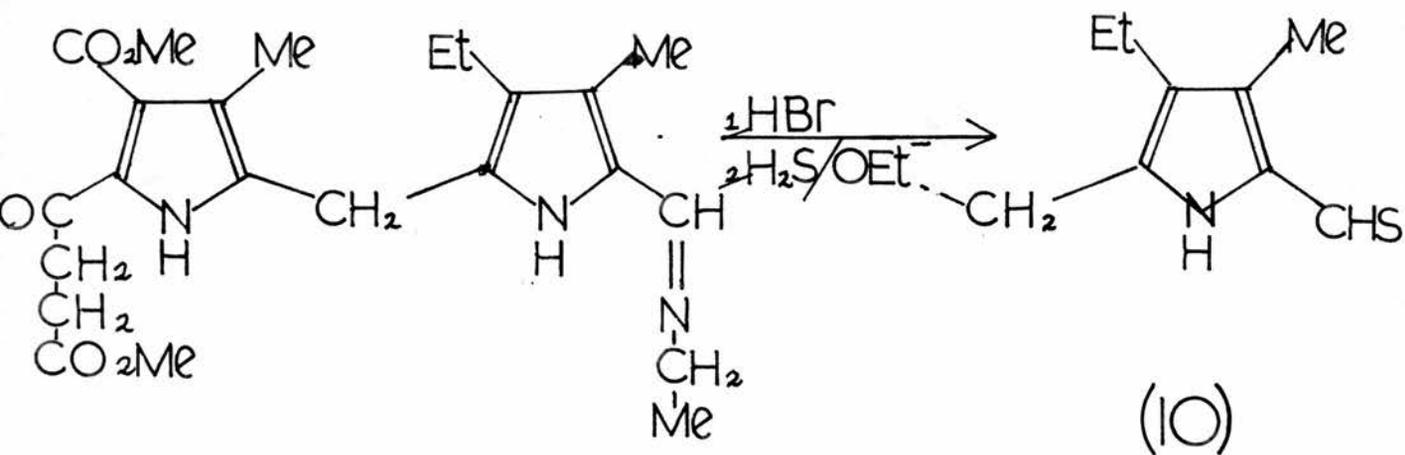
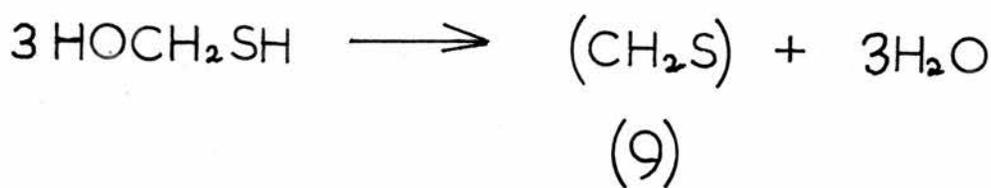
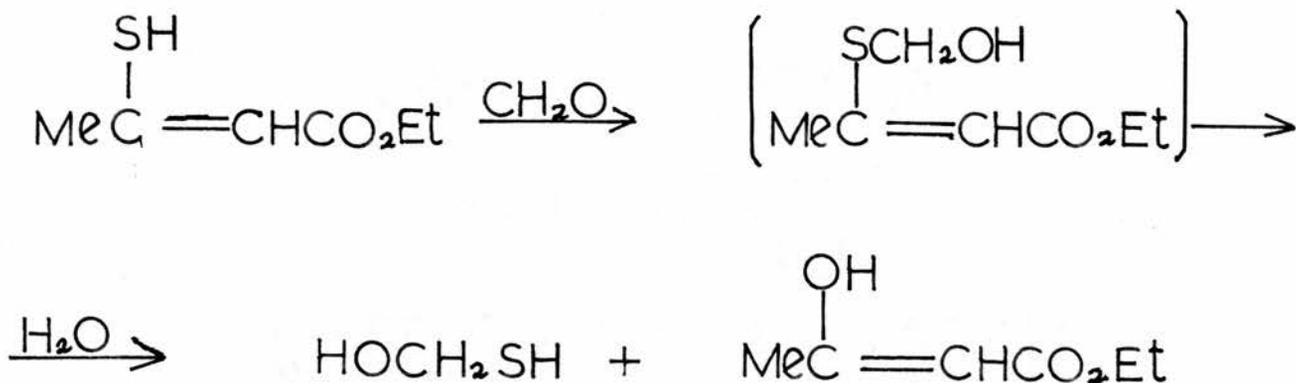
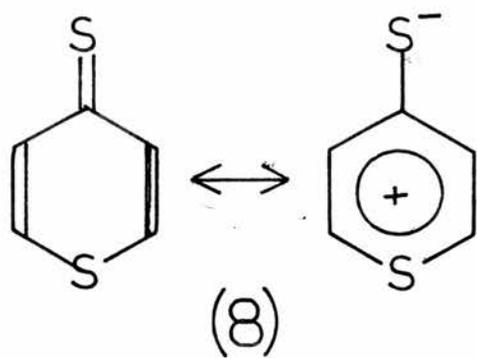
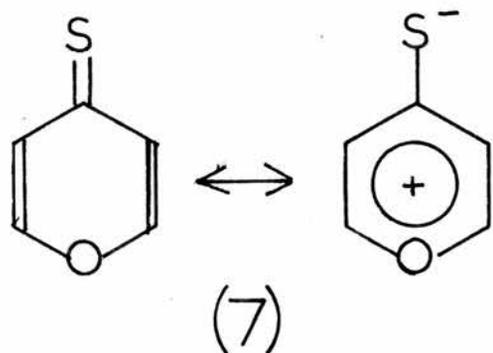
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Thioaldehydes and Thioketones

Thioaldehydes and thioketones tend to be less stable than their oxygen analogues. The thiocarbonyl group has a strong tendency to form compounds containing a C - S single bond. This may occur by enthiolization dimerization, trimerization or polymerization, the products being chains or rings, for example, structures (1), (2) and (3).

Aliphatic thioaldehydes are extremely unstable, and polymerise during attempted preparation. Aliphatic thioketones can be isolated under carefully controlled conditions but these too are generally unstable. This instability of thioaldehydes and thioketones is due to the difficulty with which sulphur forms a  $P\pi - P\pi$  double bond with carbon. Overlap of the  $2P_z$  orbital of the carbon atom with the  $3P_z$  orbital of sulphur is necessary for the formation of a double bond (5). Owing to inner-shell repulsion overlap is not so great, with the result that this type of bond is weaker than a bond of the  $2P\pi - 2P\pi$  (4). This accounts for the difference in stability between thioaldehydes and thioketones on one hand, and their oxygen analogues on the other.

The thiocarbonyl bond is polarised in the ground state and will polarise further in the sense  $^+C - S^-$ . This is demonstrated by dipole moment measurements. The work of several groups has shown the dipole of the thiocarbonyl group to be  $0.5 \times 10^{-18}$  e.s.u. greater than that of the carbonyl group. If the thiocarbonyl group were not polarised, one would



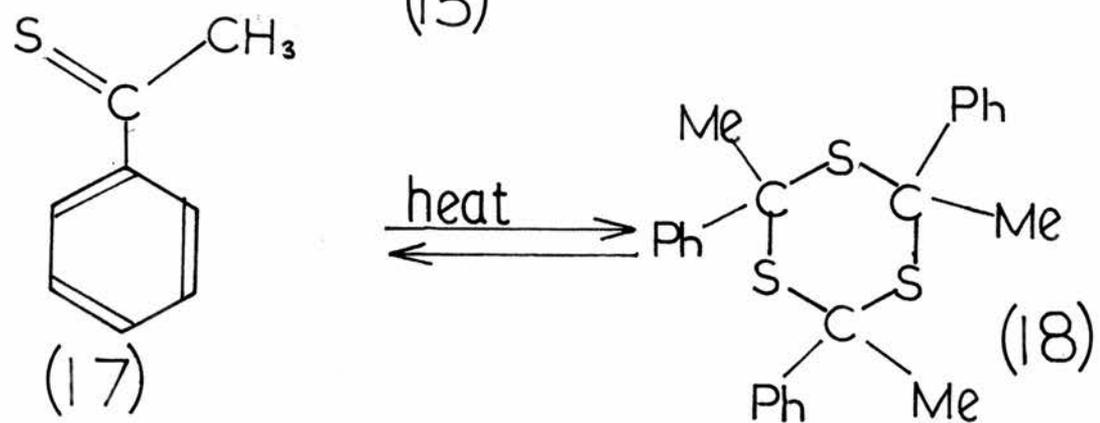
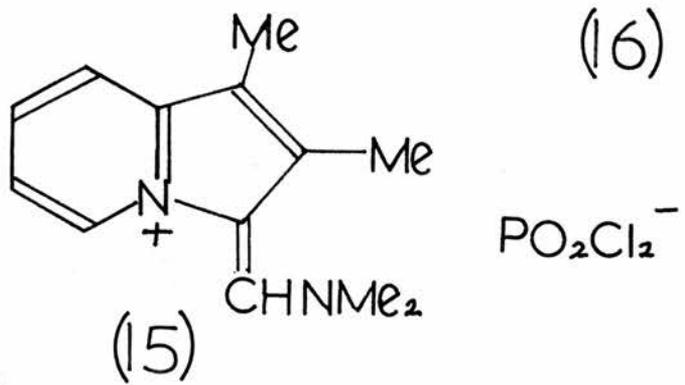
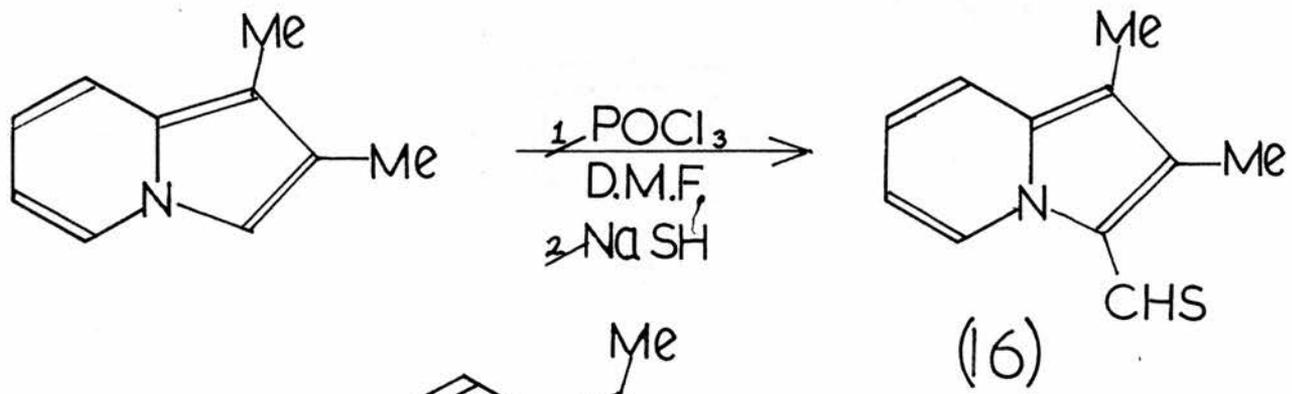
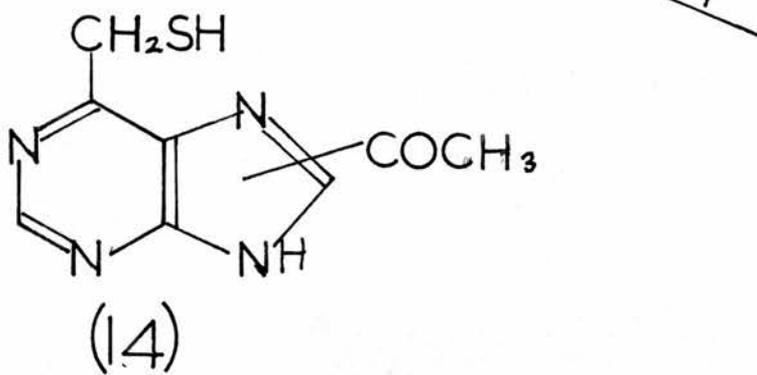
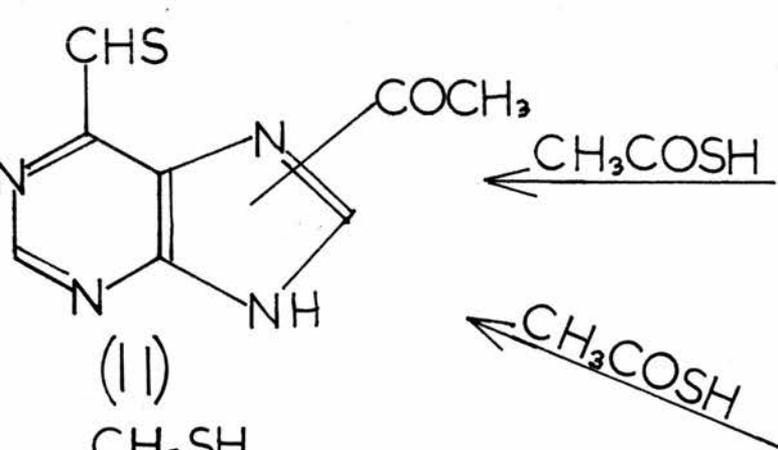
expect the carbonyl group to have the larger dipole moment, oxygen being more electronegative than sulphur. These considerations suggest that the thiocarbonyl group might be stabilised by conjugation with an electron-releasing system. Dimethylthioformamide (6) illustrates this possibility.

An extension of the same effect is demonstrated by 4H-pyran-4-thione (7) and 4H-thiopyran-4-thione (8). The aromatic system is responsible for the delocalisation of the positive charge on the carbon atom. It should be pointed out, however, that in the case of 4H-thiopyran-4-thione, experimental findings give evidence that sulphur is a weak donor, and its 3P electron pair enters into conjugation with reluctance. This inhibits the formation of the 6-electron cation with the result that 4H-thiopyran-4-thione is less stable than 4H-pyran-4-thione.

### Preparation and Properties of Thioaldehydes

#### Preparation

Early attempts to prepare thioaldehydes were usually by the treatment of a solution of the corresponding aldehyde with hydrogen sulphide in the presence of acid. The reaction was first applied by Hofmann<sup>27</sup> in 1868 to formaldehyde, the result being the formation of dimers and trimers. Various other methods have been employed. When an alcoholic solution of ethyl thioacetoacetate<sup>28</sup> which had been saturated with dry hydrogen chloride, was treated with a 40% solution of formaldehyde, heated on a steam bath, and left to stand overnight,



trithioformaldehyde was obtained (9). Similar results were obtained with aromatic aldehydes<sup>70</sup>.

All attempts to prepare a stable monomeric thioaldehyde failed until recently, when Woodward<sup>24</sup> obtained the compound (10) in his total synthesis of chlorophyll a. The only quoted property of the thioaldehyde was its melting point. In a later paper, Giner - Sorolla<sup>25</sup> claimed the preparation of the purine thiocarboxaldehyde (11) from the corresponding oxime (12) or hydrazone (13). Work in this laboratory<sup>71</sup> has shown that the thiol (14) and not the thioaldehyde had been obtained. McKenzie and Reid<sup>26</sup> adapted the Vilsmeier - Haack synthesis in their preparation of thioaldehydes. The heteroaromatic compound (an indolizine, pyrrolothiazole, or indole) was allowed to react with a mixture of dimethylformamide and phosphorus oxychloride to give Vilsmeier salts of the (15), for example, in the case of 1, 2 - dimethylindolizine. Treatment of these intermediates with a solution of sodium hydrogen sulphide gives the thioaldehyde (16). Alternatively, the aldehyde could be obtained by the Vilsmeier - Haack synthesis, which could be converted to the corresponding thioaldehyde by the action of phosphorus pentasulphide .

#### Properties<sup>108</sup>

Thioaldehydes are orange or red crystalline solids, relatively stable at room temperature. The infra-red stretching frequency of the

thioformyl bond was found to be markedly solvent dependent, and occurred in the region  $980 - 950 \text{ cm}^{-1}$ . The ultra violet spectra show an intense band in the region  $380 - 450 \text{ m.}\mu$ . corresponding to the observed orange-red colour of these compounds, and the weak, forbidden  $n - \pi^*$  transition was found in the region  $530 - 600 \text{ m.}\mu$ . Nuclear magnetic resonance studies showed that the thioformyl proton gives rise to a characteristic peak, normally in the region  $10.4 - 10.8. \delta$

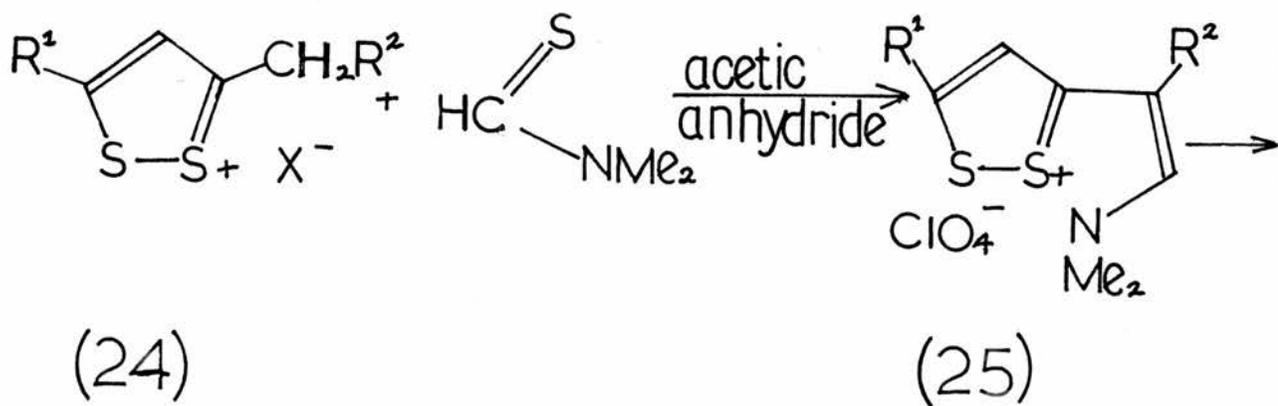
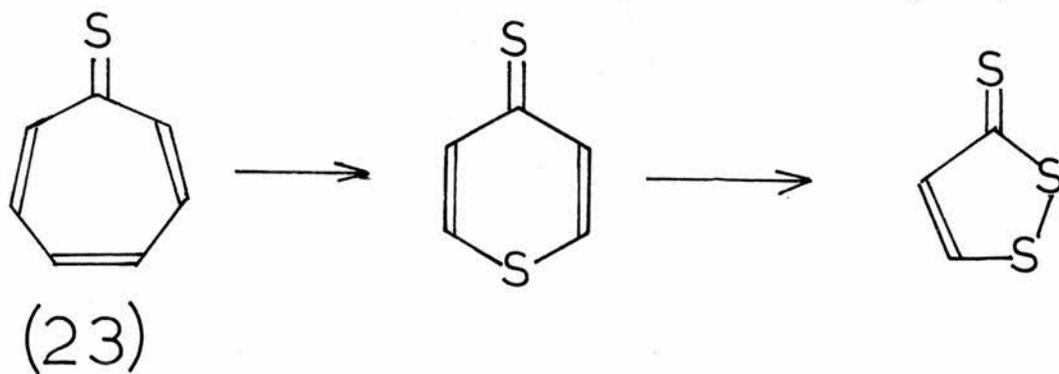
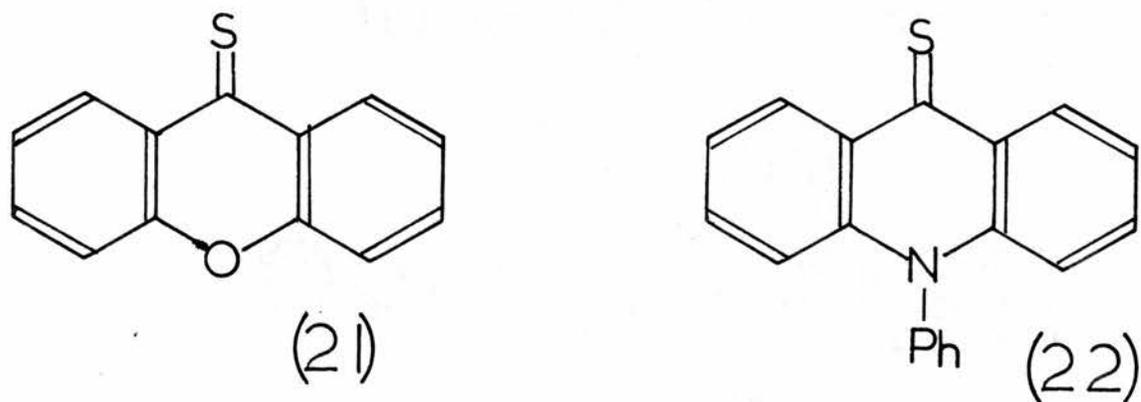
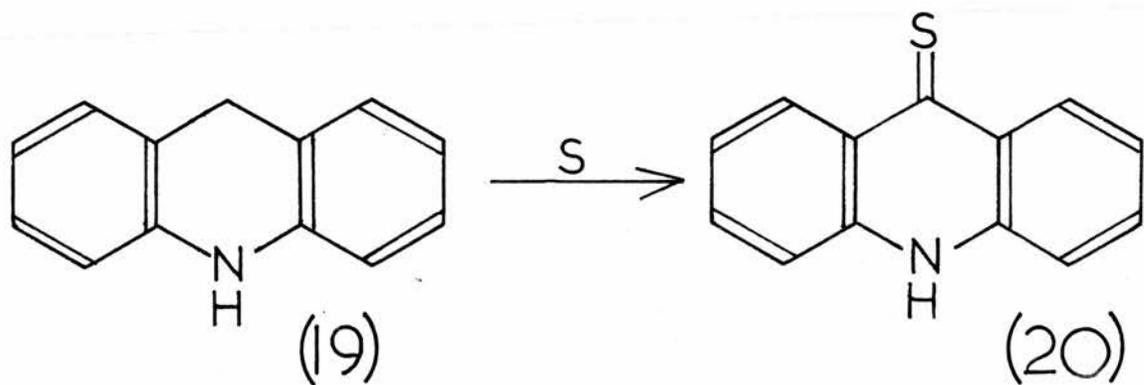
### Preparation and Properties of Thioketones

#### Preparation

Thioketones are more widely documented than thioaldehydes. This discussion will be limited to thiones of the type used in work described in this thesis.

#### (a) Alkyl - Aryl Thioketones

Very few thioketones of this type have been prepared, in contrast to the diaryl thioketones, which have been extensively studied. Alkyl - aryl thioketones are somewhat unstable, and tend to polymerise. The action of hydrogen sulphide on ketones is the only method to have received much attention in their preparation. Baumann and Fromm<sup>30</sup> passed a mixture of hydrogen sulphide and dry hydrogen chloride gas into an alcohol solution of acetophenone at  $0^\circ\text{C}$ . The initial intense blue-violet colour of the solution due to the monomeric thioacetophenone (17) faded, and the colourless trithioacetophenone (18) was deposited.



It was found that monomeric trithioacetophenone could be partially reconverted into thioacetophenone by heating above its melting point in a vacuum. Mitra<sup>32</sup> treated acetophenone with ethyl thioacetoacetate and obtained monomeric thioacetophenone. Mingoa<sup>31</sup> used the reaction of magnesium bromobisulphide with acetone to prepare trithioacetone and with acetophenone to obtain the monomeric blue-violet thioacetophenone.

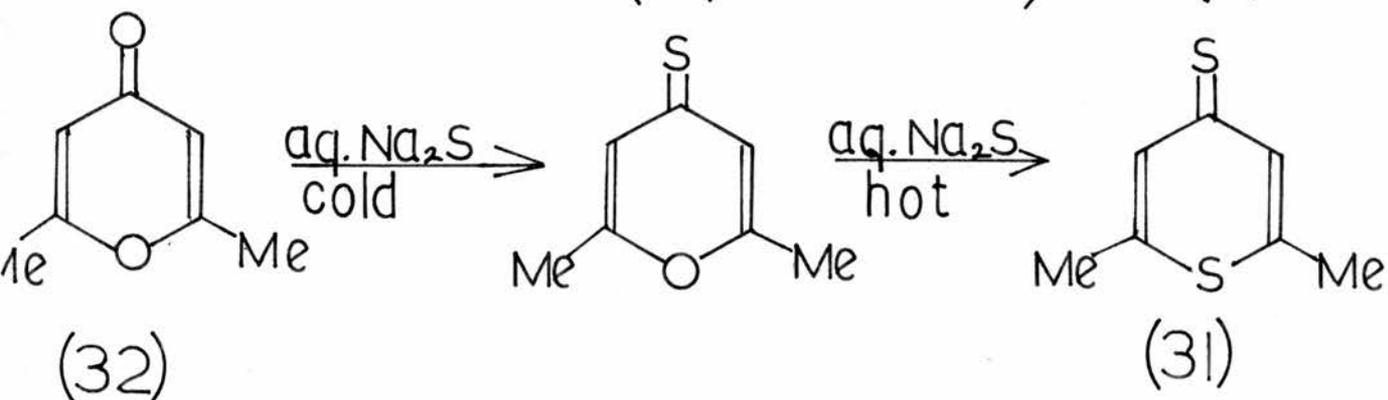
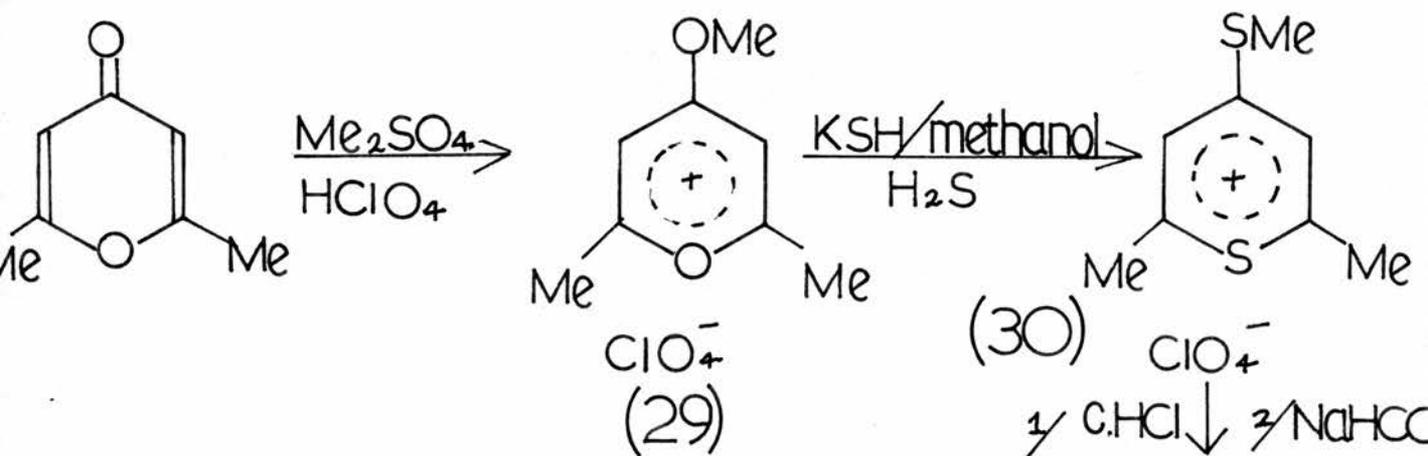
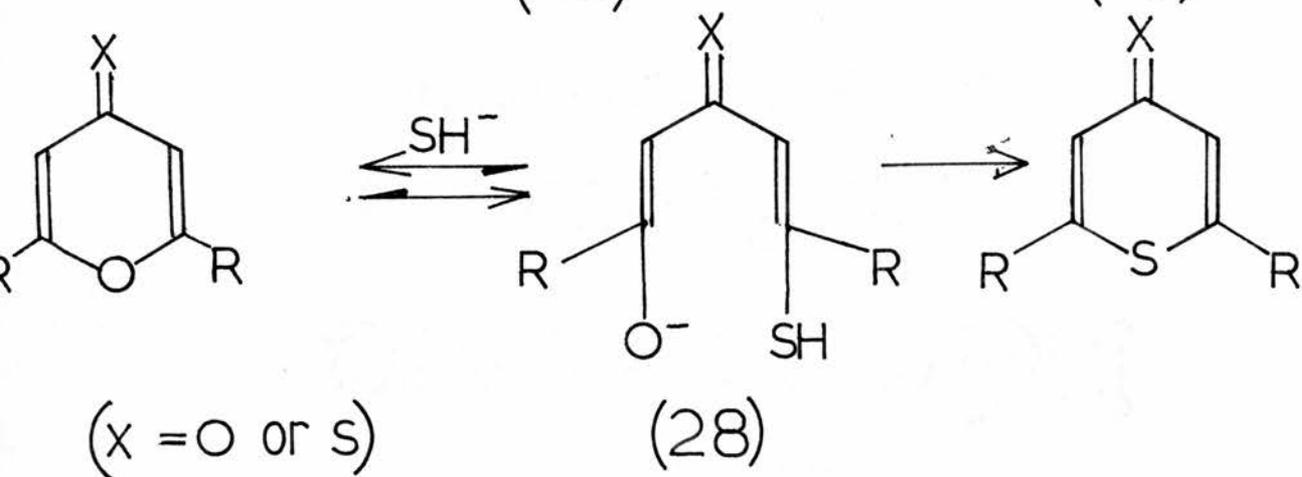
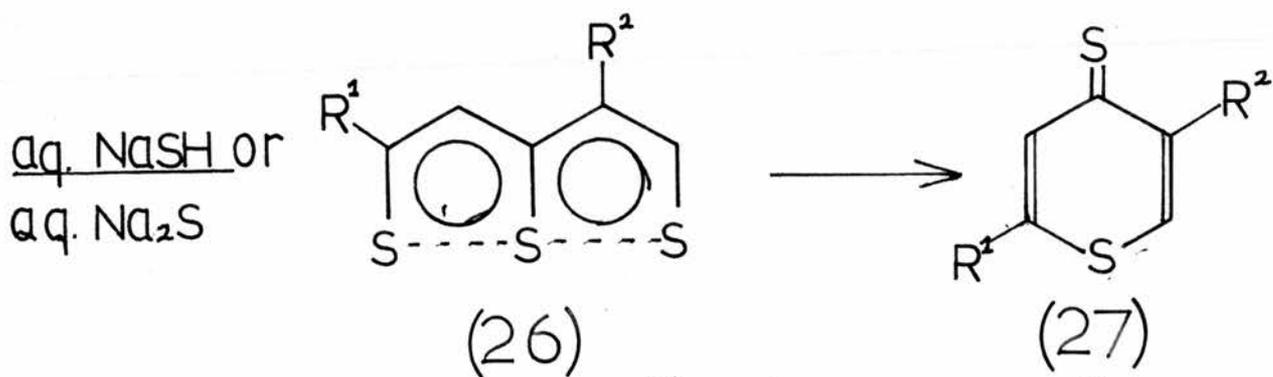
(b) Heterocyclic Thioketones

These are relatively stable, high melting compounds which can be prepared in almost all cases by the action of phosphorus pentasulphide on the appropriate ketone. Another method, first used by Edinger and Arndt<sup>33</sup> to obtain thioacridone (20) relied on heating the basic methylene derivative (19) with elemental sulphur.

Another method of interest is that of Schonberg, Schutz and Nickel<sup>34</sup>. They were able to prepare xanthione (21) and N - phenylthioacridone (22) from the corresponding methylene dichloride compounds by the reaction of thioacetic acid.

4H - Pyran - and 4H - Thiopyran - 4 - thiones

These thioketones are formally derived from thiotropone (23), not yet isolated in substance, by replacing in each case a C - C double bond by a bivalent sulphur or oxygen atom. The ring size is changed but the number of  $\pi$  - electrons remains constant. These systems



tend to be formed easily. The driving force is the formation of the  $\pi$  - electron sextet, and the delocalization of the positive charge. They can be prepared from the appropriate ketone, in almost all cases by the action of phosphorous pentasulphide in a non-polar solvent at c.100°C. However a variety of other methods may be used. Recent work by Dean, Goodchild and Hill<sup>49</sup> has shown that either silicon disulphide or boron sulphide could be used for converting pyranones to pyranthiones. In the synthesis of 6a - thiothiophthenes Reid and coworkers<sup>47,48</sup> condensed dithiolium salts (24) with dimethylthioformamide in acetic anhydride to give Vilsmeier salts (25). These salts reacted with aqueous sodium hydrogen sulphide to give 6a - thiothiophthenes (26). The thiothiophthenes rearrange, when treated with sodium hydrogen sulphide in dipolar aprotic solvents to 4H - thiopyran - 4 - thiones (27). Alternatively, the Vilsmeier salt was allowed to react with the stronger reagent, aqueous sodium sulphide, to give 4H - thiopyran - 4 - thiones without isolation of the thiothiophthene.

The conversion of pyranthiones into thiopyranthiones was first attempted by Arndt and his coworkers<sup>37,38,39,40</sup>. The pyranthione (or pyranone) was boiled in alcohol with a concentrated solution of aqueous potassium hydrogen sulphide. Ring-opening and substitution of oxygen by sulphur took place (28). A variation of this method comes from Kato<sup>45</sup> and coworkers. The pyrylium salt (29) was treated with

potassium hydrogen sulphide in methanol under a current of hydrogen sulphide. This was reported to produce the 4 - methylmercapto - 1 - thiopyrylium salt (30)! Treatment with concentrated hydrochloric acid, followed by neutralisation with sodium bicarbonate gave the required 2, 6 - dimethyl - 4H - thiopyran - 4 - thione (31) in good yield. Some doubt must be cast on these two methods by the work of Lozach<sup>46</sup>. Repetition of Arndt's work showed that a mixture of starting material and thiopyranthione was produced. These could only be separated with difficulty by chromatography. Similarly Traverso<sup>42,43,44</sup> found it necessary to use sodium sulphide solution in preparing 2, 6 - dimethyl - 4H - thiopyran - 4 - thione (31) from 2, 6 - dimethyl - 4H - pyran - 4 - one (32). Pyranthione was obtained by allowing the reaction to proceed in the cold. Thiopyranthione was obtained by heating the mixture.

#### Properties of Thioketones

Monomeric thioketones are coloured compounds, and this property is useful in deciding the point at which the trimers dissociate. Trithioacetophenone gives a blue solution in boiling xylene, which gradually fades as the solution is cooled and association takes place.

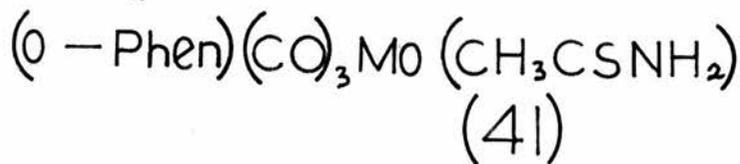
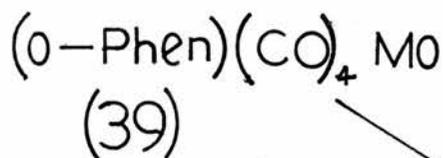
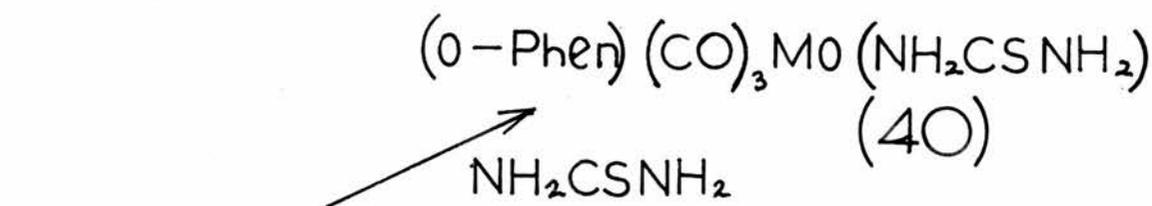
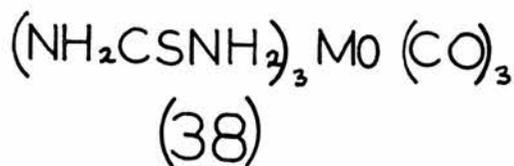
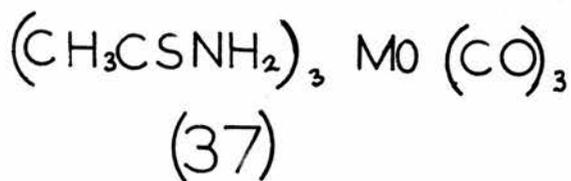
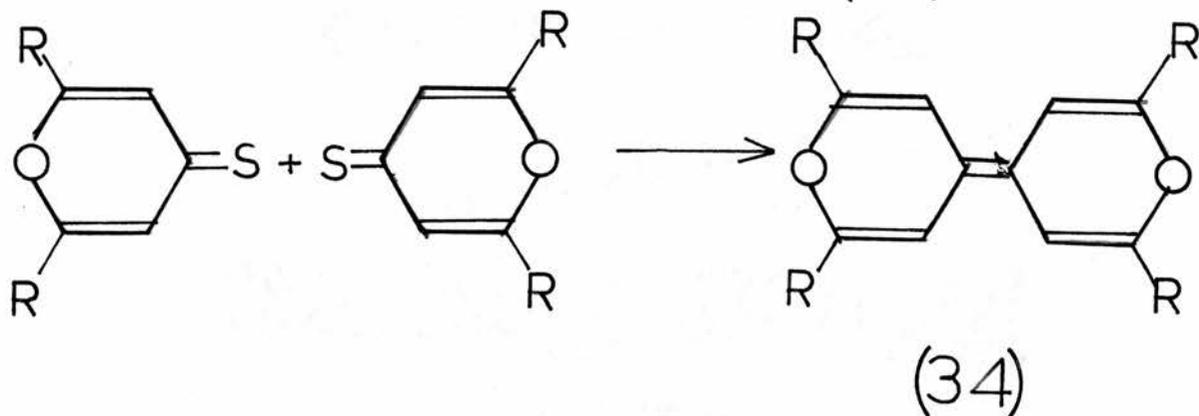
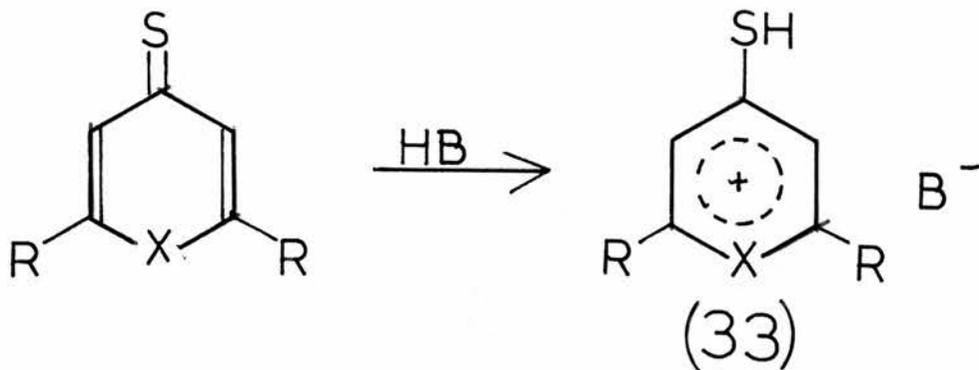
Simple alkyl thioketones are unstable red oils with extremely unpleasant odours. Alkyl - aryl thioketones are unstable as the monomer, forming trimers. Heterocyclic thioketones tend to be stable, particularly when the aromatic ring contains electron-releasing groups

favouring polarisation of the thiocarbonyl group.

Because of the instability of the simpler thioketones, there is very little information on the infra-red stretching frequencies of the C=S group. Consequently all data is from studies on thioamides and diaryl and heterocyclic thioketones. In general, there is agreement that the theoretical thiocarbonyl stretching frequency falls in the range  $1150 \pm 70 \text{ cm.}^{-1}$ . In the case of thioamides, interactions with vibrations in the same spectral range give rise to coupled vibrations. For thioacetamide, this has the effect of lowering the thiocarbonyl stretching frequency to  $975 \text{ cm.}^{-1}$ .

The ultra-violet spectra of thioketones show a weak band at c. 500 m. for aliphatic and c. 600 m.  $\mu$  for aryl thioketones. On the basis of its intensity and solvent dependence it has been assigned to the  $n - \pi^*$  transition.

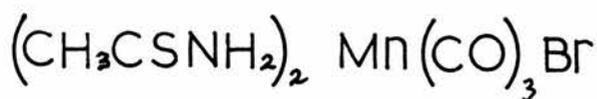
Corresponding to the negative charge on the sulphur atom, thioketones tend to be weak bases. Pyranthiones react with strong acids to give pyrylium salts (33). Pyranthiones will condense to form dipyrlylenes (34). The more developed the thioketones nature of the thiocarbonyl group, the more easily is the dipyrlylene formed. This reaction has long been known and may be brought about by heating the thioketone. Thioketones are unstable towards oxidizing agents, usually forming carbonyl compounds. With some pyranthiones of the type (35), meriquinoid salts (36) may be formed instead.



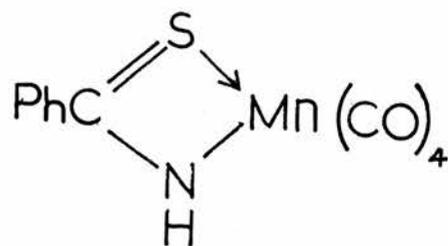
Metal Complexes with Thiocarbonyls and Related Compounds(1) Derivatives of Thioacids(a) Thioamides and Thioanhydrides

Examples of purely monodentate sulphur ligands are thioacetamide (37) and thiourea (38). They provided the first substituted metal carbonyls containing ligands which coordinate through bivalent sulphur<sup>3,4</sup>. These compounds were of the type  $Mo L_3 (CO)_3$ , and were yellow crystalline solids, ranging in stability in air, from very unstable to moderately stable.

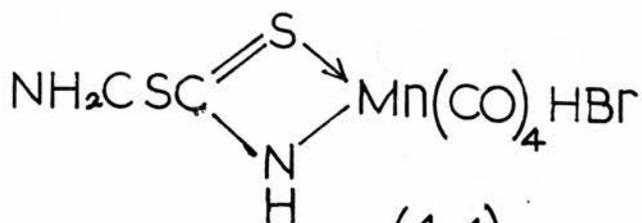
Houk and Dobson<sup>102</sup> later prepared thiourea (40) and thioacetamide (41) complexes from o - phenanthroline molybdenum (VI) tetracarbonyl (39). Hieber and Gschiedmeier<sup>22</sup> used manganese bromopentacarbonyl as starting material and thioacetamide and dithioamides as ligands to obtain the product (42) and the salt (44) respectively. Similarly, it was found that thiobenzamide was sufficiently acidic to react with manganese bromopentacarbonyl to form the derivative (43). Recent work<sup>75</sup> has produced complexes of tin and thiourea. Varying amounts of thiourea were dissolved in aqueous acid solutions of the appropriate tin (II) compound and the solid product (45) isolated and identified by chemical analysis and X-ray diffraction. The shifts to lower frequency (c.  $30\text{ cm}^{-1}$ ) of the thiocarbonyl vibration of the thiourea portion of the infra-red spectra of the complexes show that the tin - ligand bond is through



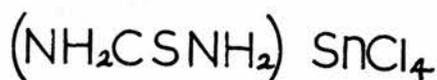
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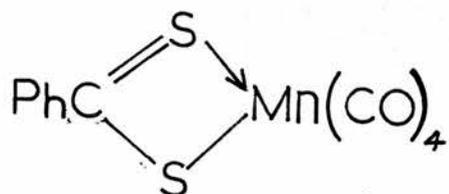
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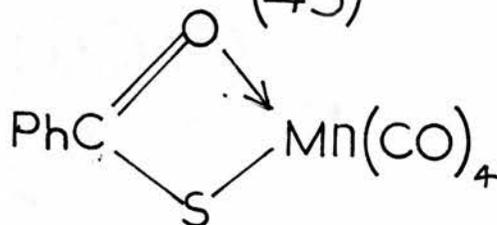
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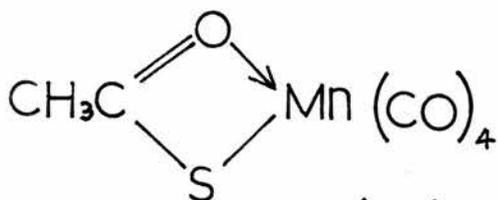
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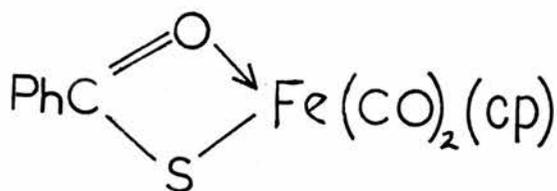
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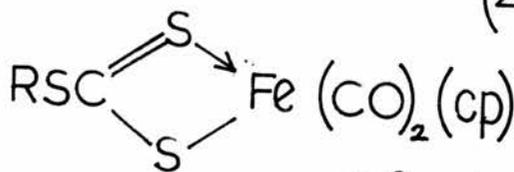
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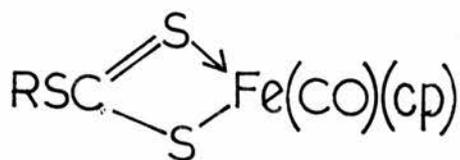
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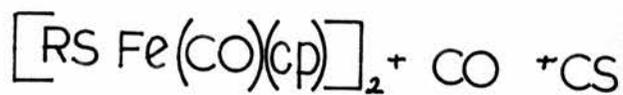
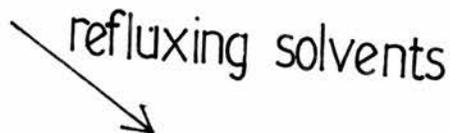
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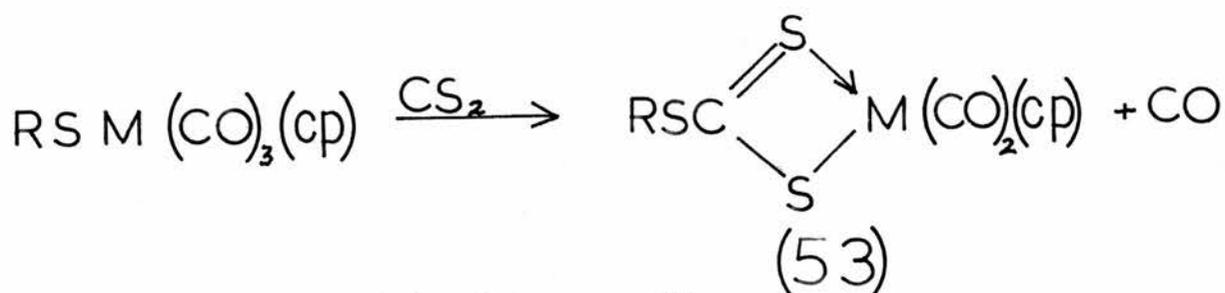
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the sulphur atom.

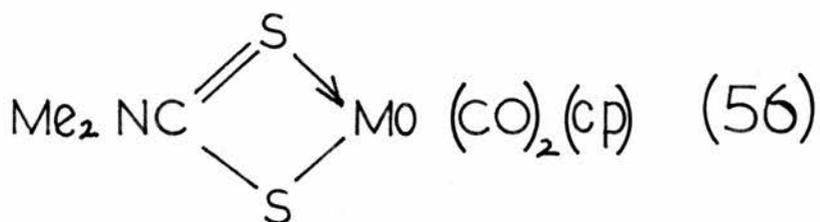
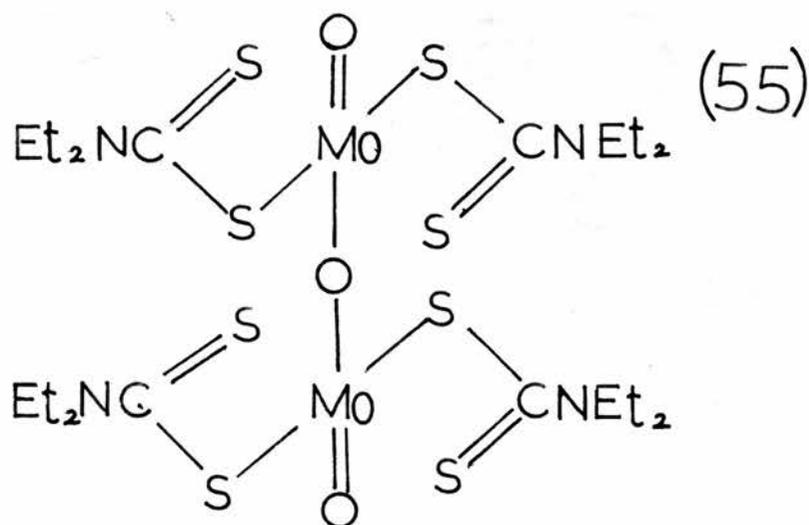
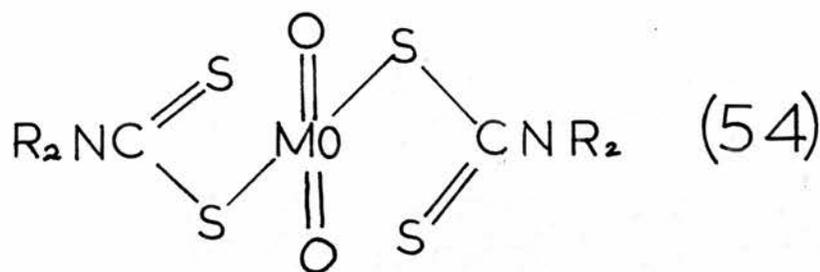
(b) Thiocarboxylates

These anions normally act as chelating ligands to metal carbonyls, although monodentate derivatives with cyclopentadienyliron have been prepared. Thus manganese pentacarbonyl bromide yields tetracarbonyl derivatives with dithiobenzoic (46), thiolbenzoic (47) and thiolacetic acids (48). The only cyclopentadienyliron derivative of these is the dicarbonyl  $\eta^5$ -thiobenzoate (49). Although a metal complex of dithiobenzoic acid had been used in the synthetic route to nickel tetracarbonyl<sup>20</sup>, Cohen and Basolo<sup>19</sup> claimed to have produced one of the first metal carbonyls coordinated to the dithiobenzoate ion (46). The product was a very stable monomeric solid, with an infra-red spectrum compatible with the  $C_{2v}$  symmetry required for bidentate attachment of the dithiobenzoate group.

Alkyltrithiocarbonates may be regarded as analogous to dialkyldithiocarbamates. The trithiocarbonate group has three sulphur atoms each in a formally different environment, and each potentially able to bond to a suitable metal. Bonding is independent or in conjunction with at least one of the other two sulphur atoms. Consequently a wide variety of different complexes can be envisaged. Bruce and Knox<sup>21</sup> prepared several complexes by reacting sodium alkyl or aryl trithiocarbonates with cyclopentadienyldicarbonyliron halides



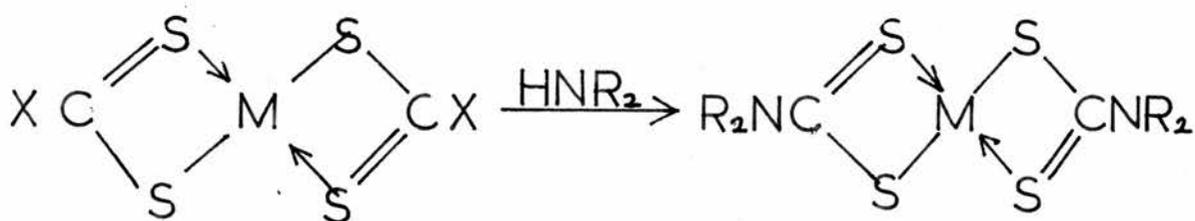
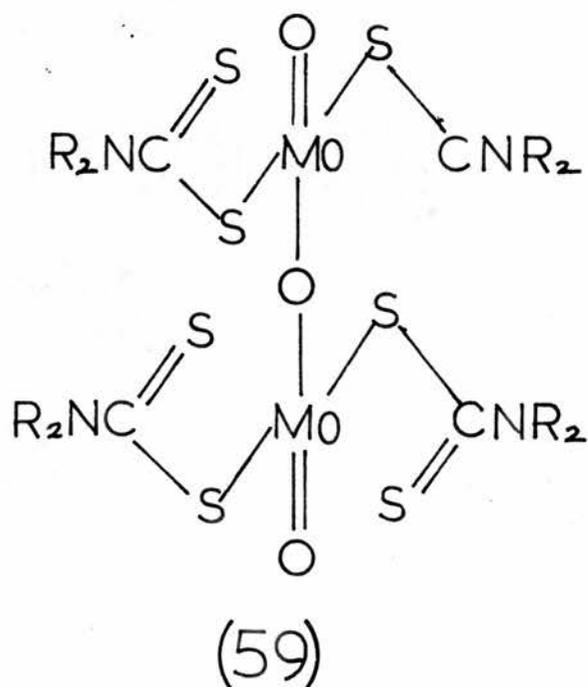
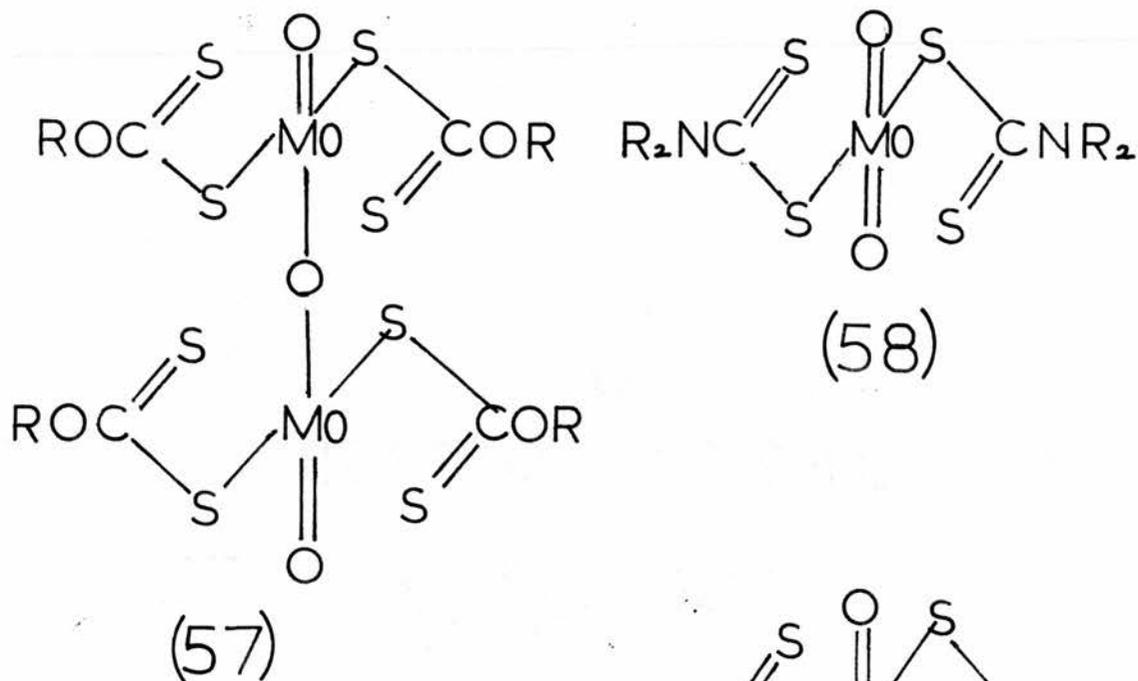
M = Mo or W



to produce complexes (50), which readily lost carbon monoxide. Owing to the instability of the sodium phenyltrithiocarbonate only a low yield was obtained in this case. On irradiation these compounds were converted into the monocarbonyl (51), and in refluxing solvents  $\text{CS}_2^-$  elimination occurs to give the derivative (52). Conversely,  $\text{CS}_2^-$  insertion can be effected in the corresponding molybdenum and tungsten systems (53).

Very few studies have been reported of the analogous oxygen compounds, the O - alkylthiocarbonates or xanthogenates. Cobalt (II) and nickel (II) solutions were allowed to react with carbon monoxide in the presence of the xanthogenates anion. This led to the formation of cobalt carbonyl hydride, or salts thereof, and nickel carbonyl, respectively.

The dithiocarbamate group,  $\text{R}_2\text{NCS}_2^-$  is a common univalent, bidentate ligand. The preparation of some dialkylthiocarbamate complexes of molybdenum (V) and molybdenum (VI) was briefly described by Malatesta<sup>94a</sup>. The molybdenum (VI) dioxobis (dialkylthiocarbamate) complexes (54), were prepared by dilute hydrochloric acid acidification of solutions containing molybdate ions and the appropriate sodium dialkylthiocarbamate. The diamagnetic molybdenum (V) complex which is formulated as  $\mu$ -oxo - dioxotetrakis (diethylthiocarbamate) molybdenum (V) (55) was prepared by the sulphur dioxide or sodium



M = Ni(II), Pd(II), Pt(II)

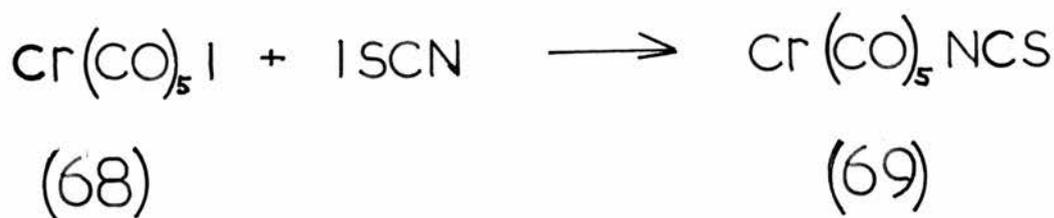
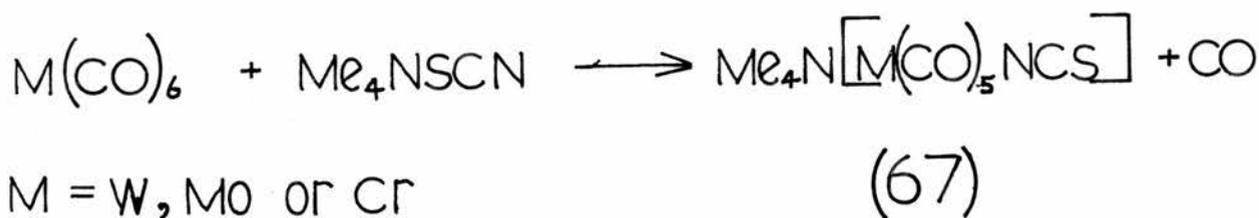
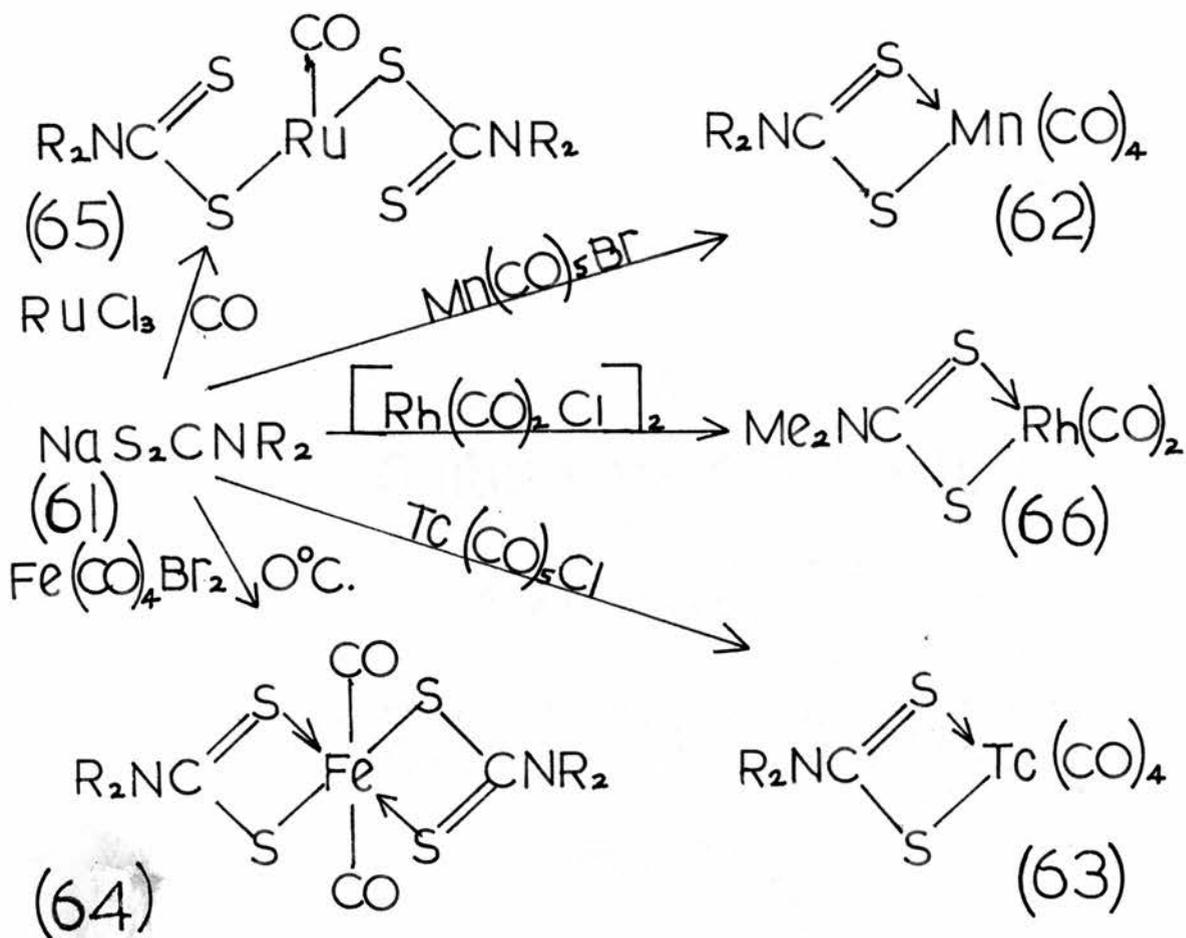
X = NH<sub>2</sub>, NHR or OCH<sub>2</sub>Ph

(60)

dithionite reduction of a solution containing molybdate and diethyldithiocarbamate ions. The related diamagnetic molybdenum (V) alkylxanthate complexes (57) have also been prepared<sup>94b</sup> and determination of the molecular structure of the ethyl derivative confirmed the dinuclear formulation with a bridging Mo - O - Mo group. Another dithiocarbamate complex isolated<sup>95</sup> was  $\pi$ -cyclopentadienyldicarbonyl (dimethyldicarbamate) molybdenum (VI) (56), prepared by the reaction of tetramethylthiuram disulphide and  $\pi$ -cyclopentadienylmolybdenum tricarbonyl dimer. Moore and Larson<sup>92</sup> prepared dialkyldithiocarbamate complexes of molybdenum (VI) of the type (58) and of molybdenum (V) of the type (59), in good yield. In the case of molybdenum (V) complexes of dimethyl and diethyldithiocarbamate and ethylxanthate, preparation was by the treatment of an aqueous solution of an alkali metal salt of the ligand with ammonium oxopentachloromolybdate (V). Infra-red bands assignable to Mo - S absorption were found in the 460 - 515  $\text{cm}^{-1}$  region and the dimeric molybdenum (V) complexes showed a band at about 435  $\text{cm}^{-1}$  due to a Mo - O - Mo stretching mode. It was concluded that Mo (VI) complexes contained a cis O = Mo = O group since their infra-red spectra contain two Mo = O bands at about 900  $\text{cm}^{-1}$ . The Mo (V) dithiocarbamates contain a ligand field band at about 19,500  $\text{cm}^{-1}$ .

The higher dialkyldithiocarbamates, like the monoalkyldithiocarbamates and alkylxanthates, are probably incapable of forming stable

molybdenum (VI) complexes because of oxidation of the ligand by molybdenum (VI). In contrast to the dithiocarbamates, the corresponding xanthate complexes, from infra-red spectral and X-ray structural evidence appear to contain the group  $RO(C=S)S^-$  rather than the group  $(RO^+CS_2^-)^-$ . Jensen's<sup>93</sup> studies with selenium analogues indicate that the C - S frequencies should be expected in the 1020 - 1070  $cm.^{-1}$  region. However, like the C - S frequencies, the frequency of metal to sulphur bands is not a true measure of the stability of the complex because other factors influence its position. In ligand field studies, the sulphur - to - molybdenum charge-transfer band of xanthate complexes appears at 6,000  $cm.^{-1}$  below that of the corresponding dithiocarbamate complexes indicating that xanthates are better reducing agents than dialkyldithiocarbamates. This agrees with the fact that no molybdenum (VI) xanthate complexes are known. Methyl and ethylxanthato complexes of Pt (II), Pd (II), Ni (II), Cr (III) and Co (III) were prepared and characterised by Watt and McCormick<sup>96</sup>. The Complexes were shown to be monomeric and square-planar. These complexes were later used by Fackler<sup>97</sup> in nucleophilic substitution reaction studies (60). Evidence suggests that the reaction occurs without rupture of the metal - sulphur bonds, and a direct nucleophilic attack was proposed for the reaction. When dialkyldithiocarbamates are allowed to react with carbonyl halides of manganese, technetium, iron, ruthenium and rhodium, the formation of

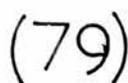
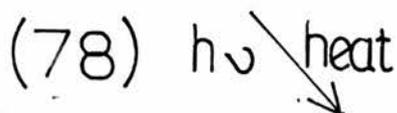
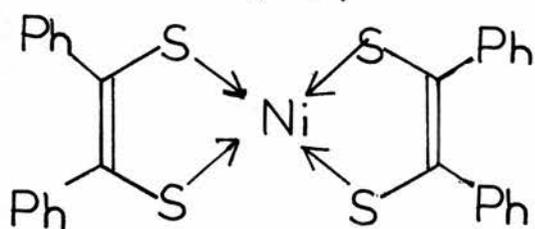
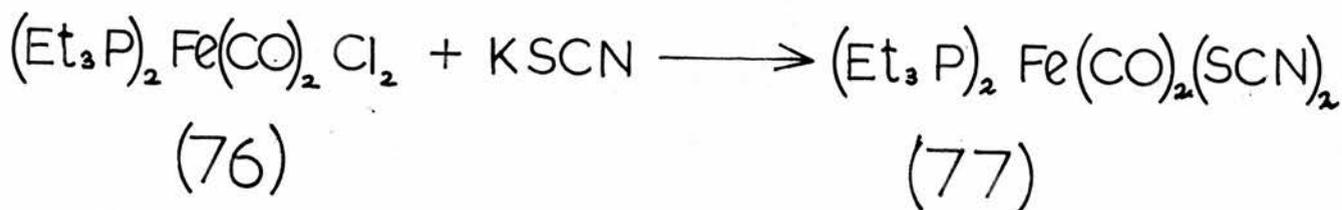
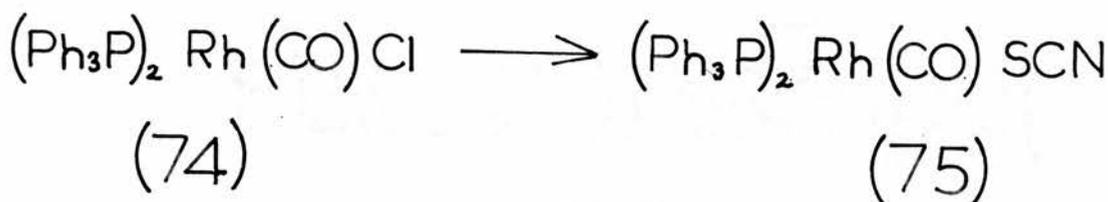
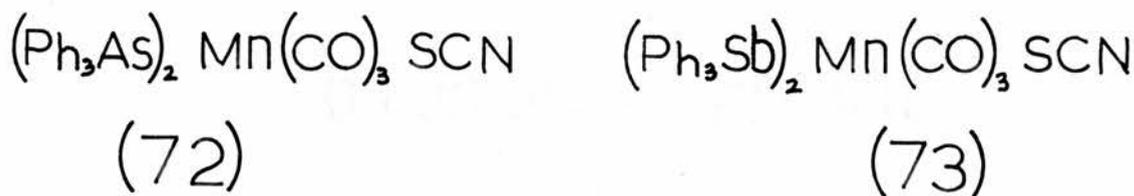


chelated derivatives (62-66) occurs.

(c) Thiocyanates

The survey will be restricted to metal carbonyl thiocyanates.

The thiocyanate ion is a pseudo - halide ion, and like halide ions, will substitute into group VI hexacarbonyls<sup>18</sup> giving N - thiocyanatopentacarbonyl metallates, isolable as tetraalkylammonium salts (67). These compounds are stable at room temperature under nitrogen and decompose only slowly on prolonged exposure to air. The molybdenum compound is markedly less stable than those of chromium and tungsten. The corresponding neutral species (69) could not be prepared from oxidative reactions in the manner of its iodine analogue (68), but was obtainable<sup>76</sup> from the latter by the action of iodothiocyanogen. This compound is N - bonded to the metal, and in contrast, the isoelectronic manganese carbonyl thiocyanate (71) is S - bonded. It is obtained<sup>77</sup> by the reaction of sodium pentacarbonylmanganate (70) with chlorothiocyanogen. Electrical conductance studies suggest S - bonding in the solid state, almost completely N - bonding in acetonitrile, and intermediate forms in solvents such as chloroform. The manner in which the thiocyanate ligand is attached depends primarily on the charge at the central metal atom. This is demonstrated by the fact that unsubstituted and monosubstituted compounds are S - bonded whereas the disubstituted and anionic derivatives are N - bonded. Exceptions to this

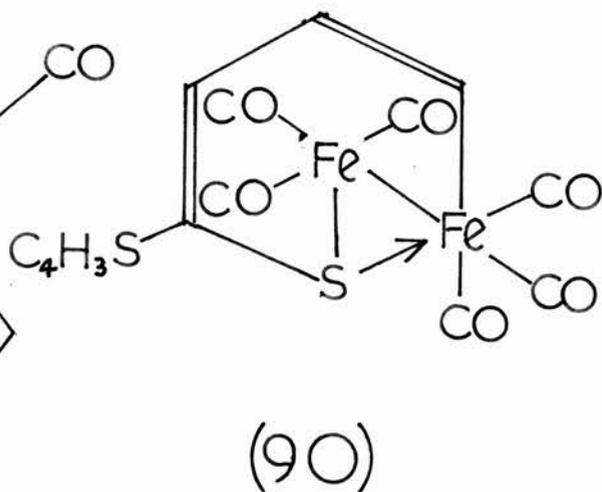
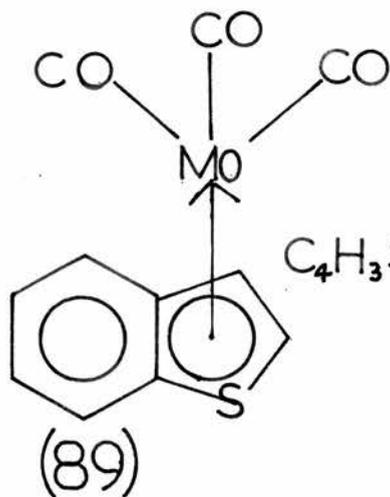
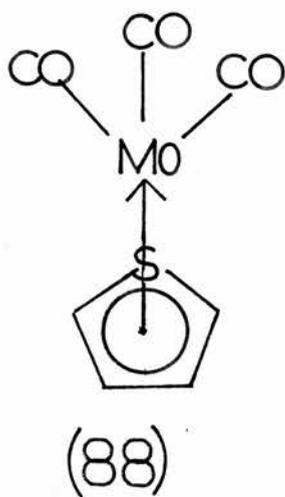
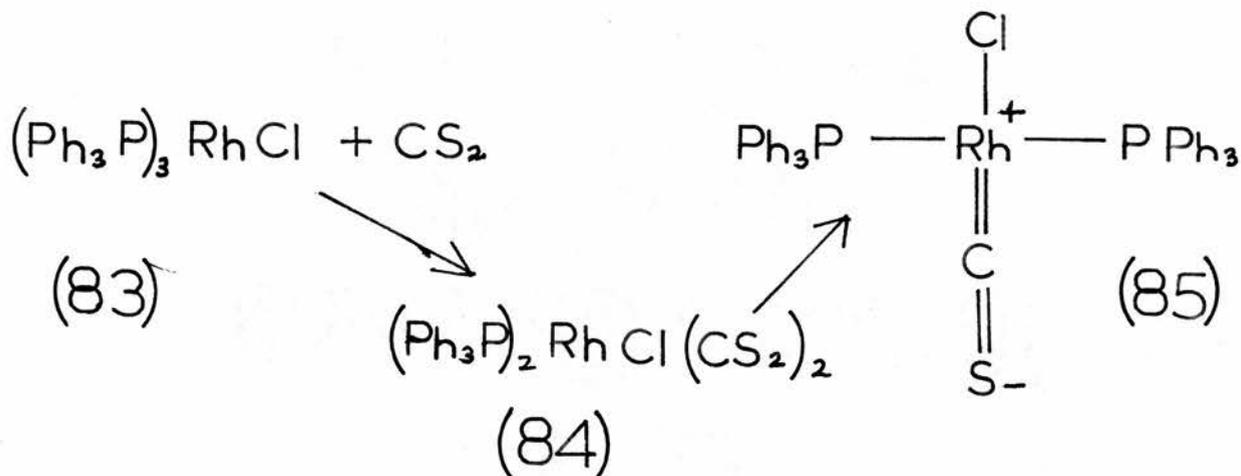
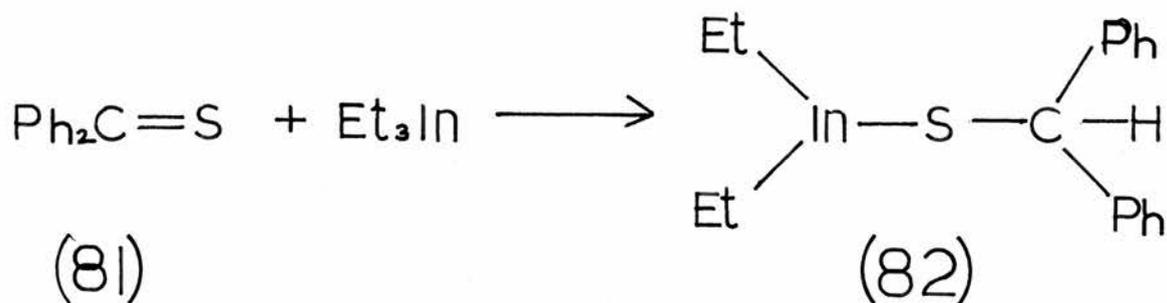


rule are the cis - bis (triphenylarsine) (72) and cis - bis (triphenylstilbene) (73) derivatives of manganese, which are S - bonded. The triphenylarsine derivative is N - bonded. This can be explained by the fact that Mn - S - CN is a non-linear grouping and unlike the bulky Mn - N - CS arrangement, can alleviate steric hindrance between bulky ligands and the thiocyanate group.

The first known<sup>78</sup> metal carbonyl thiocyanate (75) was prepared by metathesis from the corresponding rhodium (I) chloride (74). Phosphine-substituted iron carbonyl thiocyanate (77) was obtained<sup>79</sup> in a similar manner, from the chloride (76).

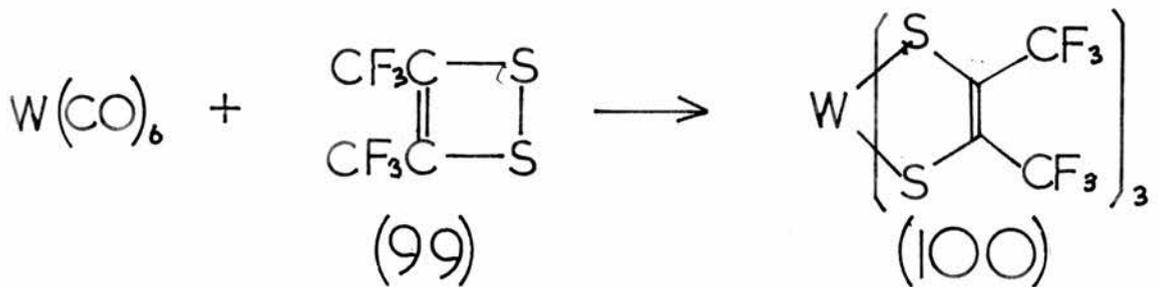
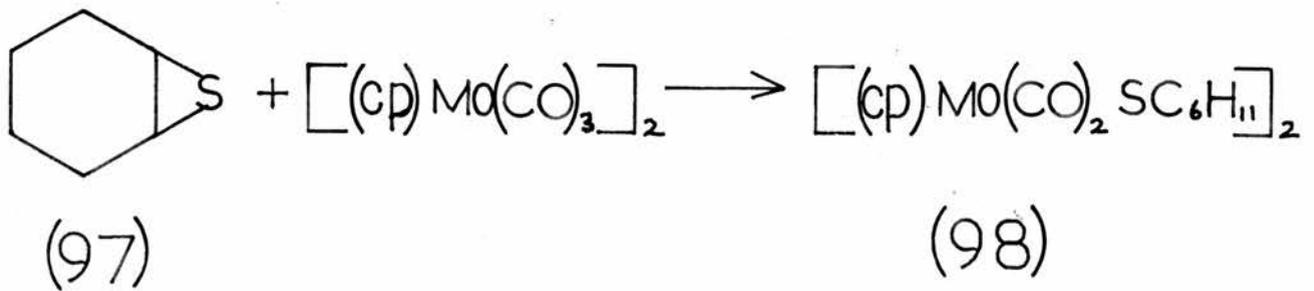
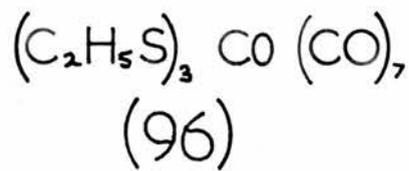
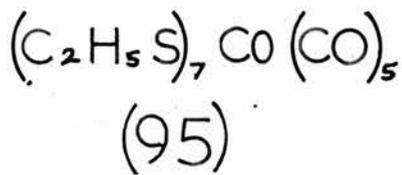
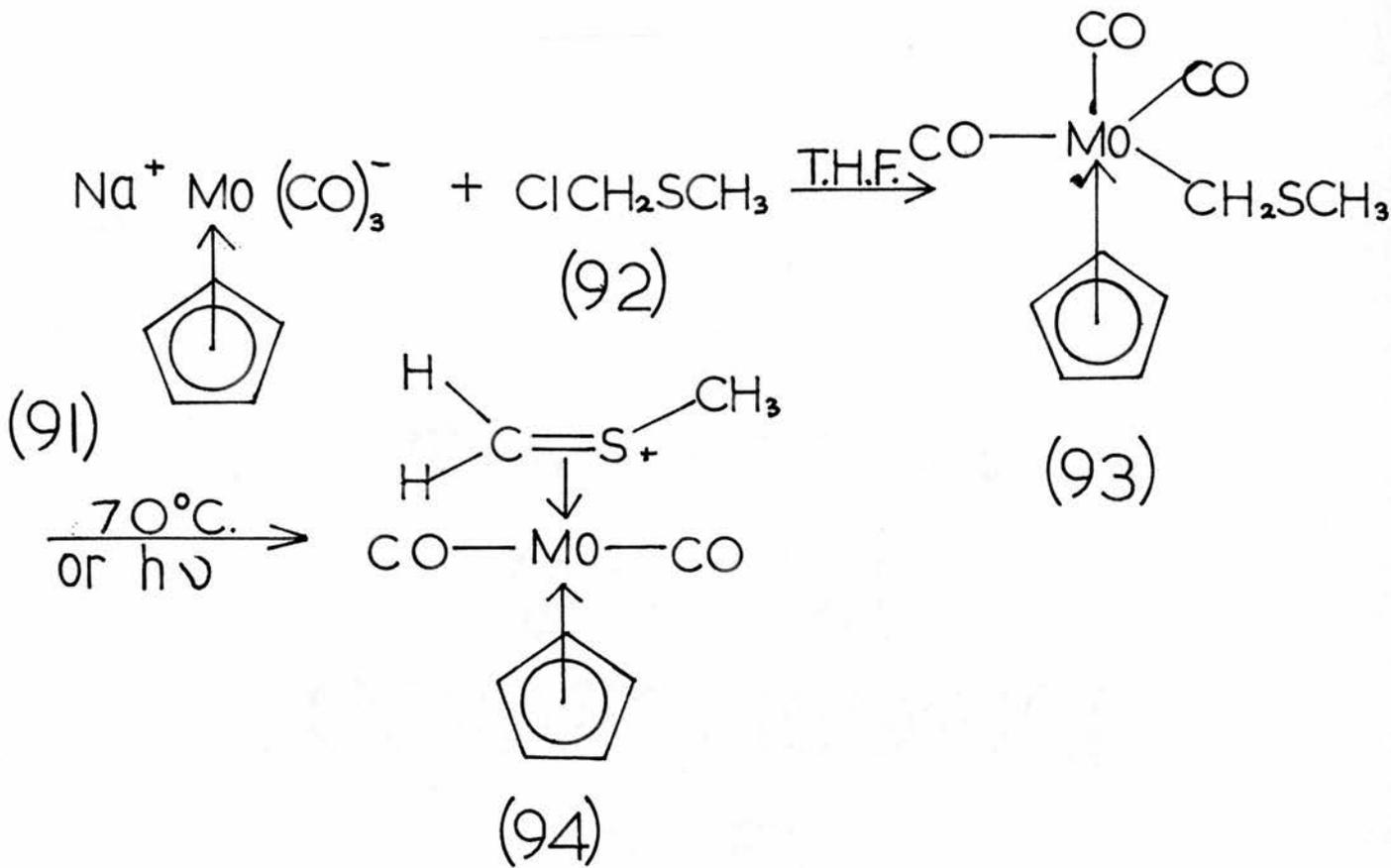
## (2) Thioketones and Thioaldehydes

No complexes have hitherto been prepared from thioaldehydes, and very few thioketones complexes have been reported. Adducts of mercuric chloride with 2H - thiopyran - 2 - thione and 4H - thiopyran - 4 - thione have been prepared<sup>50</sup>. Similarly adducts have been prepared with thiopyranthiones and Grote's reagent<sup>81</sup> although no structures are proposed. A recent paper<sup>104</sup> has tabulated the preparation and properties of some adducts of 2,6 - dimethyl - 4H - thiopyran - 4 - thione and the chlorides of Ag, Cu, Hg, Sb, Bi, Co, Fe, Pt, Ni, and Pd. No evidence has been found for the previous preparation of carbonyl complexes with thioketones. An attempt<sup>82</sup> was made, however, to prepare complexes from 4H - thiopyran - 4 - one and iron, cobalt, chromium and



molybdenum carbonyls, without success. Forcing conditions and irradiation were used. A recent paper<sup>83</sup> suggests that a thioketocarbene (79), formed as an intermediate, has reacted to produce an iron complex (80). The thioketocarbene was produced by pyrolysis of the nickel dithietene (78). The reaction is accompanied by the formation of a metal mirror consisting almost entirely of nickel. This suggests that a volatile nickel compound, probably  $\text{Ni}(\text{CO})_4$ , is formed during the reaction, and subsequently decomposes. X-ray crystallography suggested that  $\pi$ -bonding unites the metal and the ligand. Work by Tada, Yasuda, and Okawara<sup>99,100</sup> has shown that thiobenzophenone (81) reacts with triethylindium to form a complex (82) and ethylene. Although thiobenzophenone is a thioketone, the sulphur-containing ligand in the complex formed is thiolic. The complex was found to be air-stable.

Recent work has produced thiocarbonyl derivatives analogous to metal carbonyls. The first<sup>58</sup> was obtained by refluxing tris (triphenylphosphine) rhodium (I) halide (83) with carbon disulphide. The red  $\text{CS}_2$  derivative (84) formed initially subsequently breaks down into the orange thiocarbonyl (85). Marko<sup>13</sup> and his coworkers allowed dicobalt octacarbonyl to react with carbon disulphide to obtain  $\text{CS}_2$  complexes of the type (86). In a later paper<sup>16</sup>, it was claimed that these complexes broke down to form the first thiocarbonyl complexes (87) with cobalt.



Metal Carbonyl Complexes with Other Sulphur-Containing Ligands(1)  $\pi$  - Complexes

Thiophene, benzo - [b] - thiophene and 2,2' - thienyl are the only known aromatic sulphur-containing ligands to form  $\pi$  - complexes. All three replace 3 CO s from chromium hexacarbonyl at high temperatures and pressures to form a  $\pi$  - complex. The thiophene  $\pi$  - complex (88) was first proposed by Fischer and Ofele<sup>52</sup>, but later work was done on the compound by Bailey and Dahl<sup>53</sup>, who performed an X-ray study in order to determine the effect of chromium - thiophene interaction on the thiophene ring parameters. Thiophene and thiophene derivatives were later found<sup>54</sup> to react successfully with manganese pentacarbonyl chloride to give similar  $\pi$  - complexes. Benzo - [b] - thiophene gives<sup>55</sup> a similar monochromium tricarbonyl derivative (89) 2,2' - dithienyl was shown<sup>56</sup> to react with triiron dodecacarbonyl, to yield a diiron hexacarbonyl derivative with the suggested structure (90).

When the salt (91) was allowed to react with chloromethyl sulphide (92) in tetrahydrofuran solution at 25°C., the alkyl tricarbonyl derivative (93) was obtained<sup>57</sup>. On being heated to approximately 70°C., or when irradiated with u.v. light, this tricarbonyl derivative formed the dicarbonyl  $\pi$  - bonded derivative (94); the first sulphur  $\pi$  - allyl derivative.

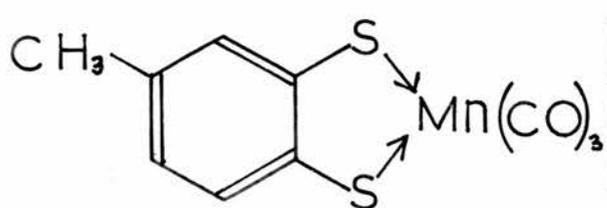
(b) Thiol Complexes

Marko and his colleagues<sup>14,15</sup> produced complexes with dicobalt

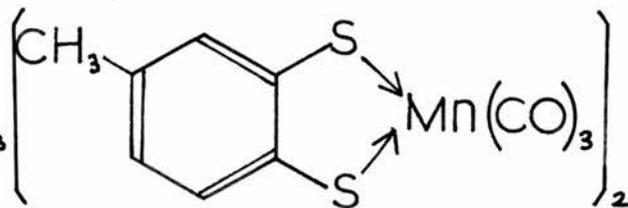
octacarbonyl and ethyl thiol (95,96). Treichel and Wilkes<sup>7</sup> found that cyclohexene sulphide (97) would react with cyclopentadienyl transition metal carbonyls to give complexes. In the case of molybdenum a dimer (98), as well as other isomers, was obtained. The overall structures were later confirmed. Dithiols have been studied in detail, in their reactions with metal carbonyls. Bis (trifluoromethyl) dithietene (99) is used as starting material in the preparation of cis - ethene - 1,2 - dithial derivatives<sup>51</sup>. With chromium molybdenum and tungsten hexacarbonyls, complete elimination of CO takes place to give tris - (dithiolates) (100), after refluxing for four and a half hours in, ethylcyclohexane. Toluene - 3,4 - dithiol, on the other hand gives monosubstituted products with manganese carbonyl bromide (101,102).

#### Physical Properties of Sulphur-containing Metal Carbonyls

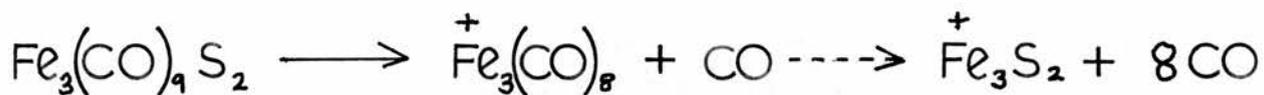
Perhaps the most useful tool for the study of these complexes is infra-red spectroscopy. Orgel<sup>84</sup> has attempted to assign the CO stretching frequencies in substituted carbonyls of the type  $L_n M(CO)_{6-n}$  where  $L_n$  is the sulphur-containing ligand, and the metal. Although not specifically for sulphur-containing ligands, this paper is of some use in the elucidation of their structure. Strohmeier<sup>85</sup> has discussed the stretching frequencies of C - O, and in some cases force constant calculations and assignments of  $\nu(C - O)$  modes have been made. Schrauzer and colleagues<sup>86</sup> have studied the ultra violet spectra of



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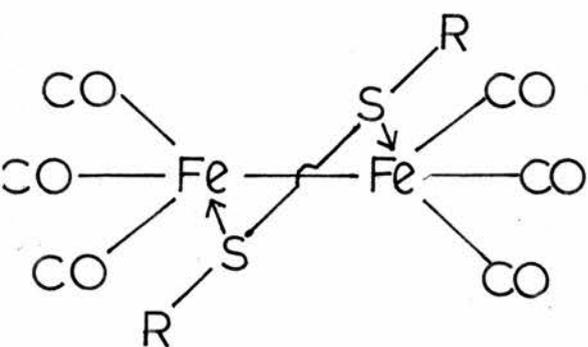


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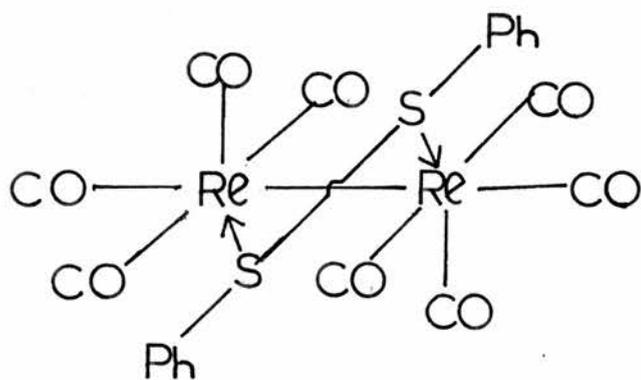


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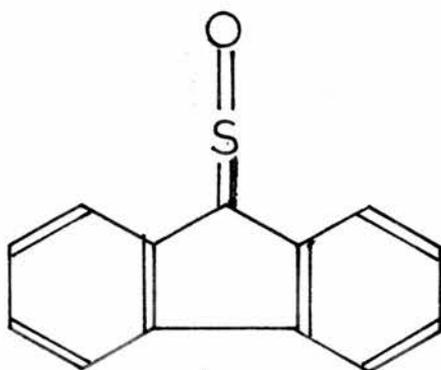
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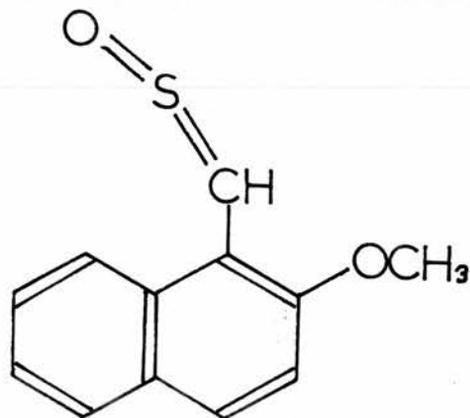
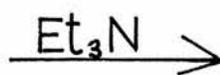
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these carbonyls although few specific assignments have been made. Similarly nuclear magnetic resonance studies<sup>89</sup> are limited to routine summaries of spectra, without conclusions.

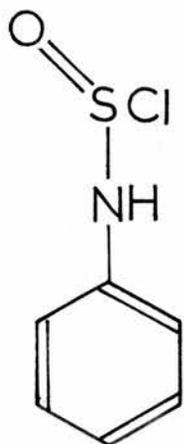
Mass spectrometric studies have shown<sup>87,88</sup> that, because sulphur is a very strong ligand to many transition metals, the complex first loses progressively all the carbonyl groups. Thus triironnonacarbonyl disulphide (103) decomposes<sup>91</sup> to the ion, triiron disulphide (104) which corresponds to the base peak of the spectrum. Similarly thio-bridged metal carbonyls such as (105) and (106) resemble phosphorus and halide analogues in retaining the M S R structure until loss of carbonyl groups is completed. Alkene loss is then observed if R is ethyl or butyl. Trimeric and tetrameric compounds<sup>90</sup> show similar features.



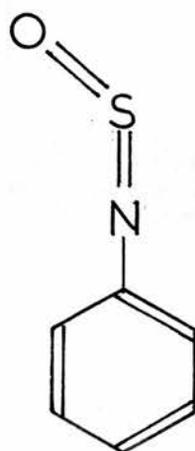
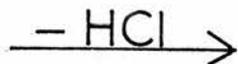
(108)



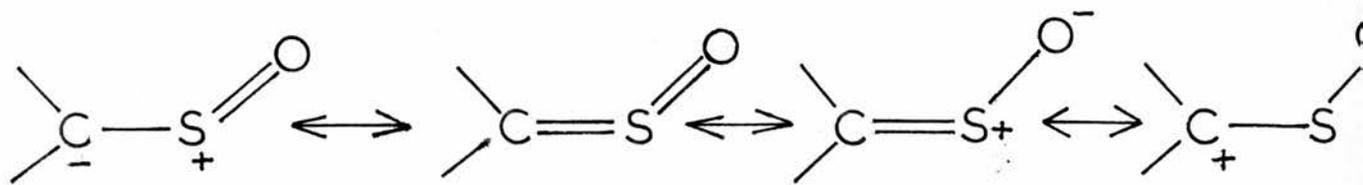
(109)



(110)



(111)



A

B

C

D

(112)

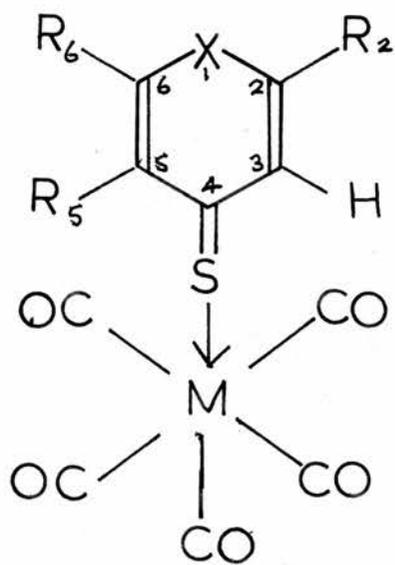
Sulphines

Sulphines were first prepared by Sheppard and Diekmann<sup>61</sup> in 1964. They are the S - oxides of thioketones. The compound obtained by these authors was fluorenylidene sulphine (107). Shortly afterwards, Strating<sup>62</sup> prepared a thioaldehyde S - oxide. This followed on from his work on the mechanism of formation of 2 - methoxy - 1 - naphthylmethylsulphinyl chloride (108), which with triethylamine lost hydrogen chloride to form the sulphine (109). Similarly N - sulphinylaniline (111) has been prepared<sup>72</sup> from its corresponding N - sulphinyl chloride (110). In a later paper<sup>63</sup>, Strating described a new preparation of sulphines. Oxidation of thioketones with perphthalic acid gave in many cases the corresponding sulphine. Hitherto oxidation of thioketones had not appeared to be an attractive method for the preparation of sulphines, although oxidation<sup>64</sup> of thioamides, thioureas, thiourethanes and trithiocarbonates had led to the formation of the corresponding S - oxides. However, in many cases, oxidation of thioketones will not be suitable for the preparation of sulphines<sup>65</sup>, because of further rapid oxidation to the corresponding ketone.

In later papers<sup>66,67</sup> Strating went on to describe the chemistry of sulphines. He put forward the proposal that the structures A,B,C, and D (112) contribute to the resonance stabilization of sulphines. A theoretical H.M.O. treatment of the sulphine system leads to the

conclusion that the carbon atom is slightly negative, the sulphur positive and the oxygen strongly negative. Although structure C (and possibly also B) is the most important one, the stability of sulphines will be governed predominantly by the possibilities of delocalization of the negative charge on the carbon atom in the ylid structure A.

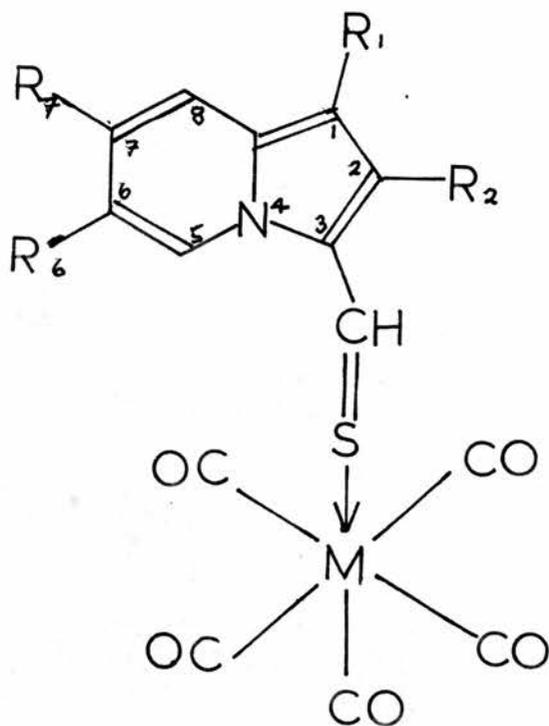
PART 2



(1)

M X R<sub>2</sub> R<sub>5</sub> R<sub>6</sub>

a	Mo	O	Me	H	Me
b	Mo	S	H	H	H
c	Cr	S	H	H	H
d	Mo	S	Me	H	H
e	Mo	S	Ph	Ph	H
f	Mo	S	Ph	H	H



(2)

M R<sub>1</sub> R<sub>2</sub> R<sub>6</sub> R<sub>7</sub>

a	Mo	Me	Me	H	H
b	Mo	H	Me	H	H
c	Mo	H	Me	Me	H
d	Mo	H	Me	H	Me

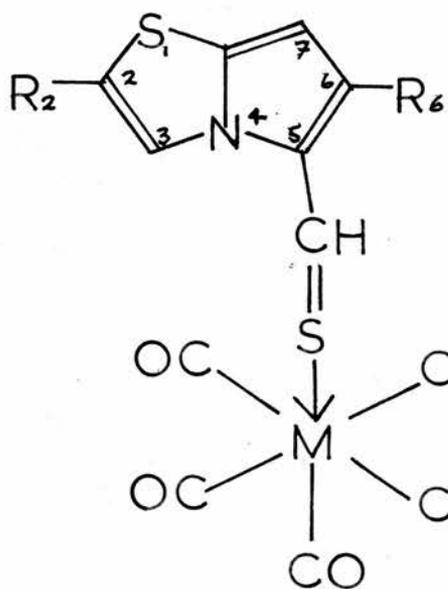
Discussion

This section is composed of two parts. The first will explain the aims of the work described in this thesis. The second and larger section tabulates and elucidates the spectra.

Preparation of Transition Metal - Organosulphur Complexes and Sulphines

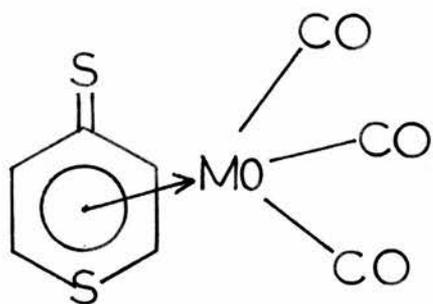
It is clear from the introduction that transition metal complexes of thiocarbonyl compounds are rather rare. It was hoped that the thiopyranthione complexes would be  $\pi$ -bonded instead of, as was found later,  $\sigma$ -bonded. A  $\pi$ -bonded complex might have been bonded in such a way (4) as to allow reactions to occur without deformation of the basic shape of the thiopyranthione molecule. Reaction of thiopyranthione (6) with sulphide ion produces thiothiophthenes under normal conditions (8). It was thought that a  $\pi$ -complexed thiopyranthione might have been held in such a way as to produce the seven-membered ring structure (5) on reaction with sulphide ion, and subsequent removal of molybdenum tricarbonyl. The structure (5) is that which was originally postulated for thiothiophthene. However, subsequent work showed that the  $\sigma$ -complexes had been formed, comprising a hitherto unknown group of compounds.

The reasons for the attempted preparation of sulphines are similar. Firstly, the preparation was attempted because of the novelty and the current interest in sulphines. Secondly, it was hoped

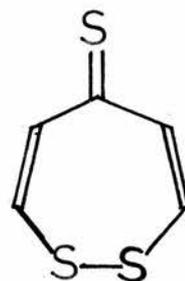
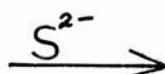


(3)

	<u>M</u>	<u>R<sub>2</sub></u>	<u>R<sub>6</sub></u>
a	Mo	H	Me
b	Mo	Me	Me



(4)

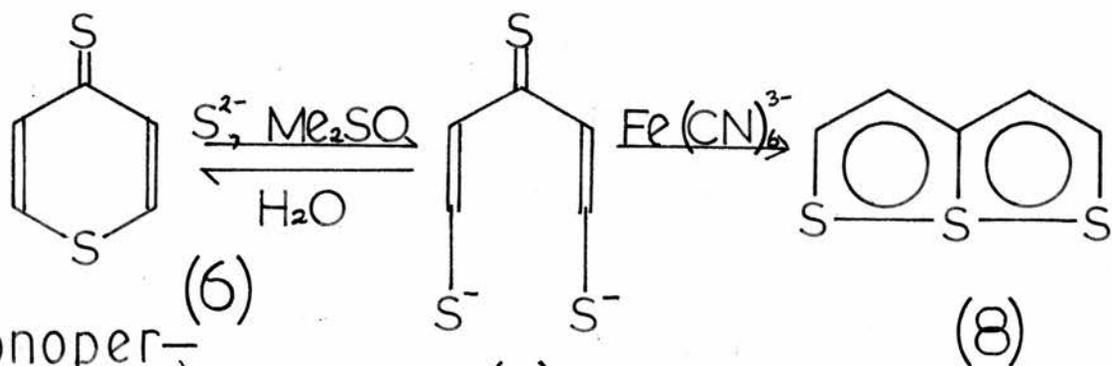


(5)

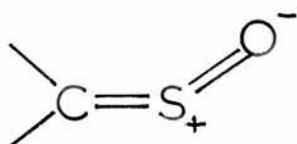
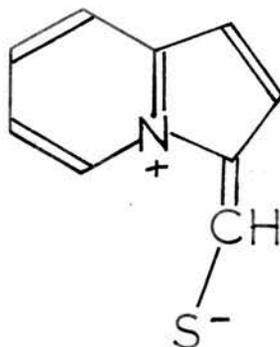
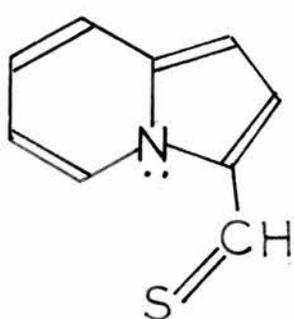
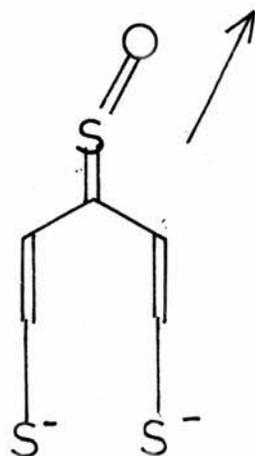
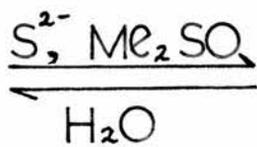
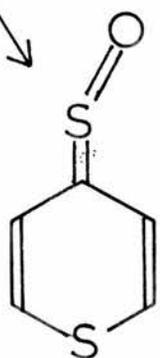
that if a thioaldehyde or methylthioketone would produce a sulphine, the reaction might succeed with thiopyranthiones. In their synthesis of thiothiophthenes Reid and coworkers<sup>105</sup> oxidised the anion (7) produced by allowing thiopyranthione (6) to react with sulphide ion in dimethylsulphoxide, using potassium ferricyanide. If the sulphine (9) had been prepared, the thiothiophthene would possibly have been produced spontaneously due to the presence of the oxygen atom, upon ring-opening. The reason for the failure to produce a sulphine depends on the charge of the sulphur atom of the sulphine system. The indolizine nucleus (10) tends to produce a negative charge at the sulphur atom, and is in no way compatible with the stable sulphine structure (11).

#### Preparation of Methylthioketones

Following the successful synthesis of stable heterocyclic thioaldehydes by Reid and coworkers<sup>108</sup>, a synthesis of methylthioketones by a similar method was attempted. The Vilsmeier reaction, however, was found to give low yields. This resulted in the new synthesis described, using thiolacetic acid and triethylamine.



monoperphthalic acid



Spectral Properties of Transition Metal - Organosulphur Complexes.(1) Proton Magnetic Resonance Spectra(a) 4H - Pyran - 4 - thione and 4H - Thiopyran - 4 - thione Complexes (Table 1,1A)

The  $^1\text{H}$  n .m.r. spectra of 4H - pyran - and 4H - thiopyran - 4 - thione complexes are similar in basic outlines to the spectra of the uncomplexed thioketone. The major difference in the case of pyran - and thiopyranthione complexes is a downfield shift of all protons. The proton signals of H - 3 and H - 5 in the complexes have shifted downfield by c. 0.25 p.p.m., in comparison with the uncomplexed thioketone. (An anomalous value is found in the case of 2,5 - diphenyl - 4H - thiopyran - 4 - thione, where the downfield shift is 0.41 p.p.m). The proton signals of H - 6 and the methyl groups have shifted downfield by c. 0.06 p.p.m. and c. 0.14 p.p.m. respectively.

Little can be said without the direct evidence of X-ray crystallography, but some hypotheses explaining these figures can be put forward. H - 3 and H - 5 of a  $\sigma$  - complex would probably lie in the vicinity of carbonyl groups. One could expect regions of deshielding near to the carbonyl groups by analogy to Pople's work<sup>109</sup> on the  $^1\text{H}$  n.m.r. spectra of carbonyl compounds. The anomalous 2,5 - diphenyl - 4H - thiopyran - 4 - thione result can be explained in terms of steric hindrance. The 5 - phenyl group could possibly be pushing

the 3 - proton nearer a carbonyl group, and further into the area of deshielding. This theory of steric hindrance is substantiated by the low yield in preparation.

The 2 and 6 protons and the 2 and 6 methyl groups are still within range of the anisotropic deshielding effect of the carbonyl groups. Hence an explanation of the downfield shift experienced by these positions. In addition, however, a certain amount of deshielding should be experienced from complex formation. On reaction of the thioketone with metal carbonyl, the thiocarbonyl sulphur atom donates two electrons to form a coordination bond with the metal atom. This tends to leave a positive charge which is distributed over the ring. This should cause deshielding of all protons.

It should be noted that the assignments<sup>106,107</sup> of 4H - thiopyran - 4 - thione itself have been assumed to be incorrect. Comparisons with the spectra of substituted thiopyranthiones, and with complexes formed lead us to believe that the values assigned to 3 - H and 5 - H should, in fact have been assigned to 2H and 6H, and vice versa.

(b) Thioformylindolizine Complexes (Table 2,2A)

The thioformylindolizine ligand is not only larger than, but also more asymmetric than the thiopyranthione ligands. Different <sup>1</sup>H n.m.r. spectra should, therefore, be expected. It was found that all protons were deshielded, with the exception of the 5 and thioformyl protons

which experienced an upfield shift.

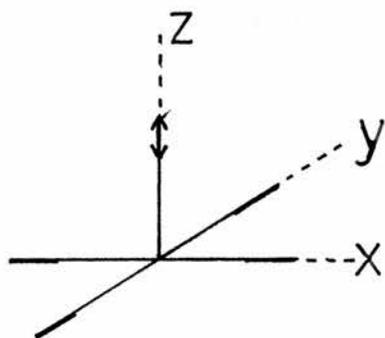
Reaction of a thioformylindolizine with a metal carbonyl will tend to leave a positive charge distributed over the ring system. This will tend to deshield the protons of the rings.

An explanation of the shielding of 5 - H and the thioformyl proton can be arrived at by assuming that the double-bond character of the thiocarbonyl group has decreased on complexing. The anisotropic shielding of 5 - H and the thioformyl proton by the thiocarbonyl group has thus been decreased, resulting in an upfield shift.

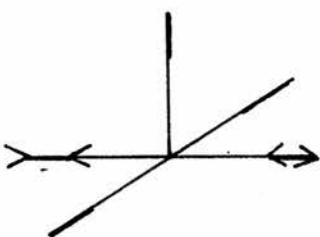
Further studies were performed on the molybdenum hexacarbonyl and 2,6 - dimethyl - 3 - thioformylindolizine complex. Studies<sup>110</sup> have shown the sulphur atom of the thioformyl group to be adjacent to 5 - H. It was thought that complex formation might alter the thioformyl group in such a manner as to cause a trans effect between 1 - H and the thioformyl proton. Spin-decoupling on the 100 Hz scale, however, gave no indication of a trans effect.

(c) Thioformylpyrrolo - [2,1-b] - thiazole Complexes (Table 3,3A)

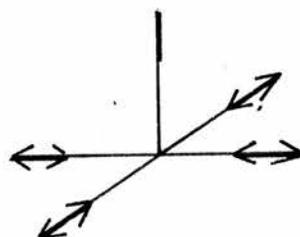
The changes in the <sup>1</sup>H n.m.r. spectra of the thioformylpyrrolo - [2,1-b] - thiazole complexes are similar to the changes exhibited by the thioformylindolizines. All protons show deshielding due to complex formation, with the exception of H - 3 and the thioformyl proton, whose signals have moved upfield. Because of the similarity



A<sub>1</sub>

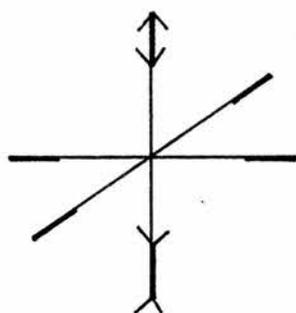


E



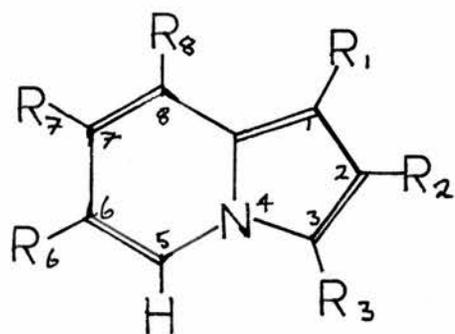
A

(12)



T<sub>1u</sub>

(13)



(14)

R<sub>1</sub> R<sub>2</sub> R<sub>3</sub> R<sub>6</sub> R<sub>7</sub> R<sub>8</sub>

a	H	Me	H	H	H	H
b	Me	Me	H	H	H	H
c	H	Me	Me	H	H	H
d	H	Me	H	Me	H	H
e	H	Me	H	H	Me	H
f	H	Me	H	H	H	Me

between the thioformylpyrrolothiazole complexes and the thioformyl-lindolizine complexes similar arguments hold.

(2) Infra Red Spectra (Table 5)

For a ligand L, coordinated to a metal hexacarbonyl  $M(CO)_6$ , to give a complex  $ML(CO)_5$ , the following spectrum would be expected. According to group theory, the symmetry is  $C_{4v}$ , and formal symmetry rules state that the vibration may be classified as two  $A_1$  transitions, one E transition and a forbidden  $B_1$  transition (12). The E vibration corresponds closely to the  $T_{1u}$  vibration (13) of the parent hexacarbonyl and should account for roughly four fifths of the total intensity of absorption. The  $A_1$  vibration relating to the stretching of the unique carbonyl is strongly allowed, and is coupled to the almost forbidden other  $A_1$  transition, to account for the remaining fifth.

The position of the stronger  $A_1$  band cannot be predicted, but the weak  $A_1$  band should be approximately  $120\text{ cm.}^{-1}$  higher than the E band. Except for 4H - thiopyran - 4 - thione and 2,6 - dimethyl - 4H - pyran - 4 - thione, all the thiocarbonyl ligands are asymmetric, and hence the complex will have a lack of axial symmetry. This should lead to small and possibly resolvable splitting of the intense E transition, and to the appearance of the B transition with low intensity<sup>84</sup>. These theoretical conclusions are in close agreement with the observed spectra of the thiocarbonyl complexes, and assignments have been

tentatively based on them.

Because of the lack of infra red data on the pyran - and thiopyranthiones, no conclusions have been reached on the exact position of the C=S stretching frequencies.

### (3) Ultra Violet Spectra (Table 6)

The u.v. spectra of the pyran - and thiopyranthione metal pentacarbonyls show two band groups of intense absorption. In the visible region, there is an absorption (c. 497 - 580 n.m.) corresponding to the observed deep purple colour of the solutions. The stronger absorption comprising two or more absorption maxima or shoulders occurred in the region 214 - 354 n.m.

Thioformylindolizine metal pentacarbonyls gave similar spectra, the two major band groups appearing within the same limits. In addition, a series of less intense absorption maxima were found in the region 310 - 455 n.m.

Thioformylpyrrolothiazole metal pentacarbonyls, differ in their u.v. spectra from those of thioformylindolizines in two respects. Firstly the peaks appear to be broadened, and secondly fewer peaks were found in the region 310 - 415 n.m.

In all cases, the cyclohexane solutions were kept for seventeen hours, and a new spectrum was obtained. These spectra gave some idea of the relative stability of the compounds in solution. In particular,

it was found that the chromium complex decomposed to a very large extent.

In comparison with the u.v. spectra of the parent compounds<sup>111,108</sup>, no direct correlations could be found.

#### (4) Mass Spectra (Table 7)

Molybdenum has seven stable isotopes the most common of which is  $^{42}\text{Mo}_{98}$  with a relative abundance of 23.78%. Molybdenum gives an outline in a mass spectrum, therefore, which is easily identifiable.

The mass spectra of the compounds 1a, 1b, 1c, and 2a were examined. No peaks were found at the calculated molecular weights of the compounds, however, Molecular ion peaks for the ligand (L) were usually identified. Successive loss of carbon monoxide was found in all cases.

#### Conclusions

Without the use of X-ray crystallography, the structure of these complexes cannot be stated with absolute certainty. However, certain possible structures can be eliminated by the available evidence.

Elementary analysis excludes all variations on the formula  $\text{L}_x \text{M} (\text{CO})_{6-x}^-$  (where L = thiocarbonyl ligand, and M = metal), except where  $x = 1$ ,

Sulphur analyses exclude carbene intermediates. Hence one is left with two possibilities. Firstly, the  $\sigma$ -complex  $\text{LM} (\text{CO})_5$ , and secondly, the  $\pi$ -complex  $\text{LM} (\text{CO})_3$ , which are virtually indistinguishable by elementary analysis.

The  $\sigma$  - complex is the most likely to be correct for various reasons. Firstly, there is the strong evidence of the apparent steric hindrance experienced by all 3,5 - disubstituted thiopyranthiones, and the lower yield obtained with 5 - substituted thiopyranthiones. This would suggest that it is the thiocarbonyl sulphur in the 4 - position that is forming a  $\sigma$  - complex. Secondly, there is the failure of other workers to form complexes with the corresponding ketones, again suggesting that the bonding is through the thiocarbonyl sulphur atom. Thirdly, there is the reasonably good agreement of the measured i.r. spectra with the calculated spectrum for a complex  $LM(CO)_5$ . Finally, the appearance in the mass spectrum of the thioaldehyde complexes of a peak corresponding to  $Mo COS$  would suggest once again that bonding is through sulphur.

TABLE (1)

<sup>1</sup>H n.m.r. spectra of Pyranthione and Thiopyranthione Metal Carbonyl Complexes in deuteriochloroform

Chemical Shifts in p.p.m., coupling constants in c. sec.<sup>-1</sup>  
d denotes a doublet m = multiplet b = broad.

<u>Compound</u>	<u>2-H</u>	<u>3-H</u>	<u>5-H</u>	<u>6-H</u>	<u>R2</u>	<u>R5</u>	<u>R6</u>
1a		7.20	7.20		2.37		2.37
1b	7.64d	8.15d	8.15d (J=10.4)	7.64d			
1c	7.61d	8.14d	8.14d (J=10.4)	7.61d			
1d		8.07m	8.07m	7.62d (J=9.8)	2.50d (J=0.8)		
1e		8.80		c.7.52	7.3-7.9m		
1f		8.40	8.13d (J=9.9)	c.7.68	7.4-7.7m		

TABLE 1A

<sup>1</sup>H n.m.r. spectra of Pyranthiones and Thiopyranthiones in deuteriochloroform

<u>Compound</u>	<u>2-H</u>	<u>3-H</u>	<u>5-H</u>	<u>6-H</u>	<u>R2</u>	<u>R5</u>	<u>R6</u>
16 <sup>106,107</sup>		6.94	6.94		2.22		2.22
21 <sup>106,107</sup>	7.58d	7.90d	7.90d (J=10.4)	7.58d			
25a <sup>48</sup>		7.80	7.81d	7.54d	2.37		
25B <sup>48</sup>		8.39		7.51	7.3-7.8m		
25c <sup>48</sup>		8.17	7.92 (J=9.8)	7.58	7.4-7.9m		

TABLE 2

Thioformylindolizine Metal Carbonyl Complexes in deuteriochloroform

<u>Compound</u>	<u>2-Me</u>	<u>Other Me</u>	<u>1-H</u>	<u>5-H</u>	<u>6-H</u>	<u>7-H</u>	<u>8-H</u>	<u>CHS</u>
2a	2.40	2.26		10.71d (J=6.5)	c.7.28m	c.7.62m	7.71m	9.70
2b	2.48b		6.53b	10.60d (J=7.0)	c.7.29	7.56m	7.62	9.82
2c	2.46d (J=0.8)	2.49 (J=1.1)	6.50b	10.47b		7.50d	7.50d	9.70
2d	2.43d (J=0.9)	2.50b	6.45b	10.51d (J=6.4)	7.01d		7.37b	9.72

TABLE 2A<sup>108</sup>Thioformylindolizines in deuteriochloroform

<u>Compound</u>	<u>2-Me</u>	<u>Other Me</u>	<u>1-H</u>	<u>5-H</u>	<u>6-H</u>	<u>7-H</u>	<u>8-H</u>	<u>CHS</u>
6	2.34	2.17		11.30d (J=6.8)	6.97m	c.7.42m	c.7.44m	10.40
7	2.45d (J=0.9)		6.39b	11.25d (J=6.8)	6.98m	c.7.41m	c.7.45	10.55
8	2.42d (J=0.8)	2.36d (J=5.10)	6.35b	11.17b		7.27d (J=8.7)	7.37d	10.46
9	2.41d (J=0.8)	2.38b	6.29b	11.15d (J=6.8)	6.81d		7.23b	10.38

TABLE 3

Thioformylpyrrolothiazole Metal Carbonyl Complexes in deuteriochloroform

<u>Compound</u>	<u>6-Me</u>	<u>Other Me</u>	<u>2-H</u>	<u>3-H</u>	<u>7-H</u>	<u>CHS</u>
3a	2.44		7.12d (J=4.3)	9.26d	6.50b	9.63b
3b	2.39	2.53d (J=1.3)		9.00b	6.40	9.53

TABLE 3A<sup>71</sup>Thioformylpyrrolothiazoles in deuteriochloroform

<u>Compound</u>	<u>6-Me</u>	<u>Other Me</u>	<u>2-H</u>	<u>3-H</u>	<u>7-H</u>	<u>CHS</u>
10	2.40		6.93d (J=4.0)	9.67d	6.33	10.37
11	2.36	2.43d (J=1.3)		9.38	6.24	10.28

TABLE 4

Differences in the Chemical Shift of the Organosulphur Compounds, and their Complexes ( $\Delta\delta$ )

Negative values represent deshielding, positive values represent shielding (p.p.m.)

<u>Compound</u>	<u>2-H</u>	<u>3-H</u>	<u>5-H</u>	<u>6-H</u>	<u>R2</u>	<u>R5</u>	<u>R6</u>
1a		-0.26	-0.26		-0.15		-0.15
1b	-0.06	-0.25	-0.25	-0.06			
1c	-0.03	-0.24	-0.24	-0.03			
1d		-0.27	-0.26	-0.08	-0.14		
1e		-0.41		-0.01			
1f		-0.23	-0.21	-0.10			

<u>Compound</u>	<u>2-Me</u>	<u>Other Me</u>	<u>1-H</u>	<u>5-H</u>	<u>6-H</u>	<u>7-H</u>	<u>8-H</u>	<u>CH3</u>
2a	-0.06	-0.09		+0.59	-0.31	-0.20	-0.27	+0.70
2b	-0.03		-0.114	+0.65	-0.31	-0.15	-0.17	+0.73
2c	-0.04	-0.13	-0.15	+0.70		-0.23	-0.13	+0.76
2d	-0.02	-0.12	-0.16	+0.64	-0.20		-0.14	+0.66

<u>Compound</u>	<u>6-Me</u>	<u>Other Me</u>	<u>2-H</u>	<u>3-H</u>	<u>7-H</u>	<u>CH3</u>
3a	-0.04		-0.19	+0.47	-0.17	+0.74
3b	-0.03	-0.10		+0.38	-0.16	+0.75

TABLE 5

Infra Red Spectra of Thiocarbonyl Complexes

All values in  $\text{cm}^{-1}$ . s = strong, m = medium, w = weak, sh = shoulder.

<u>Compound</u>	<u>Probable Transitions</u>			
	<u>A<sub>1</sub></u>	<u>B<sub>1</sub></u>	<u>E</u>	<u>A<sub>1</sub></u>
1a	2095 m	1980 m	1940 s 1925 s	1904 s
1b	2090 m	1983 m	1950 sh 1930 s	1900 s
1c	2090 m		1940 s 1920s	1900 s
1d	2098 m	1981 m	1930 s	1905 s
1e	2093 m	1995 m	1958 s	1914 s
1f	2090 m	1985 w sh	1950 sh 1928 s	1910 s
2a	2095 m	1977 m	1940 sh	1906 s
2b	2089 m	1978 m	1942 s 1921 s	1900 s
2c	2091 m	1987 m	1935 s	1899 s
2d	2091 m	1996 m	1942 s	1875 s
3a	2093 m	1985 m	1952 sh 1929 s	1880 s
3b	2094 m	1986 m	1950 s 1912 s	1882 s

TABLE 6Ultra Violet Spectra of Thiocarbonyl Complexes in Cyclohexane Solution

b = broad, sh = shoulder

<u>Compound</u>	<u>MAX (n.m.)</u>	<u>Log E</u>
1a	497 b	4.14
	312 b	4.20
	256	4.72
	236 sh	4.55
	221	4.60
1b	562 b	4.22
	344 b	4.29
	252	4.67
	221	4.61
1c	598 b	3.98
	349	4.23
	251	4.38
	214	4.37
1d	552 b	4.12
	344	4.22
	251	4.57
	223	4.54
1e	580 b	4.06
	354	4.13
	325	4.03
	255	4.68
	230	4.64
	216 sh	4.55
1f	580 b	4.10
	353	4.22
	254	4.62
	234 sh	4.50
	222	4.51
	215 sh	4.47

TABLE 6 (contd.)Ultra Violet Spectra of Thiocarbonyl Complexes in Cyclohexane Solution

b = broad, sh = shoulder

<u>Compound</u>	<u>MAX (n.m.)</u>	<u>Log E</u>
2a	574 b	4.34
	455	3.83
	429	3.79
	402 sh	3.74
	380	3.79
	326	4.09
	290 sh	4.08
	256	4.59
	234 sh	4.59
	224	4.66
2b	572 b	4.31
	441	3.68
	420	3.74
	398	3.76
	371	3.91
	352	3.87
	325	4.05
	314 sh	3.99
	274 sh	4.23
	254	4.60
	230	4.60
	222	4.61
2c	565 b	4.34
	443	3.76
	420	3.86
	397	3.92
	374	3.98
	329	4.10
	317 sh	4.01
	278 sh	4.19
	254	4.64
	234 sh	4.58
220	4.67	

TABLE 6 (contd.)Ultra Violet Spectra of Thiocarbonyl Complexes in Cyclohexane Solution

b = broad, sh = shoulder

<u>Compound</u>	<u>MAX (m.μ.)</u>	<u>Log E</u>
2a	564 b	4.38
	443	3.74
	417	3.81
	395	3.81
	371	3.96
	352 sh	3.87
	324	4.04
	260	4.64
	233	4.62
	221	4.67
3a	558 b	4.28
	426 sh	3.74
	388 b	4.02
	326 b	4.11
	290	3.93
	251	4.55
	232 b	4.60
3b	552 b	4.30
	428 sh	3.70
	386	3.99
	344 b	4.11
	253	4.57
225	4.61	

TABLE 7Mass Spectra of Thiocarbonyl Complexes

Where L = sulphur-containing ligand.

<u>Compound</u>	<u>Peak</u>	<u>Possible Assignment</u>
1a	126	Mo CO
	154	Mo (CO) <sub>2</sub>
	182	Mo (CO) <sub>3</sub>
	238	Mo L
1b	126	Mo CO
	154	Mo (CO) <sub>2</sub>
	182	Mo (CO) <sub>3</sub>
	210	Mo (CO) <sub>4</sub>
	238	Mo (CO) <sub>5</sub>
	128	L
1e	280	L
	406	L Mo CO
	434	L Mo (CO) <sub>2</sub>
	490	L Mo (CO) <sub>4</sub>
	238	Mo (CO) <sub>5</sub>
2a	157	L
	287	L Mo
	315	L Mo CO
	343	L Mo (CO) <sub>2</sub>
	158	Mo COS

PART 3

Experimental PartIntroductory Notes

Melting points were determined on a Kofler heating stage apparatus and were corrected.

Ultra violet and visible spectra were measured with a Unicam S.P. 800 instrument.

Infra red spectra were obtained with a Perkin - Elmer 237 instrument using a Nujol mull on sodium chloride plates.

$^2\text{H}$  n.m.r. spectra were carried out at c.  $34^\circ\text{C}$ . on a Perkin - Elmer R 10 spectrometer operating at 60 M Hz., at a sweep-rate of  $1.6 \text{ Hz. sec.}^{-1}$  and a sweep-width of 600 Hz. Solutions in deuteriochloroform were 0.4 M, except where this concentration was unobtainable, when saturated solutions were employed. 100 M Hz. spectra were measured at  $31.5^\circ\text{C}$ . with a Varian HA 100 spectrometer.

Mass spectra were obtained with an A.E.I. M.S. 902.

Microanalyses were carried out by Mr. James Bews, St. Andrews and Dr. A. Bernhardt, <sup>"</sup>Mulheim, Germany.

Column chromatography was carried out in all cases on activated alumina, Spence Type H 100/200 mesh, unless otherwise stated.

Thin layer chromatography was on silica (M.N. Kieselgel G.) coated plates. The plates were eluted with benzene and developed with iodine unless otherwise stated.

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

Acetonitrile, methylene chloride and chloroform were purified by refluxing over phosphorus pentoxide for 30 minutes, distilling, then redistilling.

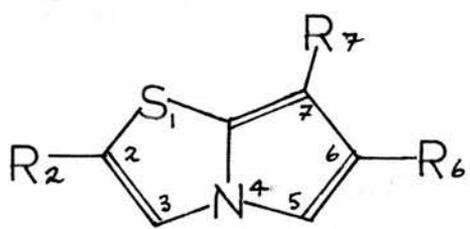
Benzene, cyclohexane, toluene xylene, light petroleum and diethyl ether were refluxed for 30 minutes of sodium wire and distilled. (Diethylether was partly pre-dried by standing over anhydrous calcium chloride for two days).

Acetic anhydride, acetic acid, methanol and ethanol were redistilled commercial materials.

Dimethylformamide was allowed to stand over calcium hydride for three days, and then distilled under reduced pressure.

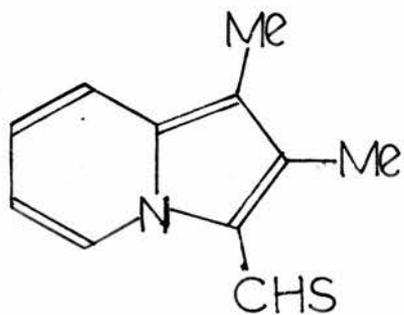
2M-aqueous sodium hydrogen sulphide solutions were obtained by saturating a 2 M-aqueous solution of sodium sulphide nonahydrate with hydrogen sulphide (2 hours).

Solutions were dried with anhydrous sodium sulphate unless otherwise stated.

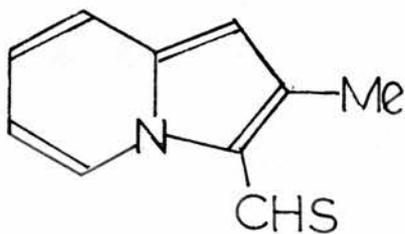


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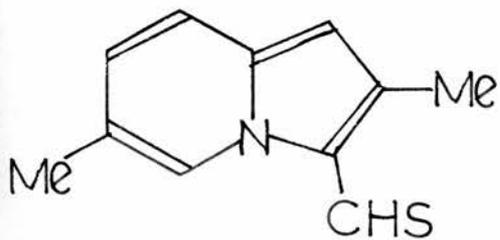
	<u>R<sub>2</sub></u>	<u>R<sub>6</sub></u>	<u>R<sub>7</sub></u>
a	H	Me	H
b	Me	Me	H
c	H	Me	Me



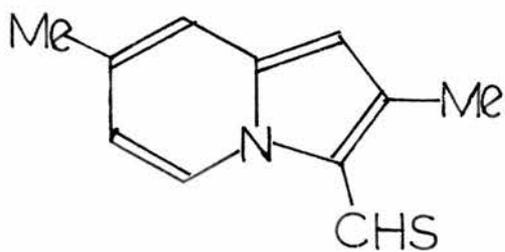
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(17)



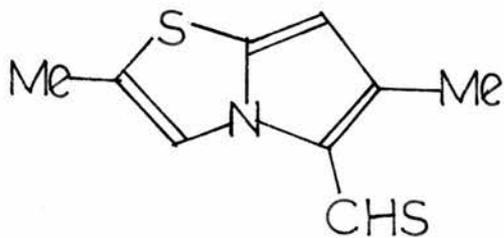
(18)



(19)



(20)



(21)

Preparation of Indolizines

2 - methyl - (14a)<sup>1</sup>; 1,2 - dimethyl - (14b)<sup>1</sup>; 2,3 - dimethyl - (14c)<sup>1</sup>; 2,6 - dimethyl - (14d)<sup>2</sup>; 2,7 - dimethyl - (14e)<sup>1</sup> and 2,8 - dimethylindolizine (14f)<sup>2</sup> were prepared as described in the references cited.

Preparation of Pyrrolo - [2,1-b] - thiazoles

6 - methyl - (15a); 2,6 - dimethyl - (15b) and 6,7 - dimethylpyrrolo - [2,1-b] - thiazole (15c) were prepared by the method of Molloy, Reid and Skelton<sup>2</sup>.

Preparation of Thioformylindolizines

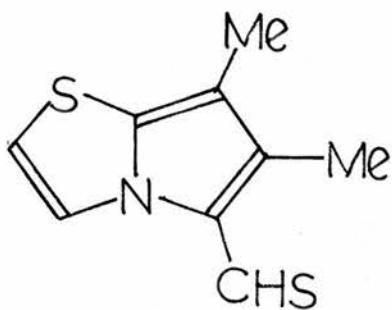
1,2 - dimethyl - (16); 2 - methyl - (17); 2,6 - dimethyl - (18) and 2,7 - dimethyl - 3 - thioformylindolizine (19) were prepared by the method of McKenzie and Reid<sup>26,108</sup>.

Preparation of Thioformylpyrrolo - [2,1-b] - thiazoles

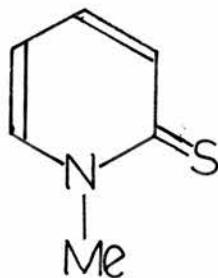
6 - methyl - (20); 2,6 - dimethyl - (21) and 6,7 - dimethyl - 5 - thioformylpyrrolo - [2,1-b] - thiazole were prepared by the method of McKenzie and Reid<sup>26</sup>.

Preparation of 2,3 - Diphenylcyclopropenethione

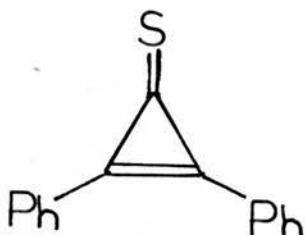
Phosphorus oxychloride (1.1 ml., 12 m. moles) was added to a solution of 2,3 - diphenylcyclopropenone (2.06 gm., 10 m. moles) in dimethylformamide (50 ml.) and the mixture was allowed to stand at room temperature for 40 minutes. 2M - Aqueous sodium thiosulphate



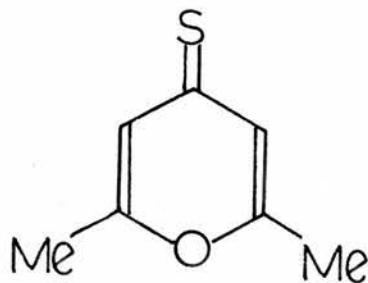
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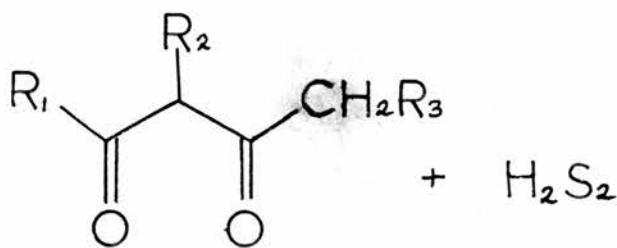
(23)



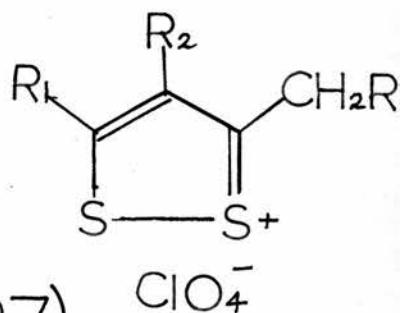
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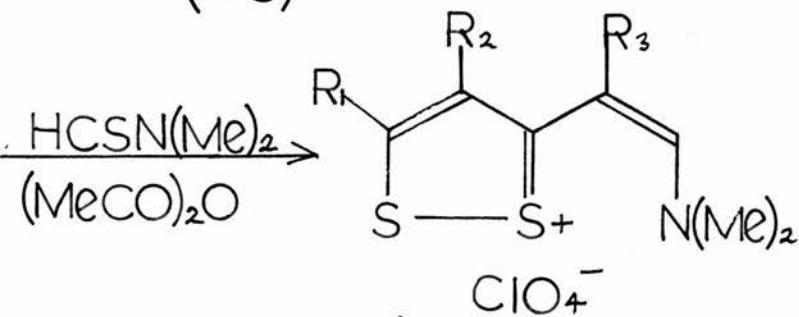
(25)



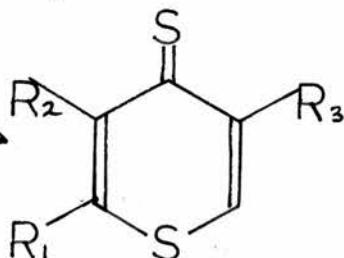
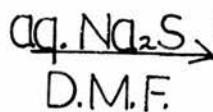
(26)



(27)



(28)



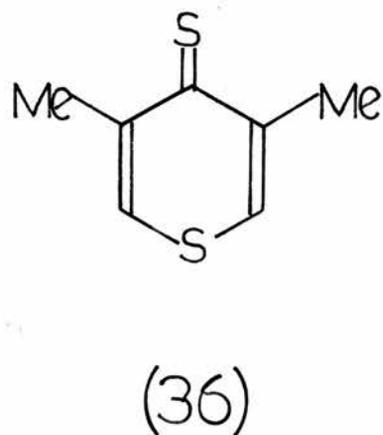
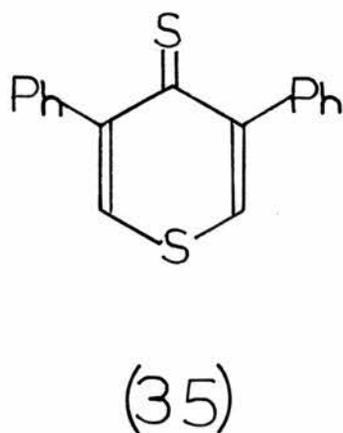
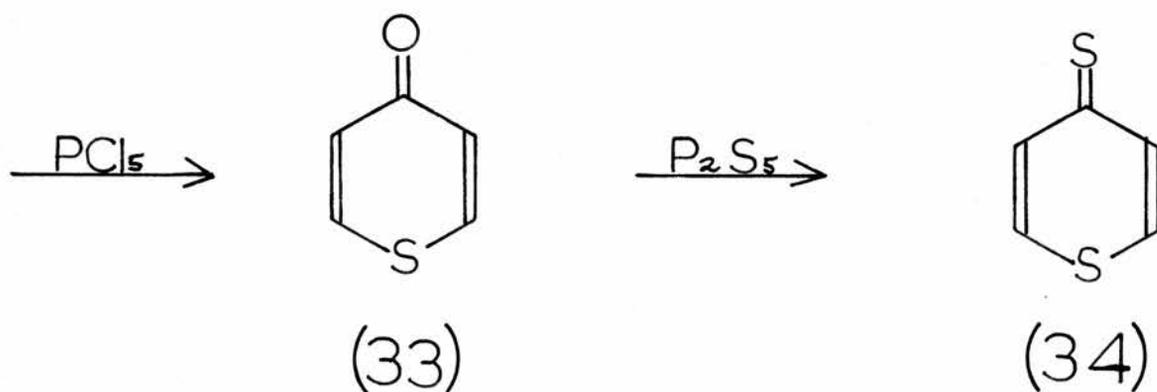
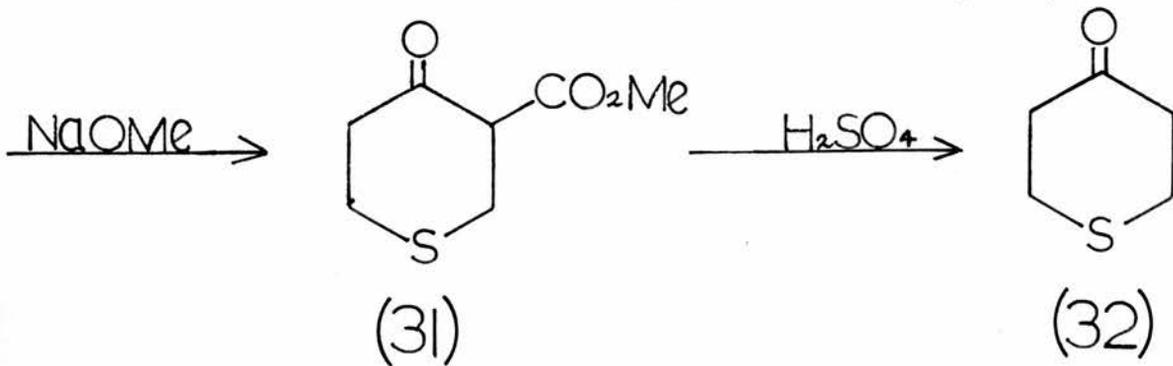
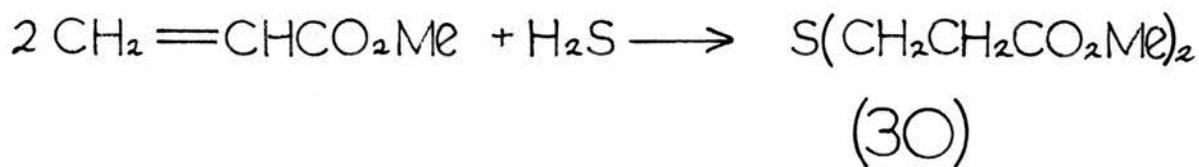
(29)

(10 ml.) was added, and the mixture was diluted with water and extracted with benzene (3 × 100 ml.). The extracts were washed with water, dried and evaporated. The dark yellow solid was chromatographed on a column of alumina (21 × 2.6 cm.) using benzene as elvant. Evaporation gave 2,3 - diphenylcyclopropenethione (24) which recrystallised from cyclohexane as yellow needles (0.59 gm., 25%), m.p. 117 - 118°C.

Preparation of 4H - Pyran - and 4H - Thiopyran - 4 - thiones

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

The preparation is an adaptation of that of Hantzsch<sup>5</sup>. A mixture of 2,6 - dimethyl - 4H - pyran - 4 - one (0.62 gm., 5 m. moles) and phosphorus pentasulphide (1.12 gm., 5.05 m. moles) in benzene (100 ml.) was boiled for two hours. The purple solution was decanted, and iced water was added to the solid residue. The residue was extracted with benzene (4 × 100 ml.) and the combined benzene solutions were washed with water, dried and evaporated. The residual solid was chromatographed on a column of alumina using benzene as eluant. Evaporation gave 2,6 - dimethyl - 4H - pyran - 4 - thione (25) which recrystallised from methanol as yellow needles (0.52 gm., 74%) m.p. 144 - 145°C.



4H - Thiopyran - 4 - thione(a) Methyl  $\beta$  - thiodipropionate<sup>6</sup>

Hydrogen sulphide was passed into a mixture of methyl acrylate (240 gm., 2.79 moles) and Triton B (2 ml., approximately 4.7 m. moles of 40% w./w. solution in water) with stirring. The temperature of the mixture rose to 70°C. and was maintained at this temperature by cooling. When absorption was complete the mixture was taken up in benzene (400 ml.), and the resulting solution was washed with dilute hydrochloric acid and water, and dried. The benzene was evaporated and the residual liquid was distilled. Methyl  $\beta$  - thiodipropionate (30) was obtained as a colourless oil (471 gm., 83%) b.p. 162°C./18 mm.

(b) 3 - Carbomethoxytetrahydro - 4H - thiopyran - 4 - one<sup>8</sup>

Methyl  $\beta$  - thiodipropionate (250 gm., 1.22 moles) was added slowly to a suspension of sodium methoxide (131.8 gm., 2.44 moles) in anhydrous ether (1.2 l.) The mixture was stirred and refluxed for three hours, allowed to cool, and poured into an ice-cold mixture of glacial acetic acid (154 ml.) in water (800 ml.). After shaking, the layers were separated, and the aqueous layer was extracted with small amounts of ether. The ether extracts were combined, washed with sodium bicarbonate solution, dried, and evaporated. The resulting oil was distilled to give 3 -

carbomethoxytetrahydro - 4H - thiopyran - 4 - one (31) (120.2 gm., 57%) b.p. 138 - 146°C./22 mm.

The method of Kutz and Weininger<sup>29</sup> was also tried. This involved the use of sodium hydride instead of sodium methoxide in a similar procedure. Low yields were obtained (c.30%).

(c) Tetrahydro - 4H - thiopyran - 4 - one<sup>9</sup>

3 - Carbomethoxytetrahydro - 4H - thiopyran - 4 - one (225 gm., 1.3 moles) and 10% sulphuric acid (2.04 l.) were boiled for two hours. The mixture was allowed to cool and extracted with ether. The ether extracts were washed with water, dried, and evaporated. Tetrahydro - 4H - thiopyran - 4 - one was recrystallised from light petroleum as white needles (141 gm., 94%).

(d) 4H - Thiopyran - 4 - one

A method derived from three groups of workers was used<sup>10,11,12</sup>. A mixture of tetrahydro - 4H - thiopyran - 4 - one (5.06 gm., 44 m. moles) and phosphorus pentachloride (27.4 gm., 132 m. moles) in benzene (20 ml.) was boiled for c. 15 minutes and filtered. The solid residue was dissolved in ice-water and the mixture was extracted with chloroform, dried, and evaporated. Sublimation at reduced pressure and recrystallisation from light petroleum gave 4H - thiopyran - 4 - one as white needles (1.68 gm., 35%).

(e) 4H - Thiopyran - 4 - thione

A method derived from two sets of workers was used<sup>11,12</sup>. A mixture of 4H - thiopyran - 4 - one (2gm., 17.9 m. moles) and phosphorus pentasulphide (5 gm., 22.8 m. moles) in benzene (100 ml.) was boiled for 2½ hours. The red solution was decanted and the residue dissolved in benzene (50 ml.) and a small amount of ammonium sulphide solution. The layers were separated, and the aqueous layer extracted with benzene. The combined benzene solutions were washed with water, dried, and evaporated. The residual dark-red oil was chromatographed on a column of alumina using benzene as eluant. Evaporation gave 4H - thione which formed from a minimum volume of acetone by the slow additions of an excess of light petroleum, as dark-red plates (1.60 gm., 70%).

Preparation of 2 - Methyl - , 2,5 - Diphenyl - and 2 - Phenyl - 4H - thiopyran - 4 - thione

The method used was that of Dingwall, McKenzie and Reid<sup>47,48</sup>. Hydrogen disulphide (9 ml., 180 m. moles) was added to a solution of the diketone (131 m. moles) (26), and perchloric acid (16.5 ml., 196 m. moles) in acetic acid (300 ml.). The solution was warmed at 65°C. for five minutes and the perchlorate (27) was precipitated by the addition of excess ether,

A solution of the perchlorate (20 m. moles) and dimethylthioformamide (8.4 ml., 100 m. moles) in acetic anhydride (80 ml.) was

boiled for five minutes, and cooled. Excess ether was added to the solution to precipitate the Vilsmeier salt (28).

2M - aqueous sodium sulphide solution (100 ml.) was added to a solution of the perchlorate (20 m. moles) in dimethylformamide (400 ml.), and the mixture was warmed at 60°C. for five minutes, poured into water and extracted with benzene. The benzene extracts were washed with water, dried, and evaporated. The resulting brown solid was chromatographed on a column of alumina, using benzene as eluant. Evaporation gave the thiopyranthione (29) which recrystallised from cyclohexane as reddish-brown plates.

2 - Methyl - 4H - thiopyran - 4 - thione, 2,5 - diphenyl - 4H - thiopyran - 4 - thione and 2 - phenyl - 4H - thiopyran - 4 - thione were prepared by this method.

#### Preparation of Transition Metal Carbonyl - Organosulphur Complexes

A solution of the thiocarbonyl compound (5m. moles) and the transition metal hexacarbonyl (6.25 m. moles) in toluene (30 ml.) (unless otherwise stated), was boiled for 10 minutes. The cooled solution was chromatographed on a column of alumina (60 x 2.7 cm.) using benzene - light petroleum mixture (1:1) for elution.

The initial eluates containing unreacted metal carbonyl were discarded. The succeeding purple fractions were collected and evaporated. The resultant solid was rechromatographed on a column

(30 × 2.6 cm.) using benzene as eluant, in order to remove traces of thiocarbonyl compound. Recrystallisation was from cyclohexane unless otherwise stated.

The following complexes were obtained:-

2,6 - dimethyl - 4H - pyran - 4 - thione molybdenum (VI) pentacarbonyl (1a) (60%), decomposition point 124°C. Formed from a minimum volume of acetone by the addition of light petroleum. (Found : C, 38.5; H, 2.2; S, 8.6%  $C_{12}H_8S_2O_6$  Mo requires C, 38.3; H, 2.1; S, 8.6%); 4H - thiopyran - 4 - thione molybdenum (VI) pentacarbonyl (1b) (67%), d.p. 114°C., (Found C, 33.2; H, 1.1%.  $C_{10}H_4S_2O_5$  Mo requires C, 33.0; H, 1.1%); 4H - thiopyran - 4 - thione chromium (VI) pentacarbonyl (1c) (18%), d.p. 125°C. Xylene as solvent. (Found: C, 37.7; H, 1.2%.  $C_{10}H_4S_2O_5$  Cr requires C, 37.5; H, 1.3%); 2 - methyl - 4H - thiopyran - 4 - thione molybdenum (VI) pentacarbonyl (1d) (66%). d.p. 117°C., (Found: C, 35.2 ; H, 1.7%.  $C_{11}H_6S_2O_5$  Mo requires C, 34.9; H, 1.6%); 2,5 - diphenyl - 4H - thiopyran - 4 - thione molybdenum (VI) pentacarbonyl (1e) (25%), d.p. 158°C., (Found : C, 51.7; H, 2.4%.  $C_{22}H_{12}S_2O_5$  Mo requires C, 51.2; H, 2.3%); 2 - phenyl - 4H - thiopyran - 4 - thione molybdenum (VI) pentacarbonyl (1f) (62%), d.p. 117°C., (Found: C, 44.0; H, 1.7%.  $C_{16}H_8S_2O_5$  Mo requires C, 43.6; H, 1.8%); 1,2 dimethyl - 3 - thioformylindolizine

molybdenum (VI) pentacarbonyl (2a) (58%), d.p. 170°C., (Found; C, 45.3; H, 2.8; N, 3.3%.  $C_{16}H_{11}NSO_5$  Mo requires C, 45.2; H, 2.6; N, 3.3%); 2 - methyl - 3 - thioformylindolizine molybdenum (VI) pentacarbonyl (2b) (47%), d.p. 130°C. Xylene as solvent. (Found; C, 43.4; H, 2.5; N, 3.8%.  $C_{15}H_9NSO_5$  Mo requires C, 43.8; H, 2.2; N, 3.4%); 2,6 - dimethyl - 3 - thioformylindolizine molybdenum (VI) pentacarbonyl (2c) (48%), d.p. 14.2°C., (Found; C, 45.5; H, 2.8; N, 3.3%.  $C_{16}H_{11}NSO_5$  Mo requires C, 45.2; H, 2.6; N, 3.3%); 2,7 - dimethyl - 3 - thioformylindolizine molybdenum (VI) pentacarbonyl (2d) (37%), d.p. 146°C., (Found; C, 45.5; H, 2.6; N, 3.4%.  $C_{16}H_{11}NSO_5$  Mo requires C, 45.2; H, 2.6; N, 3.3%); 6 - methyl - 5 - thioformylpyrrolo - [2,1-b] - thiazole molybdenum (VI) pentacarbonyl (3a) (28%), d.p. 126°C., (Found; C, 37.8; H, 1.6; N, 3.3%.  $C_{13}H_7NS_2O_5$  Mo requires C, 37.4; H, 1.7; N, 3.4%); 2,6 - dimethyl - 5 - thioformylpyrrolo - [2,1-b] - thiazole molybdenum (VI) pentacarbonyl (3b) (34%), d.p. 130°C., (Found; C, 38.8; H, 2.2; N, 3.1; S, 15.5%.  $C_{13}H_9NS_2O_5$  Mo requires C, 39.0; H, 2.1; N, 3.3; S, 14.9%).

#### Other Complexes

Attempts were made, without success, to form complexes from molybdenum hexacarbonyl and:- 3,5 - diphenyl - 4H - thiopyran - 4 - thione (35), 3,5 - dimethyl - 4H - thiopyran - 4 - thione (36),

2,3 - diphenylcyclopropenethione (24), N,N - dimethylthioformamide, N - methylpyrid - 2 - thione (23).

Chromium hexacarbonyl also reacted with those thiocarbonyl compounds with which molybdenum hexacarbonyl reacted, but gave very low yields.

Attempts were made without success to prepare complexes from dicobalt octacarbonyl, iron pentacarbonyl and diiron nonacarbonyl.

Attempted Preparation of 1,2 - Dimethylindolizine - 3 - thial - S - oxide

In this and succeeding experiments involving sulphines, reaction vessels and chromatography columns were shielded from light with aluminium foil. Reactions were carried out under nitrogen. Monoperphthalic acid was prepared by the method of Bohae<sup>74</sup>.

A solution of monoperphthalic acid (2.5 m. moles in 18 ml. of ether) was added over 5 minutes to a stirred solution of 1,2 - dimethylindolizine (0.945 gm., 5 m. moles) in chloroform (100 ml.) at - 70°C. The solution was stirred for a further 30 minutes at - 70°C., and the precipitated phthalic acid was removed by filtration. The filtrate was concentrated to c. 5 ml., and transferred to a column of silica. Elution with benzene gave starting material.

Attempted Preparation of 1,2 - Dimethylindolizine - 3 - thioacetyl - S - oxide

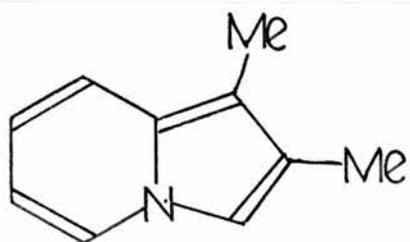
A solution of monoperphthalic acid (2.5 m. moles in 18 ml. of ether) was added over 5 minutes to a stirred solution of 1,2 - dimethyl - 3 - thioacetylindolizine in chloroform (100 ml.) at - 70°C. The solution was stirred for a further thirty minutes at - 70°C., and the precipitated phthalic acid was removed by filtration. The filtrate was concentrated to c. 5 ml., and transferred to a column of silica (25 x 2.6 cm.). Elution with benzene gave starting material.

Attempted Preparation of 6,7 - Dimethylpyrrolo - [2,1-b] - thiazole - 3 - thial - S - oxide

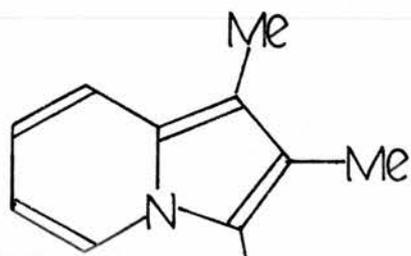
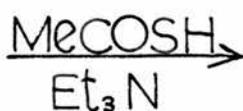
A solution of monoperphthalic acid (1.5 m. moles in 10.8 ml. of ether) was added over five minutes to a stirred solution of 6,7 - dimethyl - 5 - thioformylpyrrolo - [2,1-b] - thiazole in chloroform (80 ml.) at - 70°C. The solution was stirred for a further 30 minutes at - 70°C., and the precipitated phthalic acid was removed by filtration. The filtrate was concentrated to c. 5 ml., and transferred to a column of silica. Elution with benzene gave starting material only.

Preparation of Methylthioketones

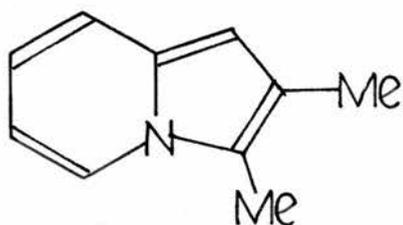
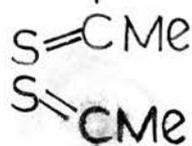
A solution of the heterocyclic base (indolizine or pyrrolothiazole) (10 m. moles) in thioacetic acid (56 ml., 60.8 gm.,



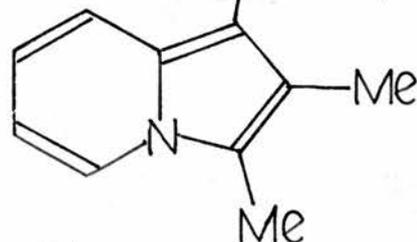
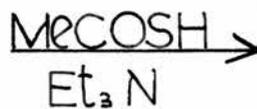
(37)



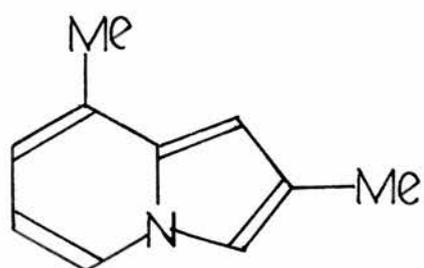
(38)



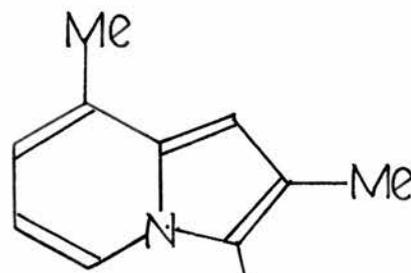
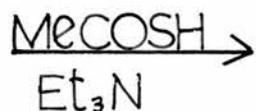
(39)



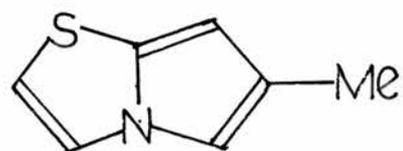
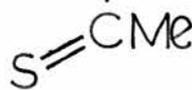
(40)



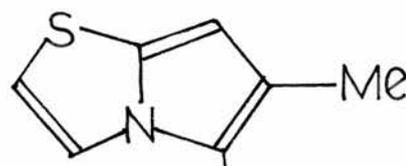
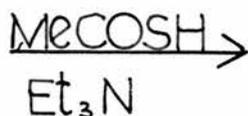
(41)



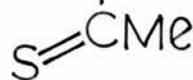
(42)



(43)



(44)



0.8 moles) and triethylamine (11.2 ml., 8.08 gm., 80 m. moles) was boiled for one minute. The mixture was diluted with ice and cold water (1 l.), and an excess of solid sodium bicarbonate was added. The crude methylthioacetone was extracted with benzene (5 × 100 ml.) and the combined extracts were washed successively with water, sodium bicarbonate solution and water. Evaporation of the dried solution yielded an orange solid which was chromatographed on a column of alumina (60 × 2.7 cm.) using light petroleum as eluant. The initial eluates (500 ml.) brought through a foul-smelling impurity, and the eluant was gradually changed to light petroleum - benzene (1;1). Unreacted heterocyclic base and a trace of thioacetic acid were removed by this solvent mixture (600 ml.) and the methylthioacetone was subsequently eluted with benzene as a red solution. Evaporation and recrystallisation from cyclohexane gave red needles of methylthioacetone. The mother liquors were rechromatographed on a short column of alumina using benzene as eluant. Evaporation and recrystallisation from cyclohexane gave methylthioacetone.

The following methylthioacetones were obtained:-

- 1,2 - dimethylindolizine (37) (1.45 gm., 10 m. moles) gave  
 1,2 - dimethyl - 3 - thioacetylindolizine (38) (1.51 gm., 74%),  
 m.p. 151 - 153°C.; 2,3 - dimethylindolizine (39) (1.45 gm., 10 m. moles)

gave 2,3 - dimethyl - 1 - thioacetylmindolizine (40) (1.06 gm., 52%), m.p. 163 - 165°C.; 2,8 - dimethylindolizine (41) (1.45 gm., 10 m. moles) gave 2,8 - dimethyl - 3 - thioacetylmindolizine (42) 1.55 gm., 76%)1, m.p. 113 - 115°C.; 6 - methylpyrrolo - [2,1-b] - thiazole (43) (1.37 gm., 10 m. moles) gave 6 - methyl - 5 - thioacetylpyrrolo - [2,1-b] - thiazole (44) (1.57 gm., 81%), m.p. 117 - 119°C.

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