Investigations of 3-Thiocyldihydropyrimidine-1,2-dithioles and Syntheses of Related Compounds.

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TO MY PARENTS
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ABSTRACT

The cyclo-addition reaction between 1,2-dithiole-3-thiones and arylacetylenes has been investigated. Three different mechanisms for the cycloaddition have been considered:

i) 1,2-Addition to the exocyclic C=S bond, followed by opening of the resulting four-membered ring, to give a 3-thioacetylthiophene-1,2-dithiole (known by the generic name 6a-thiathiophen).

ii) 1,3-Addition leading to the formation of a 2-thioacylmethylene-1,3-dithiole from which 6a-thiathiophens could be formed by rearrangement.

iii) Initial reaction between arylacetylenes and sulphur followed by addition of the resulting 1,3-dipole to the exocyclic C=S bond.

The rearrangement of 2-thioacetylmethylene-1,3-dithioles to 6a-thiathiophens has been investigated and shown to be catalysed by sulphur. A mechanism has been proposed for this rearrangement and various tests applied in order to verify this mechanism.

The products of decarboxylation of various 2-thioacetylmethylene-1,3-dithiole-4-carboxylic acids have been investigated and correlated with the rearrangement mechanism.

Cyclic polysulphides containing an anthracene nucleus have been synthesised and characterised; chloroanthraquinones were used as the starting materials.

Various routes to a naphtho bis(1,2-dithiole) have been investigated but the synthesis has not been achieved.

Further investigations have been carried out into the synthesis of 4-thioxacyl-1,2-dithiole-3-thiones, representatives of which were studied in this department. The object of the present work was to incorporate the 4-thioxacyl group into a 4,5-fused ring but none of the approaches investigated led to a successful synthesis of such a compound.
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(1,8-od:5,4-b'c')bis(dithiole).

N.m.r. Spectra

References
INTRODUCTION
PART A Dithioles and dithiolethiones

Although this thesis is mainly concerned with more complex dithiole systems it is appropriate to mention the simple dithiole ring systems and the dithiolethiones to which many of the compounds dealt with later have a vinylogous relationship.

Two isomeric, aromatic, five-membered dithiole ring systems may be formulated; the 1,2-(I) and 1,3-dithiolylium (II) cations, of which the following canonical forms may be drawn:

```
(Ia)  
\[ \begin{array}{c}
S-S^- \hline \\
\text{(Ib)} \end{array} \]

(S-S^+) 

(IIa)  
\[ \begin{array}{c}
S-S^- \hline \\
\text{(IIb)} \end{array} \]

(S-S^+) 

(S-S^-) 

(Ic)  
\[ \begin{array}{c}
S-S^- \hline \\
\text{(Id)} \end{array} \]

(S-S^+) 

(S-S^-) 

(S-S^-) 

(IIc)  
\[ \begin{array}{c}
S-S^- \hline \\
\text{(Iib)} \end{array} \]

(S-S^+) 

(S-S^-) 

(S-S^-) 

(Iod)  
\[ \begin{array}{c}
S-S^- \hline \\
\text{(Ife)} \end{array} \]

(S-S^+) 

(S-S^-) 

(S-S^-) 

(Ig)  
\[ \begin{array}{c}
S-S^- \hline \\
\text{(Ig)} \end{array} \]

(S-S^+) 

(S-S^-)
```

Sulphur can utilise its 3d orbitals in bonding and hence expand its outer shell to hold more than eight electrons, so extra canonical structures should also be considered, where either or both of the hetero atoms accommodates ten electrons in its outer shell.
By invoking the concept of isosterism these dithiole ring systems may be considered as having been derived from a seven membered ring system, the tropylium ion, by two successive replacements of $\text{CH}=\text{CH}$ by $\text{-S-}$.

\[
\begin{array}{cccc}
\text{S} & \text{S} & \text{S} & \text{S} \\
\oplus & \oplus & \oplus & \oplus \\
\text{(IId)} & \text{(IIe)} & \text{(IIf)} & \text{(IIg)} \\
\end{array}
\]

The canonical structures involving 3d orbitals in bonding are similarly isosteric if the replacements are looked upon as a substitution of $=\text{S}= \text{for } =\text{CH}=\text{CH}=$.

On the basis of the canonical forms shown previously, nucleophilic rather than electrophilic attack would be expected on the dithiolylium nucleus; in the 3-position of the 1,2-dithiolylium cation and in the 2-position of the 1,3-dithiolylium cation. Simple M.O/L.C.A.O. calculations point to a similar conclusion and these also show that free radical attack would be expected at the same positions. The 4-position, being the least
electropositive of both rings, would be where the highly improbable electrophilic attack would take place, if at all.

Further electron-donating substituents on the ring would be expected to stabilise the system since, on the basis of the resonance theory, this would lead to an increase in the number of structures contributing to the resonance hybrid, whereas electron-attracting substituents would be expected to decrease the stability of the ring.

1,2-Dithiole-3-thiones (III) and 1,3-dithiole-2-thiones (IV) are the thiones derived from these parent nuclei. These may be regarded as potentially aromatic in character since they may give rise to charge-separated structures through polarization of the thiocarbonyl group.

As with the dithiolylium salts, by invoking d-orbital resonance, further structures for these dithiole-thiones may be considered and their participation is suggested by measurements of the C-S bond lengths in a dithiolethione². If no resonance stabilization occurred in these compounds, (III) would tend to react as an $\alpha,\beta$-unsaturated thione while (IV)
would show olefinic activity.

With alkyl esters of inorganic acids, those dithiolethiones give rise to salts which may be regarded as alkylthiodithiolylium salts (V),(VI), the cations having the following contributing structures

\[
\text{(Va)} \quad \longleftrightarrow \quad \text{(Vb)}
\]

\[
\text{(VIa)} \quad \longleftrightarrow \quad \text{(VIb)}
\]

Again by invoking the concept of isostorism the dithiolethiones may be regarded as being derived from thiotropone.
Many methods are known for the preparation of 1,2-dithiolole-3-thiones and these were reviewed in 1965.5

Two important methods used in the present work are exemplified below:

i) from ketone onolates by treatment with carbon disulphide followed by phosphorus pentasulphide

\[
\text{e.g. } \text{3,3-Dimercapto-1-phenylprop-2-on-l-one (VII) is obtained by the reaction of acetophenone and carbon disulphide in sodium t-butoxido solution. The dimercaptan is readily converted to 5-phenyl-1,2-dithiolole-3-thione (VIII) by reaction with phosphorus pentasulphide.}^6
\]

\[
\text{(VII)} \quad \text{(VIII)}
\]

ii) from olefins by reaction with sulphur

\[
\text{e.g. Treatment of } 3,3^\text{-dimethylstyrone (IX)} \text{ with sulphur in boiling dimethylformamide gives } 4\text{-methyl-5-phenyl-1,2-dithiolole-3-thione (X).}
\]

\[
\text{Ph} \quad \text{Me} \quad \overset{65}{\rightarrow} \quad \text{Ph} \quad \text{Me}
\]

\[
\text{(IX)} \quad \text{(X)}
\]

Cyclo-addition Reactions of Dithiolothiones

Huisgen classifies cyclo-addition reactions according to the number of new \( \sigma \)-bonds formed or according to the size of the ring which is formed.
The most frequent case is where two reactants unite to form the cyclic compound, creating two new π-bonds at the expense of two σ-bonds.

Acyclo-addition reaction of the type 3+2 \( \rightarrow \) 5 leading to an uncharged five-membered ring cannot occur with octet-stabilized reactants which have no formal charges. Rather, a 1,3-dipole, \( a-b-c \), must be defined such that atom 'a' possesses an electron sextet, i.e. an incomplete valence shell combined with a positive formal charge and that atom 'c', the negatively charged centre, has an unshared electron pair. Combination of such a 1,3-dipole with a multiple bond system \( d-c \), termed the dipolarophile, is referred to as 1,3-dipolar cyclo-addition. The two components coalesce by means of a cyclic electron displacement with extinction of the formal charges to give a five-membered ring. The dipolarophile may be any double or triple bond.

Compounds containing an electron sextet at a carbon, nitrogen or oxygen atom are not stable. The foregoing designation would therefore acquire the physical significance of a mere resonance contributor if the 1,3-dipole were capable of isolation. Stabilization is possible if an unshared pair of electrons at atom 'b' can relieve the electron deficiency at centre 'a' by formation of an additional bond. In the new mesomeric formula in which 'b' now has the positive charge, all the centres have completely filled valence shells. Such systems are designated as 1,3-dipoles with internal octet stabilization.
1,2-Dithiole-3-thiones do not fall into any of the categories of 1,3-dipoles defined by Huisgen but are nevertheless capable of reacting with acetylenic dipolarophiles via \( (3+2) \) cyclo-addition reactions. During these reactions the original disulphide bond is cleaved and the dithiolethiones may be considered to act, in a formal sense, as 1,3-dipoles. (XI)

\[
\begin{align*}
+ & \quad \text{S} & \quad \text{S} & \quad \text{R} \\
- \quad \text{S} & \quad \text{S} & \quad \text{R} \\
\end{align*}
\]

(XI)

Reaction of 1,2-dithiole-3-thiones with Acetylenic Compounds

c) Arylacetylenes

Buchberger reported the production of 2-thioacetylactylene-1,3-dithiols (XII) and in a later paper described the conditions when toluene \( (R_1=\text{Ph}, R_2=\text{PhCO}, R_3=R_4 = -(\text{CH}_2)_3^-) \), dioxaen \( (R_1=\text{NO}_2, R_2=R_3=\text{H}, R_4=\text{Ph}) \) or xylene \( (R_1=R_4=\text{Ph}, R_2=R_3=\text{H}) \) were variously used as solvents. A mechanism involving 1,3-cyclo-addition was proposed.

\[
\begin{align*}
R_1 & \quad \text{S} & \quad \text{S} & \quad R_4 \\
R_2 & \quad \text{S} & \quad \text{S} & \quad R_4 \\
R_3 & \quad \text{S} & \quad \text{S} & \quad R_4 \\
\end{align*}
\]

(XII)
In two cases, those being the reaction of diphenylacetylene \((R_1=R_2=\text{Ph})\) with 5-phenyl-1,2-dithiolo-3-thione in dimethylformamide and the reaction of p-methoxyphenoxyacetylene \((R_1=p-\text{MeOC}_6\text{H}_4; R_2=\text{H})\) with the same thione in xylene, it was reported that 6α-thiathiophens (XIII) were obtained. It was proposed that these compounds were formed via the intermediate (XIV) formed by 1,2-addition of the acetylene across the C=S bond of the dithiolothione.

![Diagram](attachment:image.png)

(XIV)

\[
\begin{align*}
\text{a) } & R_1=R_2=\text{Ph} \\
\text{b) } & R_1=p-\text{MeOC}_6\text{H}_4; R_2=\text{H}
\end{align*}
\]

(XIII)

No explanation was offered for the apparently anomalous behaviour observed in these two reactions.

Viallo and his co-workers\[^{11,12}\] have also observed that different products are obtained when the reaction conditions are varied. They reported that when the reaction was carried out in dry xylene and the mixture heated under reflux for 15 hrs., then 6α-thiathiophens (XIII) were obtained whereas, if, before the reaction took place, hydrogen chloride was bubbled through the mixture and then the mixture was heated under reflux for 4 hrs., 1,3-addition took place to yield a 2-thiocyclohexene-1,3-
dithiole (XII). Again no explanation was proposed for this behaviour.

Those same workers also reported that if 2-thionocetylthiophene-1,3-dithiole (XII) are boiled under reflux in tetralin in the presence of phosphorus pentasulphide, rearrangement takes place to give the isomeric 6α-thiathiophthons (XIII). The rearrangement was also reported to not take place thermally, although the conditions used were not reported.

\[
\begin{array}{c}
\text{(XII)} \\
\text{(XIII)}
\end{array}
\]

a) \( R_1 = R_2 = Ph, R_3 = R_4 = H \)
b) \( R_1 = Ph, R_2 = R_3 = H, R_4 = p-XC_6H_4 \)
c) \( R_1 = p-XC_6H_4, R_2 = R_3 = H, R_4 = Ph \)

\( X = Br, Cl, OMe \)

No mechanism for the rearrangement was proposed.

Studies in this department\(^1\) showed that the rearrangement also takes place thermally at 200\(^\circ\)C, and that it is intramolecular (i.e. there is no dissociation to acetylene derivative and dithiolothione followed by 1,2-cyclo-addition).

Viallo\(^2\) had, like Behringer\(^3\), proposed that the 6α-thiathiophthons (XIII) were formed by 1,2-cyclo-addition, but in a recent report\(^4\) he stated that the 2-thionocetylthiophene-1,3-dithiole (XII) was always the first product of the cyclo-addition reaction and that the 6α-thiathiophthons (XIII) were formed subsequently with dithiolothione acting as catalyst for this rearrangement; no mechanism was proposed.
b) Dimethyl acetylonodicarboxylate

The reactions of this highly reactive acetylene with dithiolothionos have been studied in this department. In addition to 1:1 thione—ester adducts (XV) 1:2 thione—ester adducts (XVI) were also formed.

The reactions were carried out in benzene at room temperature and the 1:2-adducts became the major products when a two—fold or greater excess of ester was used. The 1:1-adduct (XVe) formed from the benzodithiolothione could not be isolated, presumably owing to its o—quinonoid nature. The structures of the 1:2-adducts (XVI) were assigned by use of the Raney nickel desulphurization reaction, the adducts (XVIa) and (XVIb) gave, respectively, dimethyl (3—phenylpropyl) succinate and dimethyl benzylsuccinate together with dimethyl succinate.

\[ \text{R}_1 \quad \text{R}_2 \]
\[ \text{S—S} \quad \text{CO}_2 \text{Me} \quad \text{CO}_2 \text{Me} \]
\[ \downarrow (a) \]
\[ \text{S—S} \quad \text{CO}_2 \text{Me} \quad \text{CO}_2 \text{Me} \]
\[ \text{S—S} \quad \text{CO}_2 \text{Me} \quad \text{CO}_2 \text{Me} \]
\[ \text{S—S} \quad \text{CO}_2 \text{Me} \quad \text{CO}_2 \text{Me} \]
\[ (XV) \]

a) \( \text{R}_1=\text{Ph}, \text{R}_2=\text{H} \)
b) \( \text{R}_1=\text{Et}, \text{R}_2=\text{Me} \)
c) \( \text{R}_1, \text{R}_2=-(\text{CH}_2)_3- \)
d) \( \text{R}_1, \text{R}_2=-(\text{CH}_2)_4- \)
e) \( \text{R}_1, \text{R}_2=-(\text{CH}==\text{CH})_2- \)

\[ \text{R}_1 \quad \text{R}_2 \]
\[ \text{MeO}_2 \text{C} \quad \text{CO}_2 \text{Me} \]
\[ \text{R}_1 \quad \text{R}_2 \]
\[ \text{MeO}_2 \text{C} \quad \text{MeO}_2 \text{C} \]
\[ \text{CO}_2 \text{Me} \]
\[ (XVI) \]
SCHEME 1

SCHEME 2
Two possible mechanisms were suggested. Route (a) is a two-stage process in which electrophilic attack by the acetylenic ester at the electron-rich exocyclic sulphur atom is followed by intramolecular nucleophilic displacement at the 2-sulphur atom. Alternatively the two stages might be concerted, the reaction proceeding via a cyclic transition state such as that shown in route (b).

In the case of the benzodithiolethione the reaction was repeated using methanol as solvent and the same 1:2-adduct (XVIe) was isolated in good yield. This result supports the concept of a concerted addition because methanol would be expected to interfere in the two-stage process by proton transfer to the anionic site of the intermediate dipolar ion.

Other workers have reported the formation of similar 1:1-adducts using diethyl acetylenedicarboxylate (XVII) and ethyl propiolacte (XVIII).

\[
\begin{align*}
\text{EtO}_2\text{CC} & \equiv \text{CO}_2\text{Et} \\
\text{PhC} & \equiv \text{CO}_2\text{Et}
\end{align*}
\]
\[
\text{(XVII)} \quad \text{(XVIII)}
\]

c) Acetylenic acids  
Bohringer et al prepared 2-thiophencylidene-1,3-dithiole-4-carboxylic acid (XIX) from 5-phenyl-1,2-dithiole-3-thione and the mono-potassium salt of acetylene dicarboxylic acid (XX). The acid was decarboxylated by heating in air at 190°C for 10 minutes and the decarboxylation product was reported as 2-thiophencylidene-1,3-dithiole (XXI), bright red plates, m.p. 136-137°C. (SCHEME 1)

The same workers also reacted 4,5-trimethylene-1,2-dithiole-3-thione (XXII) with propiolic acid in bencene at room temperature to yield 2-(4-carboxyl-1,3-dithiole-2-ylidene)cyclopentanethione (XXIII) which, on decarboxylation at 195°C, was reported to give 2-(1,3-dithiole-2-ylidene)cyclopentanethione (XXIV), red needles m.p. 134-136°C. (SCHEME 2).
d) Benzyne

Reactions of dithiolothiones with benzyne have been performed in this department. Easton used two methods to generate benzyne:

i) decomposition of phenyliodoniobenzene-2-carboxylato (XXV) in a high-boiling aprotic solvent.

\[
\begin{align*}
\text{PhI}^+ \text{CO}_2^- + \text{PhI} \rightarrow [\text{cyclopryl}] + \text{CO}_2
\end{align*}
\]

(ii) aprotic diazotization of anthranilic acid.

\[
\begin{align*}
\text{CO}_2\text{H}^- + \text{O} = \text{N} - \text{R} \rightarrow [\text{cyclopryl}] + \text{N}_2 + \text{CO}_2
\end{align*}
\]

The sole characterizable product of the reaction of benzyne with 5-phenyl-1,2-dithiole-3-thione was 4,5-benzo-2-thiophenacylidene-1,3-dithiolo (XXVI). The yield of the adduct was very low (7%) when benzyne was generated by method i), but rather higher (28%) when method ii) was used.
The product (XXVI) was readily identified since it had been obtained by two other routes, as detailed below.

i) The benzodithiolylilum salt (XXVII) reacts with sodium benzoylacetate to give a ketone (XXVIII) which is converted into the thione (XXVI) by the action of phosphorus pentasulphide\(^\text{19}\).

\[
\text{PhCOCH}_2\text{CO}_2\text{Na} + \text{XXX} \rightarrow \text{XXXI} \rightarrow \text{XXVI}
\]

ii) Benzene-1,2-dithiol (XXIX) reacts with 3-chloro-5-phenyl-1,2-dithiolylium perchlorate (XXX) in acetone at room temperature to give the same compound\(^\text{20}\).

The mechanism proposed for this reaction involves displacement of chloride ion from the 3-position in the chloro compound (XXX) by one of the thiol groups in (XXIX); the second thiol group then attacks the 3-position forming an unstable spiro intermediate (XXXI). Opening
SCHEME 3
of thol,2-lithiolo ring with loss of sulphur leads to the thiophenacylidone compound (XXVI). (SCHEME 3)

Rawlings extended this work by reacting 5-phenyl-1,2-dithiol-3-thione with benzync generated from 1-aminobenzotriazolo (XXXII) which can be oxidised to benzync and nitrogen, probably via the nitrene (XXXIII).

\[ \text{(XXXII)} \rightarrow \text{(XXXIII)} \rightarrow +2N_2 \]

In this case an improved yield (55%) of (XXVI) was obtained.

Behringer et al. have also reported the production of (XXVI) in 0.5% yield from the reaction of 5-phenyl-1,2-dithiole-3-thione in methylene dichloride, with benzync generated from benzenedicarboxylium-2-carboxylate. The physical constants (long violet needles, m.p. 130-131°C) were different from those reported by Easton (green crystals with a yellow reflex, m.p. 185-186°C.) and the violet compound was later shown to be the 6a-thienothiophen (XXXIV) possibly formed by 1,2-addition to the exocyclic C=S bond.

\[ \text{(XXXIV)} \]
Easton\textsuperscript{24} and Rawlings\textsuperscript{21} have also reported the cyclo-addition reactions of 1,3-dithiolene-2-thione (XXXV), 4-phenyl-1,2-dithiolo-3-thione (XXXVI) and 4,5-benzene-1,2-dithiolo-3-thione (XXXVII). (XXXVII) gave no identifiable product with benzene.

\begin{align*}
\text{(XXXV)} & \quad \text{(XXXVI)} & \quad \text{(XXXVII)}
\end{align*}
PART B 6a-Thiathiophthans

In 1925 Arndt et al. obtained a compound from the reaction of diacetoxylacetone (XXXVIII) and phosphorus pentasulphide to which they assigned the 1,2-dithiopin structure (XXXIX).

\[ \text{(XXXVIII)} \]

\[ \text{(XXXIX)} \]

This structure was accepted until 1958 when Bozzi et al. determined the crystal structure and found that the sulphur atoms were collinear and equally spaced at 2.36\(\text{Å} \). This compares with the normal S-S bond distance of 2.04\(\text{Å} \) and the result was explained by postulating the two equivalent resonance structures (XL).

\[ \text{(XL)} \]

Those compounds are formally 3-thioacyl-methylene-1,2-dithioles but they are given the generic name "6a-thiathiophthans". This name was evolved by regarding the compounds (XLI) as derivatives of thiophthen (XLII), assuming participation in bonding of the 6a-sulphur d-orbitals (see later). Hence the first 6a-thiathiophthon produced, mentioned above, is 2,5-dimethyl-6a-thiathiophthon (XL).
Since 1958 many synthetic routes leading to a wide variety of substituted 6α-thiathiophthons have been evolved.

i) From 1,3,5-triketones

This reaction involves the sulphurization with phosphorus pentasulphide of 1,3,5-triketones.

Arndt, in 1925, obtained 2,5-dimethyl-6α-thiathiophthon (XL) in 40% yield from diacetylacetone (XLIII; \(R_1 = R_4 = Me, R_2 = R_3 = H\)), but later workers have been unable to reproduce this yield. Loza, in 1929, in examining the reactions of 23 different ketons averaged 24% and exceeded 30% yield in only three instances. This method is suitable for obtaining bridged 6α-thiathiophthons.

ii) From acetylenes

Bohringer obtained 2-methyl-3,5-diphenyl-6α-thiathiophthon (XLIV) in 81% yield from 1-phenyl-2-phenoxyacetylethylene (XLVI) by reaction with thionoacetic acid and sodium acetate at 100°C.
Reaction of sodium disulphide with diynes (XLVIII) gives the ketone precursors of 6a-thiathiophthons (II) in nearly quantitative yields.33

iii) By condensation reactions

Many syntheses involve the condensation of a 1,2-dithiolo derivative with a thiocarbonyl or carbonyl compound. The former gives the 6a-thiathiophthon directly whilst the latter gives the ketonic precursor of the 6a-thiathiophthon (L) which is easily converted to the 6a-thiathiophthon by reaction with phosphorus pentasulphide in benzene solution.
\[ \text{Scheme 4} \]

\[ \text{Scheme 5} \]
Scheme 6
Carbonyl Condensations

a) Ketones

4-Phenyl-1,2-dithiolylium hydrogen sulphate (II), prepared from 4-phenyl-1,2-dithiole-3-thione (XXXVI), condenses with acetophenone, and other aromatic ketones, to give 3-phenacylidene-1,2-dithiolenes (LI) and hence 6a-thiathiophthons (LII) in high yield (SCHEME 4).

Aliphatic cyclic ketones (LIV) condense with 5-aryl-3-methylthio-1,2-dithiolylium iodides or with 3-aryl-1,2-dithiolylium perchlorates (LVa,b) in acetic acid solution with pyridine as base to give the ketonic precursors of 6a-thiathiophthons (LVI). In this way 6a-thiathiophthons with larger rings fused to C2-C3 have been obtained. (SCHEME 5)

b) Activated methylonic compounds

Several condensation reactions involving 1,2-dithiole derivatives with activated methylonic compounds have been reported:

Ethyl arylacetates (LVII) condense with 3-aryl-1,2-dithiolylium perchlorates (LVb) to give ketonic precursors of 6a-thiathiophthons in yields of ca. 20%. (SCHEME 6)

3-Methylthio-5-phenyl-1,2-dithiolylium iodide (LVIII) condenses with sodium benzoylacacetate to give the ketonic precursor of 2,5-diphenyl-6a-thiathiophenone, 5-phenyl-3-phenacylidene-1,2-dithiolo (LIX). (SCHEME 7)

5-Phenyl-1,2-dithiolo-3-one (LX), obtained by reaction of ethyl cinnamate and sulphur, reacts with various activated methylonic compounds in the presence of phosphoryl chloride, but not with simple ketones such as acetophenone. Thus cyanoacetophenone gives, after reaction of the ketonic product with phosphorus pentasulphide, 3-cyano-2,5-diphenyl-6a-thiathiophenone (LXI) which, in refluxing hydrobromic/acetic acid, loses the cyano group to give 2,5-diphenyl-6a-thiathiophenone (LXII). (SCHEME 8)
Closely related to this is the reaction with malononitrile, the product from which can be converted into 2-amino-3-cyano-5-phenyl-6α-thiathiophen (LXIII)\textsuperscript{38}.

\[ \text{Ph} \begin{array}{c} 
\text{CN} \\
\end{array} + \begin{array}{c} 
\text{CN} \\
\end{array} \rightarrow \text{Ph} \begin{array}{c} 
\text{CN} \\
\end{array} \]

\[ \text{alkaline hydrolysis} \]

\[ \text{Ph} \begin{array}{c} 
\text{CN} \\
\end{array} \]

3-Methylthio-4,5-benzo-1,2-dithiolylium iodide (LXIV) reacts with cyanoacetophenone to give, after further transformations, 5-phenyl-2,3-benzo-6α-thiathiophen (XXXIV)\textsuperscript{30}. This compound is of interest since it is the only 6α-thiathiophen with a benzene ring fused to it, this raises interesting structural points which are discussed later.
c) Diazoketones

5-Aryl-1,2-dithiolo-3-thiones (LXV) react with diazoketones to give the ketonic precursors of 6α-thinthiophthons (LXVI) in low yield.\textsuperscript{19,39}

\begin{align*}
\text{Ar} & \xrightarrow{\text{PhCOCHN}_2} \text{Ar} \\
\text{Ar} & \xrightarrow{150{\degree}C} \text{Ph}
\end{align*}
This method, devised in this department, provides a synthesis for 6a-thiathiophthons with rings fused to C<sub>2</sub>-C<sub>3</sub>. 3-Chloro-5-phenyl-1,2-dithiolylium perchlorate (LXVII) reacts with 1-pyrrolidino-cyclopentone or -cyclohexone in anhydrous acetone to give, after precipitation with ether, red, unstable oils presumed to be the crude dithiolylium salts (LXVIIIa,b). These react with sodium hydroxide to give the ketonic precursors of the 6a-thiathiophthons (LXIXa,b) or with potassium hydrogen sulphide to give the 6a-thiathiophthons directly (LXXa,b).

\[
\begin{align*}
\text{Ph} & \quad \text{Cl} \\
\text{S} & \quad \text{S} \\
\text{ClO}_4^- \\
\text{NcOH} \\
\text{Ph} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\text{O} \\
\text{KSH} \\
\text{Ph} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\text{NcOH} \\
\text{Ph} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\end{align*}
\]
A closely related reaction involves the use of Vilsmeier salts. Reid et al., on reacting 3-alkyl-1,2-dithiolium salts (LXXIa-c) with dimethylthioformamide (LXXII), obtained Vilsmeier salts (LXXIIIa-c) which reacted with sodium hydrogen sulphide to give 6a-thiathiophenes (LXXIVa-c). This method enables mono-substituted 6a-thiathiophenes (LXXIVa,b) to be produced. The parent compound (LXXIVd) may also be obtained by this method, albeit in low yield (13%). This compound had previously been obtained by Arndt and Traverso (see later).

![Chemical structure images](image-url)
Thiocarbonyl Condensations

The first synthesis of this type was carried out in this department\textsuperscript{19,40}. 3-Methyl-5-phenyl-1,2-dithiolylium perchlorate (LXXV) gave 2,5-diphenyl-6a-thiathiophthon (LXII) directly when heated with methyl dithiobenzote (LXXVI).

In this synthesis the methyl group on the dithiolylium ring is active whereas in some more recent syntheses\textsuperscript{42,43} the activated group has been in the dithioster; viz, the reaction to produce (LXXVII).
iv) From 4H-Thiopyran-4-thiones

Trevorso obtained 6a-thiathiophthon (LXXIVa) from 4H-thiopyran-4-thione (LXXVIII) by reaction with mercuric chloride to give the salt (LXXIX) which was hydrolysed with aqueous sodium carbonate solution to give the aldehyde (LXXX), the precursor of 6a-thiathiophthon (LXXIVa).

\[
\begin{align*}
\text{(LXXVIII)} & \quad \rightarrow \quad \text{(LXXIX)} \\
\text{(LXXX)} & \quad \rightarrow \quad \text{(LXXIVa)}
\end{align*}
\]
Roid et al.\textsuperscript{45,46} obtained 6\textsubscript{a}-thiathiophen (LXXIV\textsubscript{d}) directly from 4H-thiopyran-4-thione (LXXVIII) by reaction with sodium sulphide in aqueous dimethyl sulfoxide followed by oxidation with potassium ferricyanide in the same solvent. The dianion (LXXXI\textsubscript{c},b) was postulated as an intermediate in the reaction.

\[
\text{(LXXVIII)} \quad \rightarrow \quad \text{(LXXIV\textsubscript{d})}
\]

\[
\text{(LXXXI\textsubscript{c})} \quad \rightleftharpoons \quad \text{(LXXXI\textsubscript{b})}
\]

\[
\text{K}_4\text{Fe(CN)}_6 \quad \downarrow
\]

\[
\text{(LXXXII)}
\]

\(a) \quad R_1=\text{Ph, } R_2=R_3=\text{H} \\
\(b) \quad R_1=R_4=\text{H, } R_2=R_3=\text{Me} \)
were also obtained by this method in moderate yield.

Ring opening with sodium hydroxide in aqueous dimethylformamide gave, by a similar mechanism, the aldehyde (LXXX).

The reaction of 2-phenyl-4H-thiopyran-4-thione (LXXXIII) with sodium hydroxide resulted in the formation of the aldehyde (LXXXIV) whereas the reaction of 2-phenyl-4H-pyran-4-thione (LXXXV) with sodium hydrogen sulphide resulted in the formation of the ketone (LXXXVI). Both reactions evidently proceed by attack of the nucleophile at the 6-position.
Fine Structure of \(6\)-Thiathiophens

The fine structure of \(6\)-thiathiophens has been a very controversial question ever since the X-ray work of Bozzi\(^{26}\) in 1958.

Three structures have been variously postulated:

a) Thiathiophens possess mesomeric structures involving single-bond/no-bond resonance (LXXXVIIa ↔ LXXXVIIb).

\[
\begin{align*}
\text{(LXXXVIIa)} \quad & \leftrightarrow \quad \text{(LXXXVIIb)} \\
\end{align*}
\]

b) Thiathiophens are undergoing rapid tautomorism (LXXXVIIc ↔ LXXXVId).

\[
\begin{align*}
\text{(LXXXVIIc)} \quad & \leftrightarrow \quad \text{(LXXXVId)} \\
\end{align*}
\]

c) The d-orbitals of the \(6\)-sulphur are utilized (LXXXVIIe).

\[
\begin{align*}
\text{(LXXXVIIe)} \\
\end{align*}
\]

It will be useful to examine the conclusions arrived at by each type of physical method determination.
X-Ray Determinations

Bozzi et al.\textsuperscript{26} determined the crystal structure of 2,5-dimethyl-6a-thiophen and submitted the result that the S-S bond lengths were equal (2.36\textsubscript{A}) and thus claimed that this result was evidence for the existence of single-bond/no-bond resonance involving canonical structures (LXXXVIIIa) and (LXXXVIIIb).

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S}
\end{align*}
\]

(LXXXVIIIa)

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S}
\end{align*}
\]

(LXXXVIIIb)

An X-ray determination\textsuperscript{47} on 2,4-diphenyl-6a-thiophen (LXXXIXa,b) showed that the S-S bond lengths were not equal and that the shorter length of 2.22\textsubscript{A} indicated that (LXXXIXa) was the more important resonance structure but that (LXXXIXb) did contribute to the structure significantly since the longer S-S bond was still considerably shorter than the sum of the van der Waals radii (3.70\textsubscript{A}) for two sulphur atoms. The explanation for these results was that the sulphur atom spacing was being perturbed by unsymmetrical substitution.

At the same time as this work Paul et al.\textsuperscript{48} reported on the crystal structure of another unsymmetrical 6a-thiophen, 3-benzoyl-5-(p-bromophenyl)-2-methylthio-6a-thiophen (XCa,b).
In this case the S–S bond-lengths were 2.52Å and 2.18Å. Those workers pointed out that the values found for (XCa,b) were similar to those found for (LXXXIXa,b) although, if the 2-phenyl in (LXXXIXa,b) and the p-bromo-phenyl in (XCa,b) were considered as common reference points, then the "short" and "long" bonds were reversed in the two compounds. The "long" bond determination was made in two crystallographically independent molecules and results of 2.47Å and 2.57Å were obtained. In the first of these the S–CH$_3$ group was coplanar with the thiophthien ring system and in the second the exocyclic sulphur and carbon atoms were 0.14Å and 0.39Å respectively from the plane of the ring. They considered that comparison of the "short" S–S bond-length with the values (2.00–2.10Å) found in normal disulphide compounds provided evidence for significant single-bond/no-bond resonance in (XCa,b) and (LXXXIXa,b).
Other crystallographic results gave S-S bond-lengths in (XCl), an oxygen analogue of 6a-thiathiophthien, 50 and (XCIIa,b), a selenium analogue 51, to be 2.12 Å and 2.49 Å respectively. From these results Paul et al. 48 concluded that there might well be typical "short" (2.12-2.22 Å) and "long" (2.47-2.57 Å) S-S bond-lengths in all 6a-thiathiophthiens and that doubt was cast on the interpretation of the results for the 2,5-dimethyl compound 26 since the reported equality of the S-S bond-lengths might simply be due to random packing of the molecules or to an ordered superstructure.

Later reports on (LXXXVIIIa,b) 52 and on 2,5-diphenyl-6a-thiathiophthien (XCIIIa,b) 53 suggested that the suspicions of ambiguity 48,51 in the interpretation of the results for (LXXXVIIIa,b) 26 were unfounded. The results for (XCIIIa,b) 53 showed S-S bond-lengths of 2.30 and 2.36 Å. This, the author (I. Hordvik) pointed out, was less than the
difference between the "long" and "short" bond-lengths determined for the unsymmetrical 6α-thiathiophthons but was of the order of the difference observed in the two independent measurements of the "long" bond of (XCa,b)48. Nordvik thus concluded that the two S-S bond-lengths in any completely symmetrical 6α-thiathiophthon would be exactly equal in an isolated molecule, but that S-S bonds of total bond order less than unity (as in 6α-thiathiophthons) appear to be unusually sensitive to intermolecular as well as intramolecular environment.

\[ \text{S-S S S} \quad \text{S S S-S} \]

\[(\text{XCIVa}) \quad (\text{XCIVb})\]

A report54 on the symmetrical compound, 3,4-diphenyl-6α-thiathiophthon (XCIVa,b) quotes S-S bond-lengths of 2.232 and 2.434 Å. In this case steric interactions cause the planes of the phenyl rings to be almost perpendicular to the thiathiophthon nucleus.

All these X-ray results may be explained on the basis of molecular orbital calculations which have been carried out for 6α-thiathiophthons55,56. Gleiter and Hoffmann56 have shown that there is a clear preference for an unsymmetrical structure when the 3d-orbitals of the 6α-sulphur are not utilized and a nearly symmetrical structure with a very flat minimum of energy when the 3d-orbitals are included in the calculations. This observation would thus indicate that the structure (LXXXVIIa) is of importance.

\[ \text{S-S S S} \]

\[(\text{LXXXVIIa})\]
It is noteworthy that the relative lengths of the S—S bonds in unsymmetrically substituted 6a-thiathiophthins may often be predicted or accounted for on simple chemical grounds. In the case of (LXXXIXa,b) the X-ray results indicate that (LXXXIXa) is the more important resonance structure. This conclusion may be proposed on chemical grounds also since the thiobenzoyl group (XCV) is much more stable than the thioaldohyde group (XCVI) and should, therefore, stabilize that canonical structure of which it forms a part.

\[
\begin{align*}
\text{(XCV)} & \quad \text{(XCVI)} \\
\end{align*}
\]

Similarly for (XCa,b) the X-ray results indicate that (XCb) is the main resonance contributor. Again this matches the chemical observation that a dithiocarboxyl group (XCVII) is more stable than an arylthiono group (XCVII).

\[
\begin{align*}
\text{(XCVII)} & \quad \text{(XCVIII)} \\
\end{align*}
\]

This argument may also be applied to the selenium derivative (XCIIa,b) where thiobenzoyl (XCV) is more stable than selenoaldohyde (IC), hence (XCIIb) is the more important resonance contributor.

\[
\begin{align*}
\text{(IC)} \\
\end{align*}
\]
Both 6a-thiathiophthens (CI) and their ketonic precursors (C) have characteristic UV spectra. A comparison of the spectra of 6a-thiathiophthens with their precursors shows that the longest wavelength maximum is shifted to higher wavelength and reduced in intensity, and that a second and stronger peak appears at 200-250nm.

Although these observations appear to be applicable to many 6a-thiathiophthens they give no specific structural information.

Leaver and McKinnon proposed, on the basis of UV spectral evidence, that 6a-thiathiophthens may be undergoing rapid tautomericism (LXXXVIIa => LXXXVIIb). They observed that the UV and visible spectra of 2,5-diphenyl-6a-thiathiophthen (CII, X=S) were similar to those of (CIII, X=S) and (CIV, X=S).

(CII, X=O, S)  
(CIII, X=O, S)  
(CIV, X=O, S)
However in the latter two compounds resonance of the single-bond/no-bond type is not possible thus suggesting that the 6α-thiathiophens are undergoing rapid tautomerism rather than resonance. Furthermore, the wavelengths of the visible maxima of compounds (CII, X=S), (CIII, X=S), (CIV, X=S) differed from those of the corresponding ketonic compounds (CII, X=O), (CIII, X=O), (CIV, X=O) by roughly the same increment (67, 60 and 69 respectively) in each case.

Later observations appear to support the theory that the 6α-sulphur atom has an expanded octet. If in addition to the pairs of compounds (CII), (CIII) and (CIV), the u.v. spectra of the pairs (CV) and (CVI) are considered then an interesting conclusion emerges:

\[(CV, X=O,S) \quad (CVI, X=O,S)\]

The bathochromic shift (Δλ) caused by converting X=O to X=S is higher in (CV) and (CVI) (425 and 435) than in (CII), (CIII) and (CIV) (245, 339 and 236 nm⁻¹ respectively). The latter three compounds (X=S) have structures where there is a possible bonding interaction between the exocyclic and endocyclic heteroatoms leading to structures (CVII), (CVIII) and (CIX) whereas it is not possible to structures for (CV, X=S) or (CVI, X=S). The corresponding S=O bonding in the ketones (CII, X=O), (CIII, X=O) and (CIV, X=O) is probably not important.

50, 60
If the low $\Delta\gamma$ values mentioned above are due to the expansion of the octet of the 6a—sulphur atom leading to bonding between sulphur atoms which are formally non—bonded then, it was further reasoned, a high $\Delta\gamma$ value would be expected for the ketone—thione pair (CX, $X=0,S$) and a low value for (CXI, $X=0,S$). In the case of (CX) the angle, $A$, might be larger than normal owing to distortion of the system by the five—membered fused ring; this would prevent the thione sulphur from approaching the endocyclic sulphur. In (CXI), on the other hand, no such constraint would be expected. In accord with these postulates the $\Delta\gamma$ value for (CX) was ca. 120$\text{mm}^{-1}$ greater than for (CXI).
N.M.R. Spectra

The n.m.r. spectra of 6a-thiathiophthons have indicated the symmetry of the structure $^{19,61,62,63}$. Thus the n.m.r. spectrum $^{61}$ of 2,5-dimethyl-6a-thiathiophthon (XL) shows the equivalence of the two methyl groups and of the nuclear protons whereas in the ketonic precursor (XCl) there is no such equivalence.

![Diagrams of compounds CXII and CXIII]  

The n.m.r. spectrum of the charged 6a-thiathiophthon derivative (CXII) also indicated the equivalence of the R group protons but their non-equivalence in the charged ketonic derivative (CXIII) $^{63}$. These observations allow no distinction to be made between single-bond/no-bond resonance and rapidly established tautomerism because n.m.r. is known to be time dependent and if the compounds were tautomeric and the time of tautomeration was considerably less than the time required for the protons to absorb radiofrequency radiation, then a time average of the spectra of the tautomeric forms would result, thereby simulating the symmetry which has been attributed to resonance.

Evidence for aromaticity in 6a-thiathiophthons has been found by comparison of n.m.r. spectra with those of the ketonic precursors $^{32,64}$. Reid et al $^{32}$ have observed that whereas the chemical shift of the thioformyl proton in heterocyclic thiolaldehydes is normally in the region $-1.2$ to $-0.4$ $^\circ$, that of H-2 in 6a-thiathiophthons occurs in the
region 0.8-1.4 ppm thus indicating that H-2 is in the environment (CXIV) rather than (CXV).

\[ \text{(CXIV)} \]
\[ \text{(CXV)} \]

The other ring protons are much more deshielded than the corresponding protons in the ketonic compounds, thus indicating greater ring current and hence aromaticity.

These observations would appear to favour the bicyclic structure for 6a-thiathiophthens (LXXXVIIc) where the 6a-sulphur has an expanded octet. If the structure is to have aromatic character then the octet of the 6a-sulphur would, of necessity, be expanded since this atom would be required to donate 1 electron to the \( \pi \)-system to bring the number of \( \pi \)-electrons up to 10 as required by the Hückel (4n+2) rule.

Other Physical Evidence

Examination of i.r. spectra led to an early proposition of the structure (XL) without any suggestion of resonance but, in general, i.r. has been of no value in assigning the 6a-thiathiophthen structure.

A recent report of the electron spectrum of 2,5-dimethyl-6a-thiathiophthen (XL) using polarized light has suggested that the molecule is unsymmetrical.

In contrast to this recent measurements of the core binding energies by X-ray photoelectron spectroscopy of the symmetrical 6a-thiathiophthens, 6a-thiathiophthen (LXXIVd) and 2,5-dimethyl-6a-thiathiophthen (XL), have indicated that in such molecules there are two types of sulphur only; i.e. the 1- and 6-, and the 6a-sulphur atoms. Thus these observations indicate
that these molecules are symmetrical and that the structure is best represented by the bicyclic structure (LXXXVIIc).

The unsymmetrical 2-methyl-6a-thiathiophthen (LXXIVc) possessed three types of sulphur atom.  

**Chemical Evidence for Structure of 6a-Thiathiophthen.**

It is a chemical consequence of symmetry of the 6a-thiathiophthen nucleus that the same 6a-thiathiophthen may be formed from two different ketonic precursors. The first demonstration of this was the synthesis of 2,4-diphenyl-6a-thiathiophthen (LXXXIXa,b). This was synthesised by the reaction of 3-phonacylidene-4-phenyl-1,2-dithiole (CXVI) with phosphorus pentasulphide. Reaction of the 6a-thiathiophthen with mercuric acetate gave the aldehyde (CXVII) which reacted with phosphorus pentasulphide to regenerate the thiathiophthen.

![Chemical structures](https://example.com/chemistry.png)
SCHEME 9
An interesting demonstration of symmetry is provided by the parallel reactions of a) 5-benzyl-1,2-dithiole-3-thione (CXVIII) with carbon disulphide to give the dianion (CXIX) and b) 5-methyl-4-phenyl-1,2-dithiole-3-thione (CXX) with carbon disulphide to give the dianion (CXXI). Both dianions react with methyl iodide to give 2,5-bis(methylthio)-3-phenyl-6a-thiathiophen (CXXII), suggesting the phenomenon of single-bond/no-bond resonance in the dianions (CXIX \leftrightarrow CXXI) (SCHEME 9).

These synthetic demonstrations do not allow a conclusion to be reached as to 6a-thiathiophen fine structure since there might well be cases where the single product that is obtained is a perfectly normal compound.

In conclusion, it is perhaps reasonable to say that the bicyclic formulation (LXXXVIIc) best represents the 6a-thiathiophen structure. The n.m.r., u.v. and X-ray evidence all point to at least some contribution from this form as do the molecular orbital calculations.

In addition, the enhanced chemical stability of 6a-thiathiophens over the isomeric 2-thiophenacylideno-1,3-dithiols (CXXIII) (discussed later) also would appear to indicate some extra stabilising factor which is absent, or at least appears to be not so important, in (CXXIII), namely the octet expansion of the 6a-sulphur atom.

(CXXIII)
However, the unsymmetrical formulation best illustrates the thiocarbonyl character of the molecules and their vinlycous relationship with 1,2-dithiole-3-thiones (III). It is often the most useful formulation for consideration of syntheses and chemical properties.
Chemical Properties of 6α-Thiathiophthons

Electrophilic Substitution

Bromination, using bromine in inert solvents, to give mono-bromo derivatives (CXXIV, X=Br) of 6α-thiathiophthons (CXXV) has been reported.\textsuperscript{69, 70}

![Diagram of molecular structure](image)

The structure was assigned on the basis of n.m.r. spectra and charge density calculations.

2-Methylthio-5-phenyl-6α-thiathiophen (CXXVI) also brominates\textsuperscript{70} to give the 3-bromo derivative (CXXVII, R=Br). Nitration proceeds similarly to give (CXXVII, R=NO\textsubscript{2}), the structure of which has been assigned on the basis of an unambiguous synthesis involving the condensation of 5-phenyl-3-methylthio-1,2-dithiolylium methylsulphate (CXXVIII) with methyl nitrodithiocacetate (CXXIX).

![Diagram of molecular structure](image)
can be nitrated and nitration gives a compound (CXXX, R=COPh) from which a sulphur atom has been lost. The nitroso group is spectroscopically atypical and X-ray diffraction shows that it forms part of a bicyclic system similar to that in the thiathiophthens thenselves.

Nitrosation of (CXXVI) gives a similar compound (CXXX, R=CS₂Me).

Reaction of (CXXV, R=Ph) with dimethylformamido and phosphoryl chloride gives the 3-formyl derivative (CXXIV, X=CHO).

Formylation of 2-phenyl-6a-thiathiophen (CXXXI) in dimethylformamido and phosphoryl chloride gives 4-formyl-2-phenyl-6a-thiathiophen (CXXXII).
(CXXXIII)

\[
\begin{array}{ccc}
R_1 & R_2 & R_3 \\
H & H & \text{Me} \\
\text{Ph} & H & \text{Ph} \\
\text{Me} & H & \text{Ph} \\
\text{Ph} & \text{Ph} & H \\
H & H & \text{Ph} \\
H & H & \text{t-Bu} \\
\end{array}
\]
This is the only known example of electrophilic substitution of a 6α-thiathiophthon with an open 2-position. Attempted chlorination with sulphuryl chloride of 6α-thiathiophthons with open 2-positions resulted in decomposition.

**Nucleophilic Substitution**

The methylthio group in (CXXVI) is replaceable by thoxy by reaction with sodium ethoxide in ethanol and also by alkylamino by reaction with primary aliphatic amines.

Dingwall and Reid have shown that nucleophilic attack at the 2-position results in rearrangement to 4H-thiopyran-4-thiones (CXXXIII). This rearrangement is the reverse of their synthesis of 6α-thiathiophthons (described earlier). (SCHEME 10)

Alcoholic alkali reacts with 2,5-dimethyl-6α-thiathiophthon (XL) resulting in isomerization to give a diisoceto-thiophone derivative.

**Condensation Reactions**

Electron density calculations have shown that there is a positive charge at the 2-position in 6α-thiathiophthons. This leads to activation of the methyl groups in 2,5-dimethyl-6α-thiathiophthon (XL) which condenses with two molecules of benzaldehyde to give 2,5-distyryl-6α-thiathiophthon (CXXXIV) in high yield. Conversely, the methyl group in 3-methyl-2,5-diphenyl-6α-thiathiophthon (CXXXV) is inert.
Dehydrogenation

The bridged 6π-thiophethons (CXXXVI, X=S) and their ketonic precursors (CXXXVI, X=O) may be dehydrogenated to the charged species (CXXXVII, X=O,S) by reaction with triphenylmethyl fluoroborate in acetic acid.63.
SCHEME 11
SCHEME 12
Isostars of 6α-Thiathiophones

a) Nitrogen

Klingsborg prepared the anil (CXXXVIII) by a variety of methods from 2,6-diphenyl-6α-thiathiophthen (LXXXIX) and other methods have been reported. The anil (CXXXVIII, R=Ph) reacted further with methyl iodide to give the isothiazolium salt (CXXXIX) but this did not react with aniline to replace a second sulphur as hoped. The intermediate salt (CXII) gave, on reaction with N-methylaniline, the 1,2-dithiolyllium derivative (CXIII) (SCHEME 11).

The synthesis of the di-anil (CXII) was achieved by Reid et al via the intermediate Vilsmeier salt (CXIV) (SCHEME 12).

As with 6α-thiathiophthenes, so with the di-anil, the question arises as to whether the compound exhibits single-bond/no-bond resonance or exists as rapidly interchanging tautomers (CXIII) or whether the sulphur atom has an expanded octet thus leading to a bicyclic structure (CXIV). The reported n.m.r. results show the compound to be symmetrical down to at least -70°C. thus supporting the bicyclic structure (CXIV).

![Diagram](CXIV)

Bohringer has synthesised 5-aryl-2-anilino-3-aza-6α-thiathiophthen (CXIV) by condensing 5-aryl-3-amino-1,2-dithiolyllium chloride (CXVI) with phenylisothiocyanate and diaza-6α-thiathiophthenes such as (CXVII) and (CXVIII) are also known.
The compound (CXLVIII) is obtained via an interesting synthesis starting from S-methyliso-thiouuronium iodide (CIL) which condenses with two molecules of an arylchloride to give N,N'-diacyl-S-methylisothiouron (CL). Treatment of this with phosphorus pentasulphide gives (CXLVIII).
Compound (CXLVIII) reacts to give, in turn, the 1,2,4-thiadiazole derivatives (CLI) and (CLII).

b) Oxygon

The oxygen isosteres of 6α-thiophenothiones are their ketonic precursors (L) which may be obtained from 6α-thiophenothiones by reaction with mercuric acetate\(^{76}\) or sulphuric acid\(^{40}\).
The carbonyl group has an abnormal i.r. absorption (1520-1620 cm\(^{-1}\) compared with 1620-1720 cm\(^{-1}\)) indicating a slight accession of single-bond character. It is thus possible to propose the bicyclic structure (CLIII) but molecular orbital calculations indicate that S-O overlap is slight and indeed most compounds of this type give 2,4-dinitrophenylhydrazones, i.e. they react as ketones whereas 6a-thiathiophens are inert in comparable thiono reactions.

The S-S bond length in (CLIV) is the nearly normal value for such bonds of 2.12\(\text{Å}\) whereas the S-O distance is, at 2.41\(\text{Å}\), much greater than the normal S-O bond length of 1.69\(\text{Å}\). It is, however, less than the sum of the van der Waals radii (3.2\(\text{Å}\)) again indicating partial S-O bonding. In (CLV) the S-S and S-O bond lengths are 2.11\(\text{Å}\) and 2.38\(\text{Å}\) respectively.
When a 6a-thiathiophthon reacts with mercuric acetate it does not necessarily give the same ketonic compound from which it was formed by reaction with phosphorus pentasulphide. In addition, there are no obvious rules as to which ketone will be formed from a particular 6a-thiathiophthon. Whereas (CLVI) loses sulphur to give an aryl ketone (CLVII), the closely related 2-methyl-5-phenyl-6a-thiathiophthon (CLVIII) gives an alkyl ketone (CLIX).^40

\[
\begin{align*}
\text{(CLVI)} & \quad \text{(CLVII)} \\
\begin{array}{c}
\text{Ph} \\
\end{array} & \quad \begin{array}{c}
\text{Ph} \\
\end{array} \\
\begin{array}{c}
\text{S-S-S} \\
\end{array} & \quad \begin{array}{c}
\text{O S-S} \\
\end{array} \\
\begin{array}{c}
\text{Ph} \\
\end{array} & \quad \begin{array}{c}
\text{Ph} \\
\end{array} \\
\begin{array}{c}
\text{S-S-S} \\
\end{array} & \quad \begin{array}{c}
\text{S-S O} \\
\end{array} \\
\begin{array}{c}
\text{Ph} \\
\end{array} & \quad \begin{array}{c}
\text{Ph} \\
\end{array} \\
\begin{array}{c}
\text{S-S-O} \\
\end{array} & \quad \begin{array}{c}
\text{Me} \\
\end{array} \\
\begin{array}{c}
\text{Me} \\
\end{array} & \quad \begin{array}{c}
\text{Me} \\
\end{array} \\
\end{align*}
\]

The cyclopentone-compound (CLX) gives both ketones, (CLXI) and (CLXII), although the alkyl ketone (CLXI) is the major product^40.

These observations are yet another indication of the delicately balanced nature of the 6a-thiathiophthon system where there is a high degree of interaction between the S-S bonds and, apparently, no significant barrier to change of bond length.
c) Selenium

2,4-Diphenyl-6-seleno-6α-thiathiophthen (XCII) has been prepared from (CLV) by reaction with phosphorus pentaselenide in chlorobenzene\textsuperscript{51} and by the reaction of the Vilsmeier salt (LXXIIIc) with sodium hydrogen selenide\textsuperscript{32}. X-ray results (see earlier) indicate that the corresponding S–S bond lengths in 2,4-diphenyl-6α-thiathiophthen (LXXXIX) and (XCII) are almost identical, hence selenium replaces sulphur without disturbing the system\textsuperscript{51}.
Klingensberg has prepared the cyanine derivative (CLXIII) and an X-ray examination, carried out by Hordvik, shows that the sulphur atoms are collinear and that the central sulphurs are 3.1 Å apart. This is well below the sum of the von der Waals radii (3.7 Å) and Klingensberg suggested that canonical structures (CLXV a, b)
might make a small contribution to the resonance hybrid i.e. he suggested that there was single-bond/no-bond resonance.

Leaver, however, pointed out that there was no evidence that the disulphide bonds in the dithiole nuclei were unusually long and that the central S–S distance was no shorter than the value of 2.95Å found for the phosphacycine (CLXIV) where single-bond/no-bond resonance would be highly unlikely. Accordingly Leaver suggested that the partial intermolecular bonding in these cyclics was suitably regarded as the result of expansion of the valence-shells of the internal sulphur atoms and it would be possible to include the canonical structure (CLXVI) as a contributor to the structure of (CLXIII) rather than (CLXVa,b).

\[
\text{(CLXVI)}
\]

Staveux and Lozac'h have prepared 4- and 5-sulphur systems of the types (CLXVII), (CLXVIII) and (CLXX) and Slotton has carried out an X-ray determination on (CLXX).

\[
\text{(CLXVII)}
\]
The results of this indicate that (CLXX) has a 6a-thiathiophen type system since the fourth sulphur, at 2.97 Å from S3, would appear to have a negligible influence on the bonding of the other three sulphurs and indeed S1, S2, S3 have bond lengths comparable to those observed in 2,4-diphenyl-6a-thiathiophen (LXXXIX). Another 4-sulphur system has been described by Leaver et al.63.
Employing a method previously described for the preparation of (CLXXIa) from (CLXXIIa) by the action of phosphorus pentasulphide in boiling xylene, they prepared (CLXXIb—f). The n.m.r. spectrum of 4-(thio-p-toluoyl)-5-(p-tolyl)-1,2-dithiol-3-thione (CLXXIb) contained two methyl singlets at \( \delta \) 7.65 and \( \delta \) 7.70 thus showing that the two aryl groups are not rendered equivalent by single-bond/no-bond resonance. However, attempts to prepare (CLXXIc) and (CLXXId) from (CLXXIIc) and (CLXXIId) respectively gave identical products which, as shown by the presence of two methyl singlets in their n.m.r. spectra, were mixtures of the two isomeric thioacyl compounds. A similar result was obtained for the isomeric pair (CLXXIe) and (CLXXIf). They concluded that isomeric thioacyl compounds (CLXXI; \( R_1/R_2 \)) are interconvertible but that the tautomeric equilibrium is not rapidly established (on the n.m.r. time-scale) at room temperature.
SCHEME 13
Compounds have been reported which have dithiole groupings fused to acene systems. They have a formal relationship to other dithiols and to 6a-thiathiophons although, owing to their acene nature, chemical similarity to those classes of compounds is to some extent masked. They do, however, have considerable theoretical importance.

Marschalk et al., in a series of papers, have described the preparation and properties of tetraceno tetrasulphido (CLXXIII).  

![Tetraceno tetrasulphido (CLXXIII)](image)

Tetraceno tetrasulphido (CLXXIII) was obtained by the reaction of tetraceno (CLXXIV) with sulphur in trichlorobenzene (TCB) or, more quickly, by the reaction of tetraceno with disulphur dichloride in TCB. An intermediate in this latter reaction was identified as 9,11-dichlorotetraceno (CLXXV) which, in an independent reaction, also gave (CLXXIII) by reaction with disulphur dichloride. (Scheme 13)

Formulations considered for tetraceno tetrasulphido were (CLXXIII), (CLXXVI) and (CLXXVII). The latter two were rejected in favour of (CLXXIII) on account of the compound's stability to hydrolytic reagents, oxidising agents and thionyl chloride.
9,10,11,12-Tetramethylthio- and tetrabenzylthiotetraene (CLXXVIII), R=Me, PhCH₂ were obtained from (CLXXIII) by reaction with sodium in liquid ammonia followed by the appropriate chloro compound.

Further proof of the structure of (CLXXIII) was afforded by carrying out a similar reaction between 9,10,11,12-tetrachlorotetraene (CLXXIX) and toluene-p-
thiol (CLXXX) when a product was obtained with properties similar to those of (CLXXVIII). This product was formulated as (CLXXVIII, R=p-McC₆H₄).

\[
\text{(CLXXIX)} \quad \text{Cl} \quad \text{Cl} \quad \text{CH}_3 \\
\text{Cl} \quad \text{Cl} \quad \text{SH} \\
\text{(CLXXX)}
\]

Reaction of (CLXXIII), in an autoclave, with liquid ammonia followed by oxidation yielded 9,10-tetraacenequinone (CLXXXI).

\[
\text{(CLXXXI)}
\]

The radical-cation (CLXXXII) and dication (CLXXXIII) of (CLXXIII) were obtained by reaction with strong acid in the presence of an oxidising agent or, in the case of the dication, by direct reaction with halogen. (CLXXIII) was regenerated by reaction with a reducing agent — titanium trichloride or sodium dithionite.
The reaction of selenium with 9,11-dichlorotetracone (CLXXV) gave, along with other poorly defined materials, tetracene tetraseloned (CLXXXIV) which formed salts analogous to (CLXXXIII).

\[
\text{Se-Se}
\]

(CLXXXIV)
Recently Marschalk's work on tetracone tetrasulphido has been repeated and also the reactions between pentacone and sulphur and hexacone and sulphur have been studied and compounds believed to have the formulae (CLXXXV), (CLXXXVI) and (CLXXXVII) have been isolated\(^9\).
PART E 2-Thioacylmethylene-1,3-dithiolenes

These compounds (XII) are isomeric with 6α-thiathiophthens.

They may be obtained by the cyclo-addition of 1,2-dithiole-3-thiones and acetylenic derivatives (see earlier).

They may also be obtained by condensation reactions analogous to those reported for the synthesis of 6α-thiathiophthens. Thus sodium benzoylacetae condenses with 4-phenyl-2-methylthio-1,3-dithiylyium perchlorate (CLXXXVIII) to give 4-phenyl-2-phenoacylidene-1,3-dithiolo (CLXXXIX) which is analogous to the ketonic precursors of 6α-thiathiophthens. The ketone then reacts with phosphorus pentasulphide in benzene to give 4-phenyl-2-thiophenacylidene-1,3-dithiolo (CXC).
Another reported synthesis involves the reaction of \( \alpha \)-haloketones (CXCI) with \( \alpha, \beta \)-unsaturated gem-dithiolenes (CXCII) to give 4-hydroxy-1,3-dithiolan-2-ylidene ketones (CXCIII) which, on treatment with acid, yielded 1,3-dithiolyldene ketones (CXCIV), the kotic precursors of the required compounds.

\[
\begin{align*}
\text{CXCI} & \quad \begin{array}{c}
\text{R}_1 \\
\text{R}_2
\end{array}
\quad + \\
\text{CXCII} & \quad \begin{array}{c}
\text{R}_3 \\
\text{HS} \quad \text{O} \\
\text{HS} \quad \text{O} \\
\text{R}_4
\end{array}
\quad \rightarrow \\
\text{CXCIII} & \quad \begin{array}{c}
\text{R}_1 \\
\text{R}_2 \\
\text{S} \quad \text{O} \\
\text{S} \quad \text{O} \\
\text{R}_3 \\
\text{R}_4
\end{array}
\quad \rightarrow \\
\text{CXCIV} & \quad \begin{array}{c}
\text{R}_1 \\
\text{R}_2 \\
\text{R}_3 \\
\text{R}_4
\end{array}
\end{align*}
\]

These compounds have similarities to 6β-thiathiophlions. Thus they are converted into their kotic precursors by similar methods, their u.v. spectra are similar when both have aryl substituents \( 9, 10, 77 \), and they nitroso to similarly \( 97 \).

It has been suggested \( 40 \), on the basis of the u.v. spectra, that there is a bonding interaction between the exocyclic and endocyclic sulphur atoms which, in the extreme case, would lead to the bicyclic formulation (CXCV) involving octet expansion of the endocyclic sulphur atom.
As yet only 1 X-ray determination on a compound of this type has been reported. The compound was 4-(p-bromophenyl)-2-thiophonacyclidene-1,3-dithiole (CXCVI). The X-ray apparently showed that there was only one stereoisoromer (discussed later). The exocyclic S-S distance was 2.91\(\text{Å}\) which, although less than twice the van der Waals radius of sulphur (3.70\(\text{Å}\)), is much greater than any S-S distance reported in a 6a-thiathiophthon. This result provides evidence against a significant contribution for (CXCVI) although a single X-ray result is not conclusive.
DISCUSSION
SECTION 1
PART A Decarboxylation of 2-Thioacetyl methylene-1,3-dithiole-4-carboxylic acids

Bohringer et al. reported that the decarboxylation product of the acid (XIX) was the 1,3-dithiolo (XXI) (see introduction).

In view of his report that the 1,3-dithiolo existed as bright red plates, which would be atypical for this class of compounds, and the fact that Reid et al. had reported the melting point of the 6a-thiathiophthen (LXXIVb) to be 135°C, equal to the value reported by Bohringer for (XXI), it was decided to re-investigate the decarboxylation.

When Bohringer's conditions were reproduced it was found that two products were obtained, namely the 6a-thiathiophthen (LXXIVb) and 5-phenyl-1,2-dithiolo-3-thiono (VIII). It was found that the same two products were obtained if the decarboxylation was carried out by heating in boiling 2,6-lutidino or by sublimation at 200°C.

Thus it appears that the acid (XIX) loses carbon dioxide and then two alternative reaction paths are followed: (i) fragmentation yielding (VIII) and acetylene or
(ii) rearrangement yielding (LXXIVb). Alternatively, rearrangement may occur before decarboxylation.

A similar decarboxylation pattern was observed for 2-p-bromothiophenacylidene-1,3-dithiole-4-carboxylic acid (CXCVII).

Bohringer also reported the decarboxylation of the acid (XXIII) (see introduction) to give the 1,3-dithiol (XXIV).

Again Bohringer's conditions were reproduced and in this case the 1,3-dithiol (XXIV) was indeed obtained. Compound (XXIV) may be distinguished from the isomeric 6a-thiathiophen (CXCVIIIa,b) by the absence from the n.m.r. spectrum (XXIV) of a low-field doublet due to the proton (H-5) having partial thioaldehyde character.
Compound (XXIV) did not rearrange to give (CXCVIII) on being heated at 200°C.

Thus it appears that (XXIV) is much more resistant to rearrangement than (XXI) (discussed later).

Attempts to prepare the corresponding acid (CIC) from 4,5-tetramethyleno-1,2-dithiolo-3-thione (CC) failed to yield any identifiable product.
PART B  Cycle-addition Reactions of 1,2-Dithiolo-3-thiones with Acetylenic Compounds and Rearrangements of 2-Thiocyclymethylen-1,3-dithiols

The cycle-addition reaction between arylacetylenes (CCI) and 1,2-dithiolo-3-thiones (CCII) to give, under differing conditions, 2-thiocyclymethylen-1,3-dithiols (CCIII) and 6a-thiathiophthenes (CCIV) has been reported by various groups of workers (see introduction).

The object of this investigation was to elucidate the factors that determine the product distribution by examining substituent and catalytic effects under differing conditions.

Three possible routes for the production of (CCIV) are examined:

a) 1,2-cyclo-addition to the C=S bond followed by ring-opening of the resulting four-membered ring,

\[ \text{(CCII)} \xrightarrow{\text{R}} \text{(CCIII)} \xrightarrow{\text{R}} \text{(CCIV)} \]

b) formation, initially, of a 1,3-adduct (CCIII) followed by rearrangement to yield a 6a-thiathiophthon (CCIV),
Scheme 14

- (c) \( R_1 = p-	ext{NO}_2\text{C}_6\text{H}_4 \), \( R_2 = \text{Ph} \)
- (d) \( R_1 = \text{2-pyridyl} \), \( R_2 = \text{Ph} \)
- (e) \( R_1 = p-\text{MeOC}_6\text{H}_4 \), \( R_2 = \text{Ph} \)
c) initial reaction between sulphur and the acetylene to give a 1,3-dipolar intermediate (CCV) which then adds to the C=S bond and the resulting spiro-compound (CCVI), by ring-opening and loss of sulphur, yields the 6α-thiathiophthon (CCIV). (SCHEME 14).

In addition a mechanism for the rearrangement of the 1,3-adduct (CCIII) to the 6α-thiathiophthon (CCIV) is proposed.

Behringer and his co-workers, who studied the reaction of p-methoxyphenylacetylene (CCIa) with 5-phenyl-1,2-dithiole-3-thione (CCIIa) in boiling xylene, reported that the product obtained was 2-phenyl-5-p-methoxyphenyl-6α-thiathiophthon (CCIVa) and proposed that it might have been formed by 1,2-cyclo-addition. This reaction was considered to be worthy of re-investigation since it was one of only two cases where 1,2-cyclo-addition was proposed (the other is discussed later) and there was no apparent reason why this reaction should proceed differently from those of other arylacetylenes.

Accordingly Behringer's reaction conditions were reproduced and it was found that the main product.
obtained was the 1,3-adduct (CCIIIa) with the 6a-thiathiophthen (CCIVa) as a minor product. The adduct (CCIIIa) was again the main product when the reaction was carried out over a period of 3 hr. only and in this case an even smaller amount of the thiathiophthen (CCIVa) was obtained. It seemed possible that the difference between these results and those of Behringer might be due to the use, in the present work, of dithiolothione which had been rigorously purified to remove all traces of free sulphur.

Accordingly the same reactions were now carried out using:

a) crude dithiolothione i.e., the product obtained by rough chromatography of the tar formed by hydrolysis of the reaction mixture (see experimental section)
b) pure dithiolothione with a small amount of sulphur added.

In both these cases essentially the same result was obtained: the thiathiophthen (CCIVa) was the major product and only a small amount of the 1,3-adduct (CCIIIa) was formed. It was found, moreover, that heating (CCIIIa) in boiling xylene, in the presence of a small amount of sulphur, caused a gradual rearrangement to (CCIVa).

These observations do not preclude the possibility of 1,2-cyclo-addition but they do suggest that initial formation of (CCIIIa) by 1,3-cyclo-addition with subsequent rearrangement to the thiathiophthen (CCIVa) is more likely since the presence of sulphur in the reaction mixture should not be necessary for 1,2-cyclo-addition to take place.

Results similar to these were noted when phenylacetylene (CCIIb), p-nitrophenylacetylene (CCIIc) or 2-pyridylacetylene (CCIIId) was used. The rate of the cyclo-addition was less for phenylacetylene than for the other acetylenes and this is to be expected since both electron-donating and electron-withdrawing groups on the acetylene might be expected to accelerate the 1,3-cyclo-addition by increasing the polarity of the triple bond. A similar
acceleration was observed when the p-methoxyphenyl group was present in the thione partner (CCIIc).

The other case in which Bohringer proposed 1,2-addition was the reaction of diphenylacetylene (CCVII) with 5-phenyl-1,2-dithiole-3-thione leading to 2,3,5-triphenyl-6a-thiathiophthen (CCVIII) as the product.

\[
\text{Ph} \quad \text{S-S-S} \\
\text{Ph} \\
\text{CCVII} \\
\text{Ph} \\
\text{Ph} \\
\text{CCVIII}
\]

\[
\text{Ph} \quad \text{S-S} \\
\text{Ph} \\
\text{Ph} \\
\text{CCIX}
\]

In this case he used dimethylformamide as the solvent. When the reaction was repeated, however, the principal product was the 1,3-adduct (CCIX) accompanied by small amounts of the 6a-thiathiophthen (CCVIII). This was found to be so whether dimethylformamide or xylene was used as the solvent and whether or not the dithiolethione was pure or crude or whether sulphur was present. Moreover the 1,3-adduct (CCIX) did not yield the 6a-thiathiophthen (CCVIII) even being heated with sulphur in boiling xylene or boiling dimethylformamide. When the 1,3-adduct (CCIX) was heated at 200°C. for 2 hr. the 6a-thiathiophthen (CCVIII) was formed and had the same melting point as that reported by Bohringer (187°C.). The discrepancy between these observations and those of Bohringer remains unresolved and unexplained.
Mechanism of the Rearrangement of 1,3-Adduct (CCIII) to 6c-Thiathiophen (CCIV)

This rearrangement has been reported previously (see introduction) but as yet no mechanism has been proposed.

As has been described above it was found to be catalysed by elemental sulphur. The mechanism proposed (SCHEME 15) involves nucleophilic attack by a polysulphide chain at the 2-position of the dithiolo ring. The polysulphide is envisaged as being formed either by thermal fission of an \( S_8 \) ring (to give a zwitterion) or by attack on \( S_8 \) by a nucleophilic impurity. Ring-closure to yield a 1,2-dithiolo ring then leads to the spiran intermediate (CCVI). Opening of the 1,3-dithiolo ring, involving accessions of positive charge to sulphur in the 1,2-dithiolo ring, followed by opisulphide formation and sulphur extrusion leads to the product, the 6c-thiathiophen.

The last two stages in the proposed mechanism are analogous to those involved in the base-induced conversion of 3-phenacylthio-1,2-dithiolylium salts (CCX) into 3-phenacylidene-1,2-dithioles (CCXI).
It is important to mention here that there is no evidence that the rearrangement does not take place by a radical mechanism. Such a mechanism can easily be formulated involving the same steps as the ionic mechanism. Evidence in support of this mechanism will now be presented.

a) Use of Selenium

If selenium can take the place of sulphur in the rearrangement then the final product, from the 1,3-adduct (CCIIIb), will be 2,5-diphenyl-6α-selenathiophthon (CCXII).

When the 1,3-adduct (CCIIIb) was heated with selenium in boiling 1,2,4-trichlorobenzene, rearrangement was essentially complete in 3 hr. Mass spectroscopy showed that the product, a red solid, was a mixture, in about equal proportions, of 2,5-diphenyl-6α-thiathiophthon (CCIVb) and a compound (M⁺ 379, 380) which corresponded to (CCXII) or (CCXIII). The 6α-thiathiophthon is presumably formed as a result of reaction of the starting material with sulphur produced by the selenium reaction; it's relatively high proportion being explained by the greater reactivity and solubility of sulphur.

All attempts to separate the mixture failed but it was possible to draw a meaningful conclusion by mass spectrosopic analysis. If the mixture consists of the 6α-thiathiophthon (CCIVb) and (CCXII) then there should be a peak at m/z 133 corresponding to the fragment \(\text{Ph} = \text{C} = \text{S}\)⁺ but no peak corresponding to the fragment \(\text{Ph} = \text{C} = \text{Se}\)⁺ (m/z 180, 181). This was found to be the case.

The 6α-thiathiophthon (CCIVb) was now
treated with selenium in boiling 1,2,4-trichlorobenzene and was recovered unchanged. Thus selenium is indeed introduced by reaction with the 1,3-adduct (CCIIIb) and not simply by replacement of sulphur in the 6a-thiathiophen.

b) Steric Effects

It might be expected that a 1,3-adduct derived from a dithiolethione with an electron-attracting substituent at the 2-position would rearrange rapidly. This is because an accession of positive charge would be expected at the 2-position of the 1,3-dithiolc ring thus facilitating nucleophilic attack at that position.

\[
\text{Ph} \quad \begin{array}{c}
\text{S} \\
\text{C} \equiv \text{O}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{S}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{S}
\end{array} \quad \begin{array}{c}
\text{C} \equiv \text{O}
\end{array} \\
\text{C}_6\text{H}_4\text{OMe} \\
\text{C}_6\text{H}_4\text{OMe}
\]

(CCXIV)

It was found, however, that the p-methoxybenzoyl adduct (CCXIV) rearranged very slowly in solution, though more rapidly by heating at 200°C; it is thus relatively resistant to rearrangement. This effect may arise after initial attack by sulphur, in the negative charge in the intermediate (CCXV) being very effectively delocalized thus reducing the nucleophilicity of the negatively charged sulphur and hindering ring closure.

Another explanation was based on steric considerations. The second stage of the proposed mechanism (SCHEME 15) involves ring closure by nucleophilic attack on sulphur. It is known that such a reaction mode is favoured when the leaving and attacking atoms and the
central sulphur atom are collinear. Thus the required molecular geometry will be as in (CCXVI).

A large group X might interfere with the required geometry if the attacking atom is shifted out of collinearity owing to repulsion between X and the sulphur atoms of the 1,3-dithiole ring. Thus it might be expected that a compound with a bulky substituent X would rearrange more slowly than a 1,3-adduct with no substituent at X. This proposition was born out in the case of the adduct (CCXVII) (X=Mc) which certainly rearranged more slowly than (CCIII b) (X=H). However, the proposition appeared to be completely unfounded in the cases where X and Y were bulky aliphatic groups (CCXVIII) and (CCXIX).
In these cases the 1,3-adducts, \((\text{CCXVIII}, Ar=\text{Ph})\) and \((\text{CCXIX}, Ar=\text{Ph})\), could not be isolated, the cyclo-addition reaction between phenylacetylene and the appropriate dithiolethioncs yielding only the 6a-thiathiophens \((\text{CCXX}, Ar=\text{Ph})\) and \((\text{CCXXI}, Ar=\text{Ph})\).

Before returning to consider further these particular cases it is convenient at this point to discuss the related 1,3-adducts, \((\text{CCXXII})\) and \((\text{CCXXIII}, Ar=\text{Ph})\), containing fused cycloalkene rings. When the cycloaddition reaction was performed using 4,5-tetramethylene-1,2-dithiole-3-thione (CC) and phenylacetylene the only
product obtained was 5-phenyl-2,3-tetramethyleno-6a-thiathiophthen (CCXXXIV, Ar=Ph).

When the same reaction was carried out using 4,5-trimethyleno-1,2-dithiolo-3-thione (XXII) the only product obtained was the 1,3-adduct, 2-(4-phenyl-1,3-dithiol-2-ylideno)cyclopentenothione (CCXXXII), even when sulphur was present in the reaction mixture.

Rearrangement of the 1,3-adduct (CCXXXII) could not be brought about either by refluxing in xylene or by prolonged heating at 200°C. In the former reaction the 1,3-adduct was recovered unchanged and in the latter case a small amount of sulphur was isolated in addition to unchanged 1,3-adduct.

Two possible explanations for the failure of the adduct to rearrange will now be considered.

i) Formation of a 1,2-dithiolo ring in the spiran intermediate might be retarded relative to the formation of a trithiocyclohexone ring.

Owing to the presence of the 5-membered carbocyclic ring and consequent enlargement of exocyclic bond angles at the double bond, it is to be expected that the two sulphur atoms which would normally form the 1,2-
dithiole ring will be further apart. Nucleophilic attack might, therefore, take place at the second sulphur atom in the chain which is now more favourably placed (CCXXV). This would lead to the formation of the unstable intermediate (CCXXVI) containing a trithiacycloclohexene ring which could decompose to regenerate the starting material via a cycloelimination of S₂.

Even if the spiron intermediate (CCXXVII) could be formed, retention of the normal S−S bond length would introduce considerable angle strain. The further
shortening of this bond, consequent upon the formation of a 1,2-dithiolium cationic structure, might disfavour the process sufficiently to make the alternative mode of decomposition (CCXXVII) → (CCXXVIII) → (CCXXII) completely dominant.

\[
\begin{align*}
\text{Ph} & \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \\
\text{S} & \quad \text{S} \quad \text{S} \quad \text{S} \\
\text{S} & \quad \text{S} \quad \text{S} \quad \text{S}
\end{align*}
\]

\[
\text{(CCXXVIII)}
\]

These explanations are in accord with the observation that more rigorous conditions will not bring about rearrangement since, particularly in the case of ii), it would not be expected that these limitations could be overcome by using more rigorous conditions.

The question which now remained was whether the tetramethylenothiophthien (CCXXIV, Ar=Ph) was formed by 1,2-addition or via the corresponding 1,3-adduct (CCXXIII, Ar=Ph) by rapid rearrangement under the conditions of the reaction. Thus it was necessary to synthesise (CCXXIII, Ar=Ph) by another method.

\[
\begin{align*}
\text{Ar} & \quad \equiv \\
\text{CO}_2\text{H}
\end{align*}
\]

\[
\text{(CCXXIX)}
\]

This was achieved by the reaction of 4,5-tetramethyleno-1,2-dithiole-3-thione (CC) with phenylpropionic acid (CCXXIX, Ar=Ph) in boiling benzene. When the reaction was carried out over 3hr. the adduct (CCXXIII, Ar=Ph) was the major product whereas a reaction time of 24hr. yielded the 6a-thiophthien (CCXXIV, Ar=Ph) as the major product.
Thus the 1,3-adduct is apparently rearranging in boiling benzene even in the absence of added sulphur. In accordance with this observation it was found that, after being isolated, the adduct (CCXXXIII, Ar=Ph) did indeed rearrange in benzene solution, and in xylene it rearranged sufficiently fast to account for the formation of (CCXXXIV, Ar=Ph) in the cyclo-addition reaction with phenylacetylene. A similar result was noted for the 1,3-adduct (CCXXXIII, Ar=p-MoC₆H₄) formed from p-methylphenylpropionic acid (CCXXXIX, Ar=p-MoC₆H₄) and the dithiolothione (CC). These reactions presumably proceed via an unstable acidic intermediate of the type (CCXXX) which apparently decarboxylates in solution.

These observations do not, of course, preclude the possibility of 1,2-addition yielding the 6-ethithiophenoth (CCXXXIV) directly via an unstable acidic intermediate of the type (CCXXXI).

It now appeared feasible that the reaction with an arylpropionic acid (CCXXXIX, Ar=Ph, p-MoC₆H₄) in benzene might offer a feasible route to the formerly
unobtainable 1,3-adducts (CCXVIII) and (CCXIX) which, being substituted with aliphatic groups on the exocyclic part of the molecule, bear similarity to (CCXXXIII). However, reaction in benzene failed to yield the 1,3-adducts but gave only the 6a-thiathiophens (CCXXI, $\text{Ar} = \text{Ph}, p = \text{MeC}_{6}H_{4}$) and (CCXXI, $\text{Ar} = \text{Ph}, p = \text{MeC}_{6}H_{4}$). A similar result was obtained in boiling dichloromethane which, in those cases at least, seems indicative that 1,2-addition is taking place.

The first step in the 1,3-cyclo-addition involves the breaking of the S–S bond in the dithiolothione. In the cases (CCXXXII) and (CCXXXIII) this would generate an alkyl thione group which would certainly be much less stable than the aryl thione groups of the adducts formed from 5-aryl-1,2-dithiolo-3-thiones.

However, even if the thiathiophens (CCXX), (CCXXI) and (CCXXIV) are formed by 1,2-addition, the reason for the rapid rearrangement of the adduct (CCXXXIII) remains unexplained.

c) Evidence for SCHEME 14 and for the Existence of a Spiro-Intermediate in the Rearrangement

The formation of 2-phenyl-5-p-methoxyphenyl-6a-thiathiophen (CCIVA) by sulphur-catalysed rearrangement of 3-phenyl-2-thiophenacylideno-1,3-dithiolo (CCIIIa) in boiling xylene took appreciably longer than did the formation of a comparable amount of thiathiophen by direct cyclo-addition in the presence of sulphur. Thus it is unlikely that all of the thiathiophen produced in the latter reaction can be accounted for by rearrangement of
(CCIIIa) even though it cannot be assumed that the rate of rearrangement has a linear time-dependence. (As the amount of 1,3-adduct decreases so will the rate of rearrangement). Thus it seemed that there must be an additional route to the 6a-thiathiophthon.

The necessity for an additional route becomes more apparent in the reaction of diphenylacetylene with 5-phenyl-1,2-dithiole-3-thione. In this reaction 2,3,5-triphenyl-6a-thiathiophthon (CCVIII) is a minor product of the reaction but it has been shown (see earlier) that the corresponding 1,3-adduct (CCIX) does not rearrange at all in xylene in the presence of sulphur.

The additional route proposed is shown in Scheme 14. This involves reaction of the acetylene with sulphur to form a thioacylcarbene which, behaving as a 1,3-dipole, adds to the thione to give a spiran (CCVI) identical with the one proposed as an intermediate in the rearrangement. In order to test this hypothesis it was desirable to generate thioacylcarbenes by an alternative method and to study their reactions with dithiolethiones.

\[
\begin{align*}
\text{Ph} & \quad \text{S} \\
\text{Ph} & \quad \text{N} \\
\text{Ph} & \quad \text{N} \\
\text{(CCXXXIV)}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{S} \\
\text{Ph} & \quad \text{Ph} \\
\text{(CCXXXV)}
\end{align*}
\]

Staudinger showed that the decomposition of 4,5-diphenyl-1,2,3-thiadiazolo (CCXXXIV) at 200°C, gave 2,3,4,5-tetraphenyldithiophen (CCXXXV). Nitrogen was slowly evolved when the thiadiazolo was heated in boiling xylene. These results suggest that an intermediate of the type (CCXXXVI) is being produced and that the thiophen (CCXXXV) is formed by dimerization of (CCXXXVI) to yield the tetraphenyldithiin (CCXXXVII) which then loses sulphur. Elemental sulphur was also isolated from the reaction mixture.
Kirmse and Horner investigated the photolysis of 4-phenyl-1,2,3-thiadiazole (CCXXXVIII) and postulated the existence of the intermediate (CCXXXIX) to explain the formation of the 1,3-dithiole (CCXL)

Samples of 4-phenyl-1,2,3-thiadiazole (CCXXXVIII) and 4,5-diphenyl-1,2,3-thiadiazole (CCXXXIV) were prepared. When the thiadiazoles were heated in boiling xylene with 5-phenyl-1,2-dithiole-3-thione (CCIIa) the thione was recovered unchanged, presumably because the thiadiazoles did not decompose at this temperature. However, when the thiadiazoles were heated with the thione at 200°C, the products obtained were 2,5-diphenyl-6a-thiathiophen (CCIVb) and 2,3,5-triphenyl-6a-thiathiophen (CCVIII) respectively. These compounds can only have been produced by
Scheme 16
1,3-dipolar addition of the reactive intermediate (CCV), generated from the thiazole, to the C=S bond of the dithiolethiophene (SCHEME 14).

5-Phenyl-1,2-dithiole-3-thione (CCIIa) is not the only substrate which should accept the intermediate from the thiazole. 4-Phenyl-1,3-dithiole-2-thione (CCXLI) should be equally capable of behaving as an acceptor to form the spiro bis(1,3-dithiolo) (CCXLII), decomposition of which should lead, again, via the 2-thiocarboxylidene-1,3-dithiolo (CCIIb), to 2,5-diphenyl-6a-thiathiothiophen (CCIVb). In accord with this prediction, a small yield of the thiothiophene was obtained when 4-phenyl-1,2,3-thiazole (CCXXXVIII) was heated with the 1,3-dithiole-2-thione (CCXLI) at 200°C. (SCHEME 16).

It is known that 4,5-benzo-1,2,3-thiazole (CCXLIII) decomposes to give the intermediate (CCXLIV) which adds, as a 1,3-dipole, to the thiocarbonyl group of carbon disulfide to give 4,5-benzo-1,2-dithiole-3-thione (CCXLV).
**SCHEME 17**

(CCXLIII) → [\( \text{benzene} \cdot S \)] → [\( \text{benzene}^{+} \cdot S \)]

(CCXLIV)

(CCXLIII)

(CCXLIII)

(CCXLIII)

(SCHEM 17)

(XXVI)
When the thindiazole (CCXLIII) was heated at 200°C. with 4-phenyl-1,3-dithiole-2-thione (CCXLI), the product obtained was 4,5-benzo-2-thiophenacylidene-1,3-dithiole (XXVI) (SCHEME 17).

This product was shown, in an independent investigation, to be resistant to rearrangement under similar conditions, presumably because rearrangement would involve loss of aromaticity in the benzene ring after the formation of the spiro-intermediate (CCXLVI).

\[
\text{(CCXLVI)}
\]

This reaction, while still not indicating whether or not the reaction involves free radicals or ions (which none of these reactions do), does indicate unambiguously that the sulphur of the reactive intermediate (CCXLIV) adds onto the carbon of the θ-S bond. If it did not then the spiro-intermediate formed would be (CCXLVII) which would lose sulphur to yield the benzothiophenothion (XXXIV)
\[ \text{Scheme 18} \]

\[ \text{(CCXLVIII)} \]
The corollary of these observations is that, if the intermediate (CCV) is formed directly from the acetylene and sulphur, it should be capable of being trapped by systems other than 1,2-dithiole-3-thiones.

Thus it was found that when 4-phenyl-1,3-dithiole-2-thione (CCXLII) reacted with phenylacetylene and sulphur in boiling xylene 4-phenyl-2-thiophenacylidione-1,3-dithiole (CCIIIb) was isolated in low yield presumably via the spiro bis(1,3-dithiole) (CCXLII). (In this case the 1,3-adduct would not be expected to have rearranged appreciably during the relatively short time of reaction). With p-methoxyphenylacetylene and sulphur under similar conditions, 2-phenyl-5-p-methoxyphenyl-6a-thi thiophthion (CCIVA) was obtained. The thiathiophthion was obtained presumably because of the greater tendency to rearrangement of the 1,3-adduct obtained in this case.

Another potential acceptor of the reactive intermediate (CCV) is 4-phenyl-1,2-dithiole-3-thione (XXXVI), which did not react with arylacetylenes alone to give any identifiable product.

No identifiable product was obtained on reaction of this thione with phenylacetylene and sulphur in boiling xylene but the reaction with p-methoxyphenylacetylene and sulphur gave, in low yield, 4-phenyl-2-p-methoxyphenyl-6a-thi thiophthion (CCLVIII). (SCHEME 18)

When 4,5-benzoo-1,2-dithiole-3-thione (XXXVII) was allowed to react with phenylacetylene no identifiable product was obtained. 1,3-Addition would involve the formation of the a-quinonoid product (CCIL) and for this reason is apparently precluded. However, when sulphur was present in the reaction mixture, 5-phenyl-2,3-benzo-6a-thi thiophthion (XXXIV) was obtained in low yield. (SCHEME 19)

These observations justify the postulation of a spiro-intermediate, not only in the sulphur-catalysed cyclo-addition but also in the rearrangement. The dithioles used in the experiments provide one of the dithiole rings
Scheme 20
present in the spiro-intermediate, while the other must be produced by cyclo-addition of the 1,3-dipole (CCV) which, by its very nature, will add to the most polar bond available, namely the C=S bond of the dithioloethione. Huisgen has noted that thiocarbonyl compounds are the only effective trapping agents for 1,3-dipoles of this type (thioacylcarbenes).

d) Orientation of Substitution in Products

The intermediacy of a spiro-compound (CCL) in the rearrangement of the 1,3-adduct (CCIII) is now reasonably well established and it is appropriate to consider the factors that influence the mode by which it decomposes to products. In principle the spiro-compound (CCL) may decompose to give two products, (CCLI) and (CCLII), though, in fact, only the former is observed (SCHEME 20).

This product specificity may be attributed to the fact that the zwitterionic precursor of (CCLII) i.e. (CCIII) has, in one of its canonical forms a thioaldchyl group which thus renders this intermediate much less stable than (CCLIV) which has the much more stable thioaryl group. This pattern of rearrangement has been observed with all 1,3-adducts of the type (CCLV)

\[
\begin{align*}
\text{Ar} & \quad \text{S} \\
& \quad \text{C} \\
& \quad \text{Ar} \\
& \quad \text{X}
\end{align*}
\]

(CCLV)

However, when the 1,3-adduct has an electron withdrawing group as in (CCLVIa,b) then a different pattern is observed. Thus in the case of (CCLVIa) both 6a-thiathiophthiones, (CCLVIIa) and (CCLVIIIa), are produced on rearrangement and indeed the "abnormal" product ethyl 2-phenyl-6a-thiathiophen-4-carboxylate (CCLVIIIa) is the major one. This may be explained by the extra stability of
SCHEME 21

a) R=H
b) R=Ph

EtO₂C

R

SS

Ph

EtO₂C

R

SS

Ph

(CCLVI)

EtO₂C

R

SS

Ph

(CCLVII)

EtO₂C

R

SS

Ph

(CCLVIII)

EtO₂C

R

SS

Ph

(CCLIX)
the intermediate (CCLIXa) conferred by the electron-withdrawing group.

In the case of (CCLVIib) the corresponding intermediate which possesses the greater stability is (CCLIXb). Furthermore, in this case, there is the additional stabilising factor of the thiobenzoyl group compared to (CCLIXa) where there is a thioaldehyde group. Hence, on rearrangement of (CCLVIib), a large excess of (CCLVIIIib) is produced compared with (CCLVIIib). (SCHEME 21)

c) Effect of Vulcanisation Accelerators

A vast amount of study has been devoted to the chemistry of rubber vulcanisation and the effect of accelerators upon it, but because of the overwhelming complexity of the system, there is no unequivocal evidence for any particular mechanism, ionic or radical.

The effect of vulcanisation accelerators upon the rate of the sulphur-catalysed rearrangement of 3-phenyl-2-thiophenacyliden-1,3-dithiole (CCIIIb) was examined. It was found that, as in the vulcanisation process itself, little acceleration occurred unless both accelerator and zinc oxide were present along with sulphur. In the case where the accelerator was itself a zinc salt, zinc dibenzylidithiocarbamate (CCLX), the zinc oxide was not necessary for acceleration. Other accelerators used were 2-mercapto benzothiazole (CCLXI) and tetramethylthiuram disulphide (CCLXII).

Steearic acid, widely used in vulcanisation in conjunction with the other three components, was found to have no effect on the acceleration.

\[
\begin{align*}
\text{(CCLX)}
\end{align*}
\]
Bateman, Gleadbrook and Hooper have proposed a vulcanisation mechanism involving the formation of persulphide ions. 

E.g.

\[
\text{Me}_2\text{N} \equiv \text{S} \rightarrow \text{S} \leftarrow \text{NMe}_2
\]

(CCLXII)

Certainly such a mechanism would be a convenient explanation for the results obtained in this work since the accelerated rearrangement would be explained by the greater concentration of a more powerful sulphur-containing nucleophilic species. On the other hand, even
though this may be an explanation for the effects of accelerators no conclusions can be drawn as to the nature of the species that initiates the rearrangement when accelerators are absent.

The possession of an -SH group is apparently not a sufficient criterion for a compound to have accelerator properties in this system; p-thiocresol (CCLXIII) had no accelerator properties, either with or without zinc oxide.

\[ \text{HS-} \text{Me} \quad \text{(CCLXIII)} \]

Fackler et al.\textsuperscript{104} have prepared a series of sulphur-rich complexes of nickel II and zinc II exemplified by bis (p-porthiostoluto)zinc II (CCLXIV). Such compounds may be formed by reaction of the corresponding dithiocarboxylate complexes (e.g. CCLXV) with sulphur and can be reconverted into these precursors by the action of triphenylphosphine.

\[ \text{Me-} \text{S-} \text{Zn-} \text{S-} \text{Me} \quad \text{(CCLXIV)} \]

\[ \text{Me-} \text{S-} \text{Zn-} \text{S-} \text{Me} \quad + \text{PPh}_3 \rightarrow \quad \text{Me-} \text{S-} \text{Zn-} \text{S-} \text{Me} \quad + \text{PPh}_3 S \quad \text{(CCLXV)} \]
Fackler has suggested that such complexes may be involved in accelerated vulcanisation brought about by zinc dithiocarbamates.

When the sulphur-rich complex (CCLXIV) was heated with the 1,3-adduct (CCIIIb) in boiling xylene, it was found that rearrangement, as rapid as that obtained with sulphur and accelerator present, was induced; the addition of sulphur made no difference to this rate.

It has been reported (see introduction) that the rearrangement is induced by heating with phosphorus pentasulphide in boiling toluol. The effect of phosphorus pentasulphide in xylene solution, as discovered in this work, was to accelerate the rearrangement though not to the same extent as sulphur in the presence of vulcanisation accelerators. The time for rearrangement was unaffected by the presence of added sulphur or by preliminary purification of phosphorus pentasulphide. In all probability, phosphorus pentasulphide, even when purified, contains free sulphur and it is possible that complex polysulphido ions or radicals are formed in solution.

It is convenient at this point to mention the effect of 5-phenyl-1,2-dithiole-3-thione since this compound has been reported to catalyse the rearrangement. When its effect was investigated, it was indeed found to bring about rearrangement but at a much slower rate than did sulphur. It is possible that a mechanism exists, as yet undiscovered, whereby the dithiolethione participates in the rearrangement, though it is noteworthy that its effect as an accelerator of the sulphur-catalysed reaction was only marginal. Another possible explanation, perhaps more likely, is that the thione reacts slowly with oxygen to yield sulphur in a reaction analogous to that of thiobenzophenone (CCLXVI)\textsuperscript{105}.

\[ 2 \text{PhS} + 2 \text{O}_2 \rightarrow 2 \text{PhSO}_2 \text{SPh} \]

(CCLXVI)
an- and thiopyron-4-thione (CCLXVII, X=0,S) have recently been reported to undergo a photosensitized oxidation, to the corresponding oxo-compounds, with liberation of SO which might well disproportionate to SO$_2$ and S.

f) Resistance to Rearrangement

It was found that some 1,3-adducts would not rearrange in solution. Thus the triphenyl adduct (CCIX) only rearranged to an appreciable extent after heating at 200°C for 2 hr. No explanation for this behavior can be offered. The methylthio adduct (CCLXVIII) was also very resistant to rearrangement, requiring 6 hr. at 200°C for appreciable rearrangement. This is presumably accounted for by the reduced electron demand of a dithioester thiocarbonyl group compared to that of a thioketone; this would inhibit nucleophilic attack by a polysulfide species at the 2-position of the 1,3-dithiole ring.

The n.m.r. spectra of the 2-thionocarbonylmethylene-1,3-dithioles indicated that the compounds were mixtures of two geometrical isomers. In the case of (CCIII-), for example, the following isomers were present and the spectrum showed absorptions corresponding to both of these.
The proton on the thiophencyclidenec group appeared as a singlet for one isomer and as a doublet for the other, presumably split by the proton in the 1,3-dithiole ring; a similar effect was observed for the signals from this latter proton.

The effect was more striking in the spectra of (CCXIV) and (CCXVII). In these cases the n.m.r. spectra each showed two singlets corresponding to the methyl groups of the two isomers.

(CCXIV)
It seemed possible that if the n.m.r. spectra were observed at a sufficiently high temperature then the pairs of singlets would collapse to a lone singlet owing to free rotation about the double bond at the higher temperature. However, in all cases, the compounds rearranged to the thiothiophthens in the temperature range 170-180°C. before this effect could be observed.

These observations are in apparent contradiction to the X-ray structure determination reported for 4-(p-bromophenyl)-2-thiophenacylidene-1,3-dithiol (CXCVI) where the single isomer only was observed.

In order to obtain more information on the bond lengths and non-bonding interatomic distances in this class of compounds, and to obviate any complications arising out of geometrical isomerism, 4,5-tetramethylen-2-thiophenacylidene-1,3-dithiol (CCLXIX) was synthesised and prepared for X-ray analysis by slow crystallisation from ethyl acetate. Unfortunately, at the present time, no X-ray results are to hand.
SECTION 2

PART A  Synthesis of Aceno Polysulphides

In conjunction with investigations carried out at I.C.I. Ltd., Petrochemical and Polymer Lab., Runcorn, the synthesis and characterization of polysulphides containing anthracene and naphthalene nuclei was embarked upon.

a) Polythioanthracenes

It is well known that chlorine in chloroanthraquinones is susceptible to nucleophilic attack owing to the activating effect of the quinone carbonyl groups. It seemed possible, therefore, that reaction with sulphur-nucleophiles might provide a starting point for the synthesis of polysulphides of the anthracene series.

Reaction of 1,4,5,8-tetrachloroanthraquinone (CCLXX) with potassium hydrogen sulphide in boiling aqueous ethanol failed but reaction with the stronger nucleophile, sodium sulphide, in boiling aqueous dimethylformamide yielded a green solid with a metallic lustre, which was deposited throughout the course of the reaction. This material was found to be insoluble in a wide range of solvents.

The material was continuously extracted with hot dimethylformamide. This process removed unidentified impurities and the residue was then sublimed at 350°C. Mass spectrometry indicated (exact mass measurement) that the residue obtained from the extraction was anthrac(1,9,8-bdc: 5,10,4-b'c'd'e')bis(thiathiophthon) (CCLXXI) and was indeed more pure than the sublimate. The analytical results, however, indicated that both samples still contained unidentified impurities although the identity of the material was not now in doubt.

Owing to low solubility it was not possible to obtain an n.m.r. spectrum. The compound is formally a bis-thiathiophthon for which canonical structures (CCLXXIa,b) may be drawn but in view of its overwhelming stability and lack of reactivity these would appear to contribute little to
The structure compared to the completely symmetrical form (CCLXXI).

The mode of formation of (CCLXXI) is not at all apparent. Few reactions are known involving the replacement of oxygen in anthraquinones. In these few cases the formation of a bridge by the substituent in the 1-position is involved, thus ring closure of the 1-acetylamino-anthraquinone (CCLXXII) takes place in the presence of dilute sodium hydroxide to yield the pyridone (CCLXXXIII). \(^{129}\)
Me-CO
\[ \text{O NMe} \]
\[ \text{O Br} \]

(CCLXXII) \[ \rightarrow \]

Me-CO
\[ \text{O NMe} \]

(CCLXXIII)

In the reaction of tetrachloroaanthraquinone with sodium sulphide, nucleophilic displacement of chloride will no doubt yield an anthraquinonotetraphthalato anion (CCLXXIV) which could conceivably react with more sulphide ion, oxidatively, to yield a species such as (CCLXXV). A double ring closure would then yield the bis-dithiole (CCLXXVI) and expulsion of two hydroxide ions from this double pseudo-base would give a zwitterionic structure (CCLXXVII) which is merely one of the canonical forms contributing to the resonance hybrid of the observed hexathioanthracene (CCLXXI). Though some or all of the stages involved in this conversion are potentially reversible, the very low solubility of the product will ensure that the reaction proceeds in the forward direction. (SCHEME 22).

When 1,5-dichloroaanthraquinone (CCLXXVIII) reacted with sodium sulphide under similar conditions the product, obtained only after acidification, was 1,5-dimercaptoanthraquinone (CCLXXIX).

Since, in this case, no stable thiothiophen system can be formed the quinone structure is retained in the product.
(CCLXXIX) reacted with phosphorus pentasulphide to yield products which were initially presumed to be the salts (CCLXXX, X=Cl\(^-\), ClO\(_4\)^-). This structure was suggested on the basis of mass spectrometry (M\(^+\)=302) and the fact that acidification of the reaction mixture was necessary in order to obtain the products. However, the analytical results for the products indicated that these anions were not present and that the compounds obtained were more likely to be very impure samples of the bis-dithiolc, anthra(1,9-bc:5,10-b'c')bis(dithiole)(CCLXXXI). This did not allow for any other purification attempts to be made.
The reaction of 1,8-dichloroanthraquinone (CCLXXXII) with sodium sulphide yielded 5-oxo-5H-anthra
(1,8-bisoctothiophthen (CCLXXXIII) which was identified by mass spectrometry, n.m.r. and elemental analysis. This
compound was more soluble than the hexothioanthracone (CCLXXI) and acted as a bright-green dye for Nylon yarn
though the colour, unfortunately, was not stable to light. It is possible to envisage its formation by a route similar to
that suggested for the hexothioanthracone (CCLXXI) though no explanation can be offered for the fact that addition of
acid was necessary in order to precipitate the product.

\[
\begin{array}{c}
\text{Cl} \quad \text{O} \quad \text{Cl} \\
\text{S-S-S}
\end{array}
\]

(CCLXXXII) \hspace{1cm} (CCLXXXIII)

In 1930, von Weinberg, investigating the
reaction between anthracone (CCLXXXIV) and sulphur mono-
chloride, isolated a compound with the empirical formula C_{14}Cl_4S_6, possibly a tetrachloro-derivative of the bis-
thioanthracone (CCLXXI). This reaction was re-investigated
using boiling 1,2,4-trichlorobenzene as solvent. The first
product isolated was 9,10-dichloroanthracone (CCLXXXV) but
when the reaction was allowed to continue for a longer time
dark green needles were produced. This material, as indicated
by mass spectrometry and elemental analysis had the formula
C_{14}Cl_4S_6. The same material was obtained in an independent
reaction using 9,10-dichloroanthracone as starting material.
The product had many similarities to the bis-thiathiophthlen (CCLXXI); thus it was insoluble in a large variety of solvents. Although no evidence other than that cited above was obtainable it seemed reasonable to assign the structure 2,3,6,7-tetrachloroanthra(1,9,8-bede: 5,10,4-b'c'd'e')bis(thiathiophthlen) (CCLXXXVI) to this material.

The initial isolation of 9,10-dichloroanthracone (CCLXXXV) is analogous to the isolation of 9,11-dichlorotetracene (CLXXV) by Marschalk in his preparation of tetracene tetrasulphide (CLXXXIII). The mechanism of formation of (CCLXXXVI) is again not clear but, since sulphur must be released when the anthracone is chlorinated, it is possible to envisage a subsequent displacement of chlorine by polysulphur radicals, resulting in a species
such as (CCLXXXVII).

Homolytic fission of these pendant chains and intramolecular free-radical substitution at the peri-positions could then give an anthra bis-dithiolo which, by further substitution of a similar type, could be converted into the observed product.

b) Polythionaphthalenes

Naphthalene-1,8-disulphide (CCLXXXVIII) is a known compound\textsuperscript{131,132} but there is no report of the
corresponding \textit{1,4,5,8-tetra-sulphido-naphtho(1,8\text{-cd:} 5,4\text{-c\text{'}d\text{'}})bis(dithiole)} (CCLXXXIX).

The synthesis of this compound was attempted by a variety of routes, none of which were successful.

i) \textit{From 1,5-Diaminonaphthalene}

1,5-Dibromonaphthalene (CCXC) was prepared by a Sondmeyer reaction from 1,5-diaminonaphthalene (CCXCI). This compound was then nitrated yielding 1,5-dibromo-4,8-dinitronaphthalene (CCXCII). At this stage it was hoped to utilize an extension of the known reaction whereby 1,4,5,8-tetrachloronaphthalene (CCXCI) is obtained from 1,5-dichloro-4,8-dinitronaphthalene (CCXCIV) by reaction with phosphorus pentachloride.
Unfortunately the analogous reaction using phosphorus pentabromide failed to give the required product, 1,4,5,8-tetrabromonaphthalene (CCXCV).

Thus the final stages in the reaction sequence, which were to have involved reaction with cuprous n-butylmercaptide, dealkylation and oxidation, could not be attempted. Aryl chlorides are reported to be unreactive towards cuprous n-butylmercaptide\textsuperscript{133}.

Attempted thiocyanation of 1,5-diamino-naphthalene (CCXCI), again using reactions known in the benzene series\textsuperscript{120,121}, also failed.

ii) From Naphthalene-1,5-dithiol

The production of the chlorodisulphides (CEXCVI) from benzonodithiols (CCXCVII) by reaction with sulphur dichloride has been reported recently\textsuperscript{124}. However
the corresponding reaction in the naphthalene series, starting with naphthalene-1,5-dithiol (CCXCVIII), did not occur under the conditions reported for benzene derivatives. Time did not allow further investigation of this reaction under more vigorous conditions.

![Chemical structure](image1)

(CCXCVII) \[ \text{CCH} \rightarrow \text{SSCl} \]

(CCXCVI) \[ + 2\text{HCl} \]

iii) From Naphthazarin

Treatment of naphthazarin (CCLC) with phosphorus pentasulphide, under a variety of conditions, failed to yield the required product. This may be due to the susceptibility to attack of the olefinic double bond in the 1,4-quinone ring.
(CCIC)
Leaver and Rawlings described the four-sulphur system (CLXXI) and concluded, on the basis of chemical evidence and n.m.r. spectra, that isomeric thioacyl compounds (CLXXII, $R_1/R_2$) are interconvertible but that the tautomeric equilibrium is not rapidly established (on the n.m.r. time-scale) at room temperature (see introduction).

\[ \text{(CLXXI)} \]

\[ \text{(CCC)} \]

However, these observations may not be giving a valid indication of whether or not single-bond/no-bond resonance can occur in this system since it is possible that the preferred conformations of the compounds are such that there can be no interaction between the thione-sulphur atoms (CCC).

\[ \text{(CCCI)} \]

\[ \text{(CCCII)} \]

\[ \text{(CCCIII)} \]
SCHEME 23
In the compounds (CCCI), (CCCII), (CCCIII), (CCCV), the conformations are fixed in favourable orientations and it was hoped that their synthesis and subsequent study would throw light on the possibility of single-bond/no-bond resonance in this system.

The reaction scheme proposed for the preparation of indeno(3,2-c)-1,2-dithiolo-3,4-dithione (CCCII) is typical of those proposed for the first four of these compounds. (SCHEME 23)

The first stages of the projected syntheses involve the known reaction of 2-methylthio-1,3-dithiolanium methosulphate (CCCVI) with compounds containing activated methylene groups such as indeno-1,3-dione (CCCVII). It was then hoped that reaction of phosphorus pentasulphide with the products of these condensations, exemplified by 2-(1,3-dithiolan-2-ylidene)indeno-1,3-dione (CCCVIII), would replace the oxygens with sulphur and remove the ethylene bridges as in the known synthesis of 1,2-dithiolo-3-thiones from dithiolanlylideneketones.

The starting material in the preparation of (CCCI) was dimedone (CCCIX) and reaction with the salt (CCCVI) yielded 2-(1,3-dithiolan-2-ylidene)-5,5-dimethylcyclohexano-1,3-dione (CCCX) (as reported by Mayor and Schaefer). However, this dione, on reaction with phosphorus...
pontasulphide, yielded a dark brown tar which could not be crystallized.

The reaction may have failed because the expected product (CCCI) lacks the stabilization afforded by the presence of fused aromatic or heteroaromatic rings.

Reaction of the indanodione derivative (CCCVIII) with phosphorus pontasulphide yielded, surprisingly, 2-(1,3-dithiolan-2-ylidone)indano-1,3-dithione (CCCXI) in which the ethylene bridge was retained.

More vigorous thermal treatment either failed to remove the bridge (boiling in 1,2,4-trichlorobenzene) or caused decomposition (sublimation at 275°C.).

Reaction of 2,3-dihydro-1H-phenalono-1,3-dione (CCCXII) with the methylthiodithiolanium salt (CCCVI) gave 2-(1,3-dithiolan-2-ylidone)-2,3-dihydro-1H-phenalono-1,3-dione (CCCXIII) which proved resistant to sulphurization with pure or with "crude" phosphorus pontasulphide in xylene,
pyridino or 1,2,4-trichlorobenzene. Possibly the carbonyl groups are more sterically hindered in this compound than they are in the indanodione derivative.

\[ \text{(CCCXII)} \]

\[ \text{(CCCXIII)} \]

The starting material for the synthesis of (CCCIV) was 1,3-dimethyl barbituric acid (CCCXIV). Again this condensed with the methylthiodithiolanium salt (CCCVI) to yield the expected product, 5-(1,3-dithiolan-2-ylidene)-1,3-dimethylthioxohydropyrimidine-2,4,6-trione (CCCXV, X=O). On reaction with phosphorus pentasulphide partial sulphurization took place to yield 5-(1,3-dithiolan-2-ylidene)-1,3-dimethyl-2-thioxohydropyrimidine-4,6-dione (CCCXV, X=S). This material was resistant to further sulphurization.

\[ \text{(CCCXIV)} \]

\[ \text{(CCCXV, X=O, S)} \]
SCHEME 24
Thus, in none of these four cases did it prove possible to obtain a product of the required constitution. No further routes to these materials were investigated.

Several routes to 1,2,5,6-tetrathiapentalene-3,4-dithione (CCCV) were investigated but none of these were successful.

It was proposed that 1,1,1-trichloro-2-methylpropen-2-ol (CCCXVI) might give the required product in a single stage (Scheme 24). This proposition was an extension of the results of Brown who obtained 5-mercapto-4-phenyl-1,2-dithiole-3-thione (CCCXVII) by reaction of 2-phenylpropane (CCCXVIII) with sulphur in boiling dimethylformamide.

Replacement of the phenyl group by the trichloromethyl group introduces the possibility of further reaction, via a dithioacid, to the required product. However, the product isolated from the reaction was 5-mercapto-4-methyl-1,2-dithiole-3-thione (CCCXIX). The labile trichloromethyl group has reacted first and the methyl group has been retained.
Attempted preparation of 4-butoxycarbonyl
−5-mercapto-1,2-dithiole-3-thione (CCCXX), again by the
method of Brown, from n-butyl methacrylate (CCCXI) and
sulphur, gave a black tar.

\[
\begin{align*}
\text{CO}_2\text{nBu} & \\
\text{CCCXI} & \\
\end{align*}
\]

Another approach to (CCCV) involved the
initial preparation of 4-ethoxycarbonyl-5-amino-1,2-dithiole
−3-thione (CCCXXII) according to the method of Gewald.

\[
\begin{align*}
\text{H}_2\text{N} & \\
\text{CCCXXII} & \\
\end{align*}
\]

Reaction of the aminedithiolethione (CCCXXII)
with phosphorus pentasulphide and with sodium sulphide gave
small amounts of a yellow oil and sulphur respectively.
Diazotisation of (CCCXXII) also yielded sulphur as the only
identifiable product.

Finally, the compounds diethyl 1,3-dithiolan
−2-ylidene malonate (CCCXXIII) and diethyl dimercapto-
methylene-malonato (CCCXXIV) were prepared, according to
established procedures, from diethyl malonate.

However, sulphurization of these materials
with phosphorus pentasulphide, under various conditions,
failed to produce the desired product.
(CCCXXIII)  

(CCCXXIV)
EXPERIMENTAL
Notes

1) The following instruments were used for obtaining spectroscopic data:
   - **I.R.** Unicam SP200 Infrared Spectrophotometer.
   - **N.M.R.** Varian HA100 NMR Spectrometer.
   - **Mass** A.E.I. MS902 Mass Spectrometer.

2) The alumina used for the column chromatography was 'Activated Alumina Type H' from Leporte Industries Ltd.

3) The melting points quoted are uncorrected.
SECTION 1 Cyclo-addition Reactions of 1,2-Dithiole-3-thiones

and Rearrangements of 2-Thiophencarboxylidene-1,3-dithioles and Related Reactions

1) Dithiolethiones

   a) 3,3-Dimercapto-1-arylprop-2-en-1-ones

   The method used was a modification of that of Thuillier and Viaille. The procedure used for the phenyl
   compound is typical.

   Sodium hydrate (9.8g, 50% oil dispersion) was suspended in benzene (155ml, Na dried) and t-butyl
   alcohol (20ml.) was added dropwise with stirring. A vigorous
   reaction occurred and stirring was continued for 30min. To
   the resulting grey mass were added acetoephone (45ml.) and
   then hydrogen disulphide (24ml.) dropwise with stirring. An
   immediate reaction took place to give an orange mass which
   was allowed to stand for about 12 hrs. Water (ca. 300ml.)
   was then added wherupon the orange solid dissolved. The
   aqueous fraction was separated, extracted with ether (2x100ml.)
   and acidified (after addition of ice) with concentrated
   sulphuric acid. The yellow product which precipitated was
   extracted into ether and the extract was dried. Removal of
   the solvent gave orange crystals of 3,3-dimercapto-1-phenyl-
   prop-2-en-1-one which were washed with a little light
   petroleum (b.p. 60-80°C).

   Yield = 21g. (230)
   m.p. = 60-63°C. (lit. m.p. = 63°C.)

   The same procedure was used for the preparation
   of:

   3,3-dimercapto-1-(p-bromophenyl) prop-2-en-1-one
   (42g) m.p. = 105-107°C. (lit. m.p. = 105°C.)

   3,3-dimercapto-1-(p-methoxyphenyl) prop-2-en-1-one
   (30g) m.p. = 96-97°C. (lit. m.p. = 98°C.)

   b) 5-Aryl-1,2-dithiole-3-thiones

   Prepared from the corresponding 3,3-
   dimercapto-1-arylprop-2-en-1-ones and phosphorus pentasulphide
in pyridine by the method of Thuillier and Vielle\(^6\):

5-phenyl-1,2-dithiole-3-thione (45\(^*\))

\[ \text{m.p.} = 125-127^\circ \text{C.} \quad (\text{lit. m.p.} = 125-127^\circ \text{C.}) \]

5-(p-bromophenyl)-1,2-dithiole-3-thione (47\(^*\))

\[ \text{m.p.} = 128-130^\circ \text{C.} \quad (\text{lit. m.p.} = 130-131^\circ \text{C.}) \]

5-(p-nitrophenyl)-1,2-dithiole-3-thione (93\(^*\))

\[ \text{m.p.} = 109^\circ \text{C.} \quad (\text{lit. m.p.} = 109^\circ \text{C.}) \]

c) 4-Methyl-5-phenyl-1,2-dithiole-3-thione

Prepared by the reaction of \(\beta,\beta\)-dimethyl-styrene with sulphur in dimethylformamide.

i) \(\beta,\beta\)-Dimethylstylene

Phenyl magnesium bromide was prepared from bromobenzene (31.4g., 0.2 molo) and magnesium (5g., 0.2 molo) in ether (70ml.).

The flask was cooled and a solution of isobutyraldehyde (11.5g., 0.16 molo) in ether (20ml., \(\text{Na} \) dried) was added dropwise, with swirling, at such a rate that the mixture just refluxed. Finally the mixture was refluxed on a water bath for 15 min. When cool the mixture was poured onto a mixture of ice (ca.150g.) and 10% sulphuric acid (100ml.). The aqueous layer was separated and extracted with ether and the two etheral layers were combined, washed with 10% sulphuric acid and water, and dried. Removal of the ether gave a pale yellow oil (23.7g.) which was identified by n.m.r. and i.r. as 1-hydroxy-1-phenyl-2-methylpropane. The alcohol was dehydrated by refluxing overnight in 10% hydrochloric acid (300ml.) and the olefin was then obtained by steam distillation. The olefin was identified by n.m.r. and i.r. spectroscopy as \(\beta,\beta\)-dimethylstylene and was used without further purification.

ii) 4-Methyl-5-phenyl-1,2-dithiole-3-thione

The olefin (13.2g., 0.1 molo) and sulphur (8g., 0.25 molo) were refluxed in dimethylformamide (ca.50ml.) for 4 days. After this time t.l.c. gave a single orange spot. The solvent was removed and the residual orange oil
crystallized on cooling to give an orange solid which was purified by chromatography, using benzene as eluant, and recrystallization from acetone to give chunky orange plates.

Yield = 19.5 g. (87.1\%)

m.p. = 114°C. (lit. m.p. = 114–115°C.11).

d) 5-(t-butyl)-4-neopentyl-1,2-dithiole-3-thione

Prepared by a modification of the method of Spindt, Stevens and Baldwin.107

Sulphur (8 g., 0.25 mole) was dissolved in dimethylformamide (ca. 50 ml.) and di-isobutene (11.2 g., 0.1 mole) was added slowly to the refluxing solution. The solution rapidly became dark and, during the course of 48 hrs. under reflux, the colour changed from a dark bluish-grey to a dark brownish-orange. After cooling the solvent was removed and the residue, an orange oil, was chromatographed on alumina using benzene as eluant. An orange band gave, on removal of solvent, deep orange crystals which were dissolved in the minimum amount of cold benzene and filtered to remove unreacted sulphur. The orange solid was shown, by n.m.r. spectroscopy, to be a 50:50 mixture of 4-neopentyl-1,2-dithiole-3-thione and 5-(t-butyl)-4-neopentyl-1,2-dithiole-3-thione. No further attempt was made to separate the components of the mixture.

Yield = 11 g. (54\%)

c) 5-(t-Butyl)-4-neopentyl-1,2-dithiole-3-thione

Prepared from tri-isobutene and sulphur in dimethylformamide, a modification of the method of Landis and Hamilton.108

Tri-isobutene (16.8 g., 0.1 mole) was added dropwise to a boiling solution of sulphur (16 g., 0.5 mole) in dimethylformamide (ca. 50 ml.). After a further 4 days under reflux the solvent was removed and the resulting red oil distilled under reduced pressure (oil pump). A small amount of tri-isobutene (ca. 2 g.) was collected followed by a red oil (12.8 g., 56\%) which was identified by n.m.r. spectroscopy as 5-(t-butyl)-4-neopentyl-1,2-dithiole-3-thione.
b.p. = 155-170°C./1 mm.Hg
(lit. b.p. = 155-185°C./1-3 mm.Hg

f) 4,5-Tetramethylene-1,2-dithiole-3-thione
Prepared by the method of Meyer et al. 109
from 1-pyrrolidinocyclohexone, carbon disulphide and sulphur.
Yield = 19.5 g. from 30 g. amino (52%)
m.p. = 100-101°C. (from acetone)
(lit. m.p. = 102°C.)

g) 4-Phenyl-1,3-dithiole-2-thione
Prepared by the method of Leaver et al. 110
By reaction of O-ethyl S-phenyl dithiocarbonate with
phosphorus pentasulphide in tetralin. The tetralin was
removed under reduced pressure (oil pump) and the residue
chromatographed on alumina with benzene as eluant. A yellow
band yielded 4-phenyl-1,3-dithiole-2-thione which, on
recrystallization from acetone, gave pale yellow needles (77%).
m.p. = 116-117°C. (lit. m.p. = 117-118°C.)

2) Substituted Acetylenes

c) p-Methoxyphenylacetylene
Prepared by a modification of the method of
Bodendorf and Meyer 111.
p-Methoxyacetophenone (15 g., 0.1 molar)
was dissolved in dimethylformamide (20 ml.) and phosphoryl
chloride (12 ml., 0.13 molar) was added dropwise with stirring
so that the temperature of the reaction mixture did not
exceed 60°C. Stirring was continued for 4 hr. and the resulting
brown, clear, viscous liquid was allowed to stand overnight.
This liquid was dissolved in water and a concentrated
aqueous solution of sodium acetate (6 g.) was added dropwise
with stirring. Stirring was continued for 1 hr. and the
solution allowed to stand for 24 hr. during which time
orange crystals were precipitated. The solid was filtered off
and a further crop was obtained by keeping the filtrate.
Yield = 9.86 g. (50%)
The orange crystals were shown, by n.m.r.
spectroscopy, to be 3-chloro-3-(p-methoxyphenyl)prop-2-enyl.
No further purification was attempted.

The chloroaldehyde (2g.) was dissolved in dioxan (20ml.) and the solution heated to boiling. A hot solution of sodium hydroxide (4g.) in water (10ml.) was added drop-wise and the temperature maintained for 1 hr. During this time the colour of the solution changed from orange to red-brown. The solution was then steam-distilled until the distillate became clear. The combined distillate was extracted with ether to give p-methoxyphenylacetylene which did not crystallise immediately, probably owing to the presence of residual dioxan.

Yield = 0.82g. (61.6)

m.p. = 30°C. (lit. m.p. = 31-32°C.)

b) Diphenylenecetylene

Prepared by the method of Smith and Falkoff.112

Yield = 15.4g. from 30g. of trans-stilbene (52%) m.p. = 60°C. (lit. m.p. = 60-61°C.)

3) Decarboxylation of 2-Thiophencarboxylic ester-1,3-dithiole-4-
carboxylic acid

The acid was prepared by the method of Bohringor et al.10

Yield = 8g. from 10g. of potassium salt (60%)

m.p. = 175-190°C. (decomp.)

(lit. m.p. = 185-190°C. (decomp.)

The decarboxylation was carried out by three methods:

c) Heating without solvent

The acid (1.5g.) was heated for 10 min. at 200°C. A dark brown tar was produced which was chromatographed on alumina with benzene as eluant to give:

i) a rod solid (0.03g., m.p. 134°C., from light petroleum b.p. 80/100°C.) which was shown to be identical (mixed m.p.,
i.r. and n.m.r. spectra) with an authentic sample of 2-phenyl-6a-thiothiophthen.

ii) an orange solid (0.06g., m.p. 123-124°C (from acetone) identical with an authentic specimen of 5-phenyl-1,2-dithiolo-3-thione (mixed m.p., i.r.).

b) Refluxing in 2,6-lutidine

The acid (1.5g.) was refluxed in 2,6-lutidine (ca. 25 ml.) for 1 hr. After this time the solution was acidified with dilute hydrochloric acid and extracted with ether. The brown tarry residue obtained on removal of the ether was chromatographed as in c) and the same red (0.1g.) and orange (0.2g.) compounds were obtained.

c) Sublimation

The acid (1.5g.) was mixed with an equal volume of sand and heated in a sublimation apparatus to 200°C. Before this temperature was reached the apparatus was evacuated at the pump. The temperature was maintained until sublimation had ceased (ca. 4 hr.). The sublimate was chromatographed as in a) and the same red (0.08g.) and orange (0.18g.) compounds were obtained.

4) Decarboxylation of 2-(p-bromo)thiophenacylidene-1,3-dithiolo-2-carboxylic acid

The acid was prepared from 5-(p-bromo-phenyl)-1,2-dithiolo-3-thione and acetylenedicarboxylic acid, monopotassium salt, by the method of Ehringer et al. 10

Yield = 9.6g. from 15g. potassium salt (71%)

m.p. = 180-195°C. (decomp.)

The acid was used without further purification.

Similar procedures were followed as described in the previous section. In all cases there was obtained a red solid, 2-(p-bromophenyl)-6a-thiothiophthen and an orange solid, 5-(p-bromophenyl)-1,2-dithiolo-3-thione.

a) Yield red solid = 0.08g.

m.p. = 174-175°C. (from ethyl acetate)
It)

Yield thiathiophthone = 0.09g.
Yield dithiolothione = 0.24g.

5) Ethyl 2-thiophenesulfonyl-1,3-dithiol-4-carboxylate

a) Preparation

5-Phenyl-1,2-dithio-3-thione (3g.) and ethyl propiolate (2.3g.) (molar ratio 1:2) were heated in boiling benzene (50ml.) for 5hr. The solution was then reduced in volume to ca. 10 ml. and chromatographed on alumina using benzene as eluant. A greenish-brown band on evaporation, gave bronze crystals of ethyl 2-thiophenesulfonyl-1,3-dithio-4-carboxylate.

Yield = 3.2g. (72.7%)

m.p. = 159-160°C. (from ethanol)

C_{11}H_{17}BrS_{3} Requires 41.91 2.22 30.48 25.40
Found 41.62 2.31 30.41 25.36

b) Rearrangement

i) Heating in the absence of solvent

The adduct (0.5g.) was heated at 200°C for 15 min. and the product was chromatographed on alumina using benzene as eluant. While the column was being developed it was protected from light in order to prevent irreversible adsorption which was probably due to light-assisted hydrolysis of ester groups in the products. From the column was obtained:

Firstly, an orange band yielding an orange-red solid which recrystallized from ethanol to give orange-red plates of ethyl 5-phenyl-6-thiophenothione-3-carboxylate.

Yield = 0.25g. (40.4%)

m.p. = 116-117°C.
Secondly a rod band yielding a rod solid which recrystallized from ethanol to give deep red needles of ethyl 5-phenyl-6-thiophen-2-carboxylate.

Yield = 0.15 g. (30%)

m.p. = 111-112°C.

\[ \text{C}_{14} \text{H}_{12} \text{O}_{2} \text{S}_{3} \]

\[ \text{C} \quad \text{H} \quad \text{S} \]

Requirements:

<table>
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<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>Required</td>
<td>54.54</td>
<td>3.90</td>
<td>31.17</td>
</tr>
<tr>
<td>Found</td>
<td>54.59</td>
<td>3.98</td>
<td>30.69</td>
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</table>

ii) Refluxing in xylene in the absence of sulphur

The adduct (0.1 g.) was heated in boiling xylene (12.5 ml. S free). The reaction was followed on t.l.c. which showed no rearrangement to have taken place during 3 days.

iii) Refluxing in xylene in the presence of sulphur

The above reaction was repeated with sulphur (0.1 g.) present. Complete rearrangement, to give the two isomeric 6-thiophenethiones mentioned above in the same ratio, was observed after 15 hr.

6) Rerarrangement of Ethyl 5-phenyl-2-thiophenovlidene-1,3-dithiole-4-carboxylate

a) Heating in the absence of solvent

The 1,3-adduct (0.1 g.) was heated at 200°C. for 3 hr. The product was then chromatographed on alumina with benzene as eluent to give:

i) A bright red band which gave a red solid. Crystallization from ethyl acetate gave red plates of ethyl 2,5-diphenyl-6-thiophen-3-carboxylate, identical (mixed m.p. and i.r. spectrum) with a specimen synthesized as described later.

Yield = 0.029 g. (29%)

m.p. = 136-137°C.

\[ \text{C}_{20} \text{H}_{16} \text{O}_{2} \text{S}_{3} \]

\[ \text{C} \quad \text{H} \quad \text{S} \]

Requirements:

<table>
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<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>Required</td>
<td>62.50</td>
<td>4.17</td>
<td>25.00</td>
</tr>
<tr>
<td>Found</td>
<td>62.56</td>
<td>4.06</td>
<td>24.69</td>
</tr>
</tbody>
</table>
ii) A deeper rod band which gave a red solid. Crystallization from ethyl acetate gave deep red needles of ethyl 3,5-diphenyl-6α-thiothiophthen-2-carboxylate.

Yield = 0.006 g. (6%)

m.p. = 130-131°C.

C H S
C₂₀H₁₆O₂S₃  Require 62.50 4.17 25.00
Found 62.61 4.11 24.64

N.B. The chromatography column was wrapped with silver foil to prevent irreversible adsorption.

b) Refluxing in Xylene

The 1,3-adduct (0.1g.) was heated in boiling xylene (ca. 12.5 ml.) both in the absence and in the presence of sulphur (0.01g.). In both cases no rearrangement was observed after 3 days.

c) Synthesis of Ethyl 2,5-diphenyl-6α-thiothiophthen-3-carboxylate

Ethyl 2-benzoyl-2-(5-phenyl-1,2-dithiol-3-ylidene) acetoate (0.03g.) and phosphorus pentasulphide (0.1g.) were refluxed in benzene (25 ml.) for 4 hr. The solvent was partially removed and the concentrated residue was chromatographed on alumina with benzene as eluent to give:

i) A red band yielding a red solid which crystallized from ethyl acetate to give ethyl 2,5-diphenyl-6α-thiothiophthen-3-carboxylate (0.02g.), bright red plates, m.p. 136-137°C.

ii) A faint rod band which gave a very small amount of a non-crystalline rod material which was not identified.

7) Decarboxylation of 2-(1-Carboxy-1,3-dithiol-2-ylidene) cyclopentanethione

The acid was prepared by the method of Behringer et al.¹⁰

Yield = 0.22g. from 0.2g. of 4,5-trimethyleno-1,3-dithiole-3-thione (78%).

m.p. = 189-193°C. (lit. m.p. = 191-196°C.)

The acid was decarboxylated by the method of
Bohringer et al.\(^{10}\) The product consisted of dull red needles (m.p. = 134\(^\circ\)-135\(^\circ\)C.) which were identified by n.m.r. spectroscopy as 2-(1,3-dithiol-2-ylidene)cyclopentanone-thione.

Yield = 0.16g. from 0.2g. of acid (61%).

8) **Attempted Preparation of 2-(\(-\text{Carboxy}-1,3\)-dithiol-2-ylidene)cyclohexanethione**

4,5-Tetramethyl-1,2-dithiole-3-thione (0.2g.) and propionic acid (0.08g.) were reacted according to the procedure of Bohringer et al.\(^{10}\). A black tarry solid (0.18g.) was produced which had a poorly defined i.r. spectrum and, on sublimation, gave no identifiable products.

9) **Preparation of 4,5-Tetramethyl-2-thiophenecarboxylidene-1,3-dithiole**

a) **2-Butenocyclohexanone**

Prepared by the method of Belcher, Hoyle and West\(^{113}\).

Yield = 5.2g. from 50g. of cyclohexanone (58%).

b) **Cyclisation**

3,3-Dimercaptopropano-1-phenylprop-2-on-1-one (3.92g.) and sodium bicarbonate (1.68g.) were suspended in ethanol (50 ml.) and bromocyclohexanone (3.54g.) was added. The mixture was stirred for 24 hr. and the yellow crystals which had deposited were filtered off.

Yield = 3.36g.

m.p. = 1.14-1.15\(^\circ\)C.

c) **Reaction with Hydrogen Chloride**

The yellow compound, obtained above, was dissolved in dry chloroform (500 ml.) and dry hydrogen chloride was bubbled through the solution for 3 hr. at room temperature. The solution was then washed with water, dried, and evaporated to dryness. The orange solid obtained was chromatographed on alumina with benzene as eluant to give a yellow band which yielded orange crystals (2.1g.).

This product was dissolved in hot ethanol and filtered when a pale yellow solid (0.52g.) was obtained which was identified by i.r. spectrum as 2,4-bis(phenecarboxylidene)-1,3-dithiacyclo-
The filtrate yielded orange crystals (1.5 g.) the n.m.r. spectrum of which was in general agreement with the structure of 4,5-tetramethylen-2-phenacylidene-1,3-dithiole.

d) Sulphurisation

The keto-compound (0.3 g.), obtained above, and phosphorus pentasulphide (1 g.) were heated in boiling benzene (25 ml.) for 15 min. The solution was reduced in volume and chromatographed on alumina with benzene as eluant to yield a red-brown band which gave a dark red solid (0.19 g., 60%) which was identified as 4,5-tetramethylen-2-thiophenacylidene-1,3-dithiole by n.m.r. spectroscopy and by thermal rearrangement to a thiathiophene (see below).

m.p. = 163 °C. (from ethyl acetate).

C\(_{15}\)H\(_{14}\)S\(_3\) Requires 62.07 4.83 33.11

Found 62.22 4.71 32.89

e) Rearrangement

The 1,3-adduct (0.05 g.) was heated at 200°C for 20 min. The product was chromatographed on alumina with benzene as eluant to yield a red solid (0.03 g., m.p. = 153–154°C) identical (mixed m.p., i.r.) with 2-phenyl-4,5-tetramethylen-6a-thiathiophene.

10) Cycloaddition Reactions of Arylacetylenes and Dithioclethiones

In all cases the procedure adopted was identical. The detailed results are shown in TABLE 1. The melting points and analysis results for new compounds are tabulated along with the n.m.r. spectra.

The 1,2-dithiole-3-thione and the acetylene in the molar ratio 1:2 were heated in boiling xylene (ca. 50 ml./0.0125 mole dithioclethione). The reaction mixture was reduced in volume and chromatographed on alumina with benzene as eluant to give:

- a) a bright red band which consisted of the 6a-thiathiophene.
b) a yellow band which consisted of recovered dithiolethione.
c) a red-brown band which consisted of the 2-thioethyl-
methylene-1,3-dithiole. In the cases of this band moving
slowly, it was eluted with ether.

The first group of reactions shown in the table was carried out in the absence of sulphur and the
second in the presence of a catalytic quantity (ca. 0.01g./
10 ml, xylene).

The yields given are based on the amount of
dithiolethione consumed.
Reactions carried out in the absence of sulphur:

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>% Recover. (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
<td>2.5</td>
</tr>
<tr>
<td>$p$-NOOC$_6$H$_4$</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>$p$-NOOC$_6$H$_4$</td>
<td>5.8</td>
</tr>
<tr>
<td>2-pyridyl</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
<td>1</td>
</tr>
<tr>
<td>2-pyridyl</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
<td>40.4</td>
</tr>
<tr>
<td>2-pyridyl</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
<td>82.7</td>
</tr>
<tr>
<td>$p$-NO$_2$C$_6$H$_4$</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
<td>61.5</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
<td>47.1</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>Mo</td>
<td>Ph</td>
<td>34.2</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
<td>S$_2$Mo</td>
<td>10.9</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>Mo</td>
<td>t-Bu</td>
<td>0</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>CH$_2$C(Mo)$_3$</td>
<td>t-Bu</td>
<td>30.8</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>COC$_6$H$_4$OMo</td>
<td>Ph</td>
<td>3.1</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>$-(CH=CH)_2$-</td>
<td>Ph</td>
<td>46.4</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>$-(CH_2)_3$-</td>
<td>Ph</td>
<td>30.2</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>$-(CH_2)_4$-</td>
<td>Ph</td>
<td>12.0</td>
</tr>
<tr>
<td>Yield (B)</td>
<td>Yield (C)</td>
<td>Time</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>-------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>&lt;1</td>
<td>5 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>1.5</td>
<td>3 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>10.5</td>
<td>7 hr.</td>
<td>g, a, b, c, g</td>
<td></td>
</tr>
<tr>
<td>34.4</td>
<td>6.3</td>
<td>3 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>21.6</td>
<td>1.1</td>
<td>40 min</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>9.4</td>
<td>28.1</td>
<td>1 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>0</td>
<td>9 hr.</td>
<td>c, c, g</td>
<td></td>
</tr>
<tr>
<td>32.8</td>
<td>4.5</td>
<td>1 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>13.6</td>
<td>0</td>
<td>7 hr.</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>36.7</td>
<td>&lt;1</td>
<td>18 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>39.4</td>
<td>&lt;1</td>
<td>8 hr.</td>
<td>d, c, g</td>
<td></td>
</tr>
<tr>
<td>17.6</td>
<td>4.2</td>
<td>6 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>60.2</td>
<td>&lt;1</td>
<td>14 hr.</td>
<td>e, c, g</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>16.2</td>
<td>4 hr.</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>18.0</td>
<td>5 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>35.7</td>
<td>18.7</td>
<td>3 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>60 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>75.6</td>
<td>0</td>
<td>3 hr.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>73.7</td>
<td>4 hr.</td>
<td>g</td>
<td></td>
</tr>
</tbody>
</table>
Reactions carried out in the presence of sulphur: 

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>$%$ Recov. ($A$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$\text{p-MoOC}_6\text{H}_4$</td>
<td>H</td>
<td>Ph</td>
<td>5.8</td>
</tr>
<tr>
<td>H</td>
<td>$\text{p-MoOC}_6\text{H}_4$</td>
<td>H</td>
<td>Ph</td>
<td>0.3</td>
</tr>
<tr>
<td>H</td>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
<td>1.2</td>
</tr>
<tr>
<td>H</td>
<td>2-pyridyl</td>
<td>H</td>
<td>Ph</td>
<td>25.3</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
<td>40.4</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
<td>31.7</td>
</tr>
<tr>
<td>H</td>
<td>Ph</td>
<td>$-(\text{CH}_2\text{CH})_2-$</td>
<td></td>
<td>34.3</td>
</tr>
<tr>
<td>H</td>
<td>Ph</td>
<td>$-(\text{CH}_2)_3-$</td>
<td></td>
<td>30.7</td>
</tr>
</tbody>
</table>

**Notes on Tables**

a) These reactions were also carried out using chlorobenzene as solvent when essentially the same results were obtained.

b) Repeat of Bohringer's reaction using 1.5 m ole $\text{p-MoOCH}_2\text{Ph}$ /mole of dithiolothione.

c) Reactions carried out in benzene.

d) Repeat of Bohringer's reaction using equimolar quantities of reagents and dimethylformamide as solvent.

e) In these reactions the 2-thiocycloalkylene-1,3-dithioles came off the column before the dithiolothione.

f) A brown band in front of the 6a-thiophthone gave a brown oil which could not be crystallized.

g) A trace of recovered arylacetylone was obtained from a pale pink band in front of the red 6a-thiophthone band.
<table>
<thead>
<tr>
<th>% Yield (B)</th>
<th>% Yield (C)</th>
<th>Time</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>38.1</td>
<td>7 hr.</td>
<td>a,b,g</td>
</tr>
<tr>
<td>&lt;0.1</td>
<td>30.3</td>
<td>3 hr.</td>
<td>c</td>
</tr>
<tr>
<td>0.4</td>
<td>20.2</td>
<td>5 hr.</td>
<td>g</td>
</tr>
<tr>
<td>0.7</td>
<td>26.3</td>
<td>30 min.</td>
<td>g</td>
</tr>
<tr>
<td>35.9</td>
<td>0.1</td>
<td>18 hr.</td>
<td>g</td>
</tr>
<tr>
<td>36.1</td>
<td>1.2</td>
<td>8 hr.</td>
<td>d,g</td>
</tr>
<tr>
<td>0</td>
<td>1.1</td>
<td>60 hr.</td>
<td>g</td>
</tr>
<tr>
<td>7.8</td>
<td>0</td>
<td>3\frac{1}{2} hr.</td>
<td>g</td>
</tr>
</tbody>
</table>
11) Solution Rearrangements of 2-Thiocyclohexylene-1,3-
Aithiols

The procedure employed was the same in all cases.

The 1,3-adduct (0.5g.) was heated in boiling xylene (10 ml.) in the presence of sulphur (0.005g.) until t.l.c. indicated that rearrangement was essentially complete. The product was chromatographed on alumina with benzene as eluent to give:

a) a red band which yielded the 6a-thiophen.  
b) a brown band which yielded unchanged starting material.

The results obtained are summarized in TABLE II.
TABLE II

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
</tr>
<tr>
<td>$p$-MoOC$_6$H$_4$</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>$p$-MoOC$_6$H$_4$</td>
</tr>
<tr>
<td>$p$-NO$_2$C$_6$H$_4$</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
</tr>
<tr>
<td>2-pyridyl</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
<td>Smo</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>COC$_6$H$_4$O Mo</td>
<td>Ph</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>$-(CH_2)_4^-$</td>
<td>Ph</td>
</tr>
<tr>
<td>$p$-MoC$_6$H$_4$</td>
<td>H</td>
<td>$-(CH_2)_4^-$</td>
<td>Ph</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>$-(CH_2)_3^-$</td>
<td>Ph</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>$-(CH_2)_3^-$</td>
<td>Ph</td>
</tr>
</tbody>
</table>

**Notes**

c) Those rearrangements also took place in boiling benzene over a period of 12 hr. in the presence and in the absence of sulphur.
<table>
<thead>
<tr>
<th>Yield (B)</th>
<th>% M. Conv. (A)</th>
<th>Time</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>87</td>
<td>7.2</td>
<td>12 hr.</td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>8.6</td>
<td>7 hr.</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>8.4</td>
<td>7 hr.</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>6.5</td>
<td>5 hr.</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>10.1</td>
<td>5 hr.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>92</td>
<td>60 hr.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>9.5</td>
<td>60 hr.</td>
<td></td>
</tr>
<tr>
<td>83</td>
<td>5.2</td>
<td>17 hr.</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>2.1</td>
<td>24 hr.</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>1</td>
<td>1 hr.</td>
<td>a</td>
</tr>
<tr>
<td>97</td>
<td>1</td>
<td>1 hr.</td>
<td>a</td>
</tr>
<tr>
<td>0</td>
<td>83</td>
<td>60 hr.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>76</td>
<td>60 hr.</td>
<td></td>
</tr>
</tbody>
</table>
12) **Thermal Rearrangements of 2-Thioacylethylene-1,3-dithiols**

The procedure employed was the same in all cases.

The 2-thioacylethylene-1,3-dithiolo (o.i.e.) was heated at 200°C, until t.l.c. indicated that rearrangement was essentially complete. The product was chromatographed on alumina with benzene as eluant to give:

a) a red band which yielded the 6α-thiathiophthen.

b) a brown band which yielded recovered starting material.

The results obtained are summarized in TABLE III.
<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>H</td>
<td>H</td>
<td>Ph</td>
</tr>
<tr>
<td>p-\text{OC}<em>{6}H</em>{4} &amp; H</td>
<td>H</td>
<td>Ph</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>H</td>
<td>Ph</td>
</tr>
<tr>
<td>Ph</td>
<td>II</td>
<td>Ph</td>
<td>SiIco</td>
</tr>
<tr>
<td>Ph</td>
<td>II</td>
<td>H2o</td>
<td>Ph</td>
</tr>
<tr>
<td>Ph</td>
<td>II</td>
<td>COC_{6}H_{5}OMo</td>
<td>Ph</td>
</tr>
<tr>
<td>Ph</td>
<td>II</td>
<td>$(CH_2)_3^-$</td>
<td>Ph</td>
</tr>
<tr>
<td>H</td>
<td>II</td>
<td>$(CH_2)_3^-$</td>
<td>Ph</td>
</tr>
<tr>
<td>% Yield (B)</td>
<td>% Yield (A)</td>
<td>Time</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>1</td>
<td>10 min.</td>
<td></td>
</tr>
<tr>
<td>75.8</td>
<td>1</td>
<td>10 min.</td>
<td></td>
</tr>
<tr>
<td>68.2</td>
<td>11</td>
<td>2 hr.</td>
<td></td>
</tr>
<tr>
<td>70.6</td>
<td>32</td>
<td>6 hr.</td>
<td></td>
</tr>
<tr>
<td>56.4</td>
<td>1</td>
<td>30 min.</td>
<td></td>
</tr>
<tr>
<td>53.1</td>
<td>1</td>
<td>40 min.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>40.4</td>
<td>8 hr.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>31.2</td>
<td>8 hr.</td>
<td></td>
</tr>
</tbody>
</table>
13) *Reactions involving Selenium*

a) Rearrangement of 4-Phenyl-2-thiophencyclobutene-1,3-
dithiolo

The 1,3-dithiolo (0.1g.) and selenium (0.05g.) were heated in boiling 1,2,4-trichlorobenzene (10 ml.) for 3 hr. The mixture was chromatographed on alumina using benzene as eluant to give a red band which, on removal of the solvent, yielded a red solid (0.075g.). The mass spectrum of this solid indicated that it was unchanged thiophenothion and that it contained no selenium compound.

b) Reaction of Thiophenothion with Selenium

2,5-Diphenyl-6a-thiathiophthyphthep (0.15g.) and selenium (0.05g.) were heated in boiling 1,2,4-trichlorobenzene (10 ml.) for 3 hr. The mixture was chromatographed on alumina using benzene as eluant to give a red band which, on removal of solvent, yielded a red solid (0.075g.). The mass spectrum of this solid indicated that it was unchanged thiophenothion and that it contained no selenium compound.

14) Rearrangement of 4-Phenyl-2-thiophenceylidene-1,3-
dithiolo in Xylene with Various Additives

The procedure employed was the same in all cases.
(0.1g.) and 0.01g. each of all catalysts were heated in boiling xylene (ca. 12.5 ml.). The reaction was followed on t.l.c. until it was observed that rearrangement was essentially complete. Chromatography on alumina with benzene as eluent yielded 2,5-diphenyl-6a-thiathiophthen (0.065-0.085g., 80-90%) and recovered starting material (0.005-0.01g.). The times for rearrangement are given in TABLE IV.

### TABLE IV

<table>
<thead>
<tr>
<th>ADDITIVES</th>
<th>TIME (hr.) REQUIRED FOR REARRANGEMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>70 (very small amount of rearrangement, material showed signs of decomposition).</td>
</tr>
<tr>
<td>5-phenyl-1,2-dithiole-3-thione (1 equiv.)</td>
<td>60 (40% rearrangement)</td>
</tr>
<tr>
<td>S</td>
<td>21</td>
</tr>
<tr>
<td>ZnDBDT</td>
<td>14</td>
</tr>
<tr>
<td>S + ZnDBDT</td>
<td>3</td>
</tr>
<tr>
<td>S + ZnO</td>
<td>13</td>
</tr>
<tr>
<td>S + MBT</td>
<td>15</td>
</tr>
<tr>
<td>S + ZnO + MBT</td>
<td>3</td>
</tr>
<tr>
<td>S + TMTD</td>
<td>9</td>
</tr>
<tr>
<td>S + ZnO + TMTD</td>
<td>3</td>
</tr>
<tr>
<td>BPZ</td>
<td>3</td>
</tr>
<tr>
<td>S + BPZ</td>
<td>3</td>
</tr>
<tr>
<td>P₂S₅ (purified)</td>
<td>5</td>
</tr>
<tr>
<td>S + P₂S₅ (purified)</td>
<td>5</td>
</tr>
<tr>
<td>S + TPC</td>
<td>17</td>
</tr>
<tr>
<td>S + ZnO + TPC</td>
<td>17</td>
</tr>
</tbody>
</table>

ZnDBDT = zinc dibenzyldithiocarbamate;
MBT = 2-mercaptobenzothiazole;
TMTD = tetramethylthiuram disulphide;
BPZ = bis(p-porphthioluato)zinc II;
TPC = thio-p-cresol.
Bis(p-perthiotoluato)zinc II

Prepared by the method of Fackler et al.\textsuperscript{104}.

Yield = 9.4 g. from 12 g. of p-toluic aldehyde (41%).

m.p. = 192–193°C. (lit. m.p. = 192–195°C.)

The ammonium sulphide solution used was prepared as follows:—

Sulphur (12 g.) was added to a mixture of concentrated ammonia (50 ml.) and water (50 ml.) and hydrogen sulphide was bubbled through until all the sulphur had dissolved. Bubbling was then continued for a further 30 min. The mixture was shaken from time to time to disperse the sulphur.

**Purification of Phosphorus Pentasulphide**

The crude phosphorus pentasulphide (10 g.) was placed in a Soxhlet apparatus and continuously extracted with carbon disulphide (150 ml.) for 4 hr. Pale yellow crystals of phosphorus pentasulphide (5.2 g.) separated. Those were filtered and again subjected to the same procedure to give white prisms (3.8 g.).

15) **Reaction between Arylpropionic acids and Dithiolethiones**

The 1,2-dithiole-3-thione (0.1 mol) and the arylpropionic acid (0.1 mol) were heated in boiling benzene (25 ml.). The reaction mixture was reduced in volume and chromatographed on alumina with benzene as eluant to give:—

- a) a bright red band which yielded the 6a-thiathiophthcn.
- b) an orange band which yielded recovered dithiolethione.
- c) a brown band which yielded the 2-thioacetyl-methylene-1,3-dithiole.

The results obtained are summarized in

**TABLE V.**

The yields quoted are based on the amount of dithiolethione consumed.
\[
\begin{align*}
\text{CO}_2 \text{H} & \quad \text{Ar} \\
\text{S-S} & \quad \text{S=S} \quad \text{R}_1 \quad \text{R}_2 \quad (A)
\end{align*}
\]

<table>
<thead>
<tr>
<th>Ar</th>
<th>R₁</th>
<th>R₂</th>
<th>% Recov. (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MoC₆H₄</td>
<td>-(CH₂)₄⁻</td>
<td></td>
<td>42.5</td>
</tr>
<tr>
<td>p-MoC₆H₄</td>
<td>-(CH₂)₄⁻</td>
<td></td>
<td>41.1</td>
</tr>
<tr>
<td>Ph</td>
<td>-(CH₂)₄⁻</td>
<td></td>
<td>40.9</td>
</tr>
<tr>
<td>p-MoC₆H₄</td>
<td>Me</td>
<td>t-Bu</td>
<td>34.3</td>
</tr>
<tr>
<td>p-MoC₆H₄</td>
<td>CH₂C(Me)₃</td>
<td>t-Bu</td>
<td>30.4</td>
</tr>
<tr>
<td>Ph</td>
<td>Me</td>
<td>t-Bu</td>
<td>36.4</td>
</tr>
<tr>
<td>Ph</td>
<td>CH₂C(Me)₃</td>
<td>t-Bu</td>
<td>30.7</td>
</tr>
</tbody>
</table>

**Notes**

a) Those reactions were carried out in boiling dichloromethane.
<table>
<thead>
<tr>
<th>Yield (B)</th>
<th>Yield (C)</th>
<th>Time</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.1</td>
<td>5.1</td>
<td>3 hr.</td>
<td></td>
</tr>
<tr>
<td>6.6</td>
<td>41.1</td>
<td>24 hr.</td>
<td></td>
</tr>
<tr>
<td>18.7</td>
<td>4.1</td>
<td>3 hr.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>20.0</td>
<td>4 hr.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>17.2</td>
<td>4 hr.</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>21.3</td>
<td>20 hr.</td>
<td>a</td>
</tr>
<tr>
<td>0</td>
<td>19.7</td>
<td>20 hr.</td>
<td>a</td>
</tr>
</tbody>
</table>
16) **Reactions Involving 1,2,3-Thiadiazoles**

a) **4-Phenyl-1,2,3-thiadiazole**

Prepared by the method of Kirase and Hornor.

Yield = 5.5g. from 10g. of acotophonone othoxy-carbonyl-hydrazone (70%).

m.p. = 79-80°C. (from methanol)

(lit. m.p. = 80.81°C.)

b) **4,5-Diphenyl-1,2,3-thiadiazole**

Prepared by the same method as 4-phenyl-1,2,3-thiadiazole.

Yield = 0.33g. from 10g. of deoxybenzoin othoxy-carbonyl-hydrazone (5%).

m.p. = 90-92°C. (lit. m.p. = 93-94°C.)

c) **4,5-Benzof1,2,3-thiadiazole**

Prepared from 2-amino benzothiol by diazotization followed by reduction.

Yield = 0.34g. from 10g. of 2-amino benzothiol (31%).

m.p. = 33°C. (from light petroleum b.p. 40/60°C.)

(lit. m.p. = 35°C.)

d) Reaction between 5-Phenyl-1,2-dithiolo-3-thione and 4-Phenyl-1,2,3-thiadiazole

5-Phenyl-1,2-dithiolo-3-thione (0.21g., 0.001 mole) and 4-phenyl-1,2,3-thiadiazole (0.16g., 0.001 mole) were heated together at 200°C. for 1½ hr. The product was chromatographed on alumina with benzene as eluant to give:

i) a red solid (0.06g.) which was shown to be identical (mixed m.p., i.r. spectrum) with 2,5-diphenyl-6a-thiophththion.

m.p. = 160-161°C. (from ethyl acetate).

ii) an orange solid (0.05g.) which was shown to be unchanged 5-phenyl-1,2-dithiolo-3-thione.
c) **Reaction between 4-Phenyl-1,2-dithiole-2-thione and 4-Phenyl-1,2,3-thiadiazole**

A procedure similar to that described for the previous experiment was used. The products obtained were 2,5-diphenyl-6a-thiathiophthene (0.02 g.) and unchanged dithiolethione (0.02 g.).

d) **Reaction of 4,5-benzo-1,2,3-thiadiazole with 4-Phenyl 1,3-dithiole-2-thione**

The thiadiazole (0.14 g., 0.001 mole) and the dithiolethione (0.21 g., 0.001 mole) were heated together at 200°C. for 1 hr. The product was chromatographed on alumina with benzene as eluant to give a green solid with a metallic lustre (0.0016 g., m.p. = 186-187°C.) identical (mixed m.p.) with 4,5-benzo-2-thiophenacylidene-1,3-dithiol. (lit. m.p. = 186-187°C.).

e) **Reactions of 4,5-Diphenyl-1,2,3-thiadiazole with 3-Phenyl-1,2-dithiole-3-thione and with 4-Phenyl 1,3-dithiole-2-thione**

In both cases the thiadiazole (0.24 g., 0.001 mole) and the dithiolethione (0.21 g., 0.001 mole) were heated together at 200°C. for 1 hr. The product was chromatographed on alumina with benzene as eluant, to give, in each case, a red solid (m.p. = 186-187°C.) identical with 2,3,5-triphenyl-6a-thiathiophthene (mixed m.p.) (lit. m.p. = 187-188°C.).

Yields = 0.03 g. from 5-phenyl-1,2-dithiole-3-thione

and 0.01 g. from 4-phenyl-1,3-dithiole-2-thione.

17) **Reactions of p-Methoxyphenylacetylene and Sulphur with Dithiolethiones**

a) **with 4-Phenyl-1,3-dithiole-2-thione**

The dithiolethione (0.21 g., 0.001 mole), p-methoxyphenylacetylene (0.13 g., 0.001 mole) and sulphur (0.01 g.) were heated in boiling xylene (ca. 12.5 ml.) for
The mixture was chromatographed on alumina with benzene as eluant to give:

i) A fast moving red band which gave a red solid (m.p. = 185-186°C, from ethyl acetate) identical (mixed m.p.) with 2-phenyl-5-(p-methoxyphenyl)-6a-thiathiophthen (lit. m.p. = 185-186°C).

\[ \text{Yield} = 0.06 \text{g.} (17.6\%) \]

ii) A slow moving purple-brown band which extended to the top of the column. No identifiable products were obtained from this band.

b) with 4-Phenyl-1,2-dithiole-3-thione

A procedure similar to that described for the previous experiment was used. Chromatography yielded:

i) A fast moving red band which gave a red solid (m.p. = 152-154°C, from ethyl acetate) identified by n.m.r. and elemental analysis as 2-(p-methoxyphenyl)-4-phenyl-6a-thiathiophthen.

\[ \text{Yield} = 0.08 \text{g. (23.4\%)} \]

\[
\begin{array}{ccc}
\text{C} & \text{H} & \text{S} \\
\text{Required} & 63.12 & 4.12 & 28.08 \\
\text{Found} & 63.11 & 4.04 & 27.92
\end{array}
\]

ii) A slow moving dark-brown band which extended to the top of the column and from which no identifiable products were obtained.

Similar experiments in the absence of sulphur yielded no identifiable products other than the original dithiolethiones (0.14g. and 0.15g. respectively) even after 24 hr. boiling.

16) Reactions of Phenylacetylone and Sulphur with Dithiolethiones

a) with 4-Phenyl-1,3-dithiole-2-thione

The dithiolethione (0.21g., 0.001 mole), phenylacetylone (0.1g., 0.001 mole) and sulphur (0.01g.) were heated in boiling xylene (ca. 12.5 ml.) for 3 hr. After this time t.l.c. indicated that 4-phenyl-2-thiopheneceylidene-1,3-dithiole was present in the reaction.
mixture (by comparison with an authentic specimen). The product was chromatographed on alumina with benzene as eluant to give:

i) Fast moving pale yellow and pale pink bands which gave no identifiable products.

ii) A pale brown band which yielded a small amount of amorphous brown material. This material was again chromatographed on alumina with benzene as eluant to yield a brown solid (0.004g., mp = 198°C. from ethyl acetate) identical with 4-phenyl-2-thiophenacylidone-1,3-dithiolo (mixed mp, t.l.c.).

iii) A purple-brown band which stretched to the top of the column and from which no identifiable products were obtained.

b) with 4-Phenyl-1,2-dithiolo-3-thione

A procedure similar to that described for the previous experiment was used. Boiling was continued for 24 hr. Chromatography on alumina with benzene as eluant yielded no product other than starting material (0.11g.).

Similar experiments in the absence of sulphur yielded no identifiable products other than the original dithiolothiones (0.12g. and 0.14g. respectively) even after 24 hr. boiling.
SECTION 2 Preparation of Compounds Containing an Anthracene Nucleus

1) Reaction of 1,4,5,8-Tetrachloroanthraquinone with Potassium hydrogen sulphide

Potassium hydroxide (28 g.) was dissolved in the minimum amount of ethanol (ca. 300 ml.) and hydrogen sulphide was bubbled through the mixture for 20 hr. 1,4,5,8-Tetrachloroanthraquinone (3 g.) was added and the mixture was refluxed for 3 hr. The reaction mixture was poured into water (ca. 500 ml.) and acidified with dilute hydrochloric acid. A brown precipitate (1.4 g.) was produced which was shown by mass spectrometry and i.r. to be the starting material contaminated with sulphur.

2) Anthra[b,1,9,8-bis(10,4-benzimidazolyl)]bis(thiothiophthen)

1,4,5,8-Tetrachloroanthraquinone (6.92 g., 0.02 mole) and sodium sulphide nonahydrate (42.9 g., 0.18 mole) were heated in a boiling mixture of water (100 ml.) and dimethylformamide (200 ml.) for 6 hr. Throughout this time a green precipitate was produced. On cooling and filtration a green solid (2.81 g.) with a metallic lustre was obtained; m.p. 350°C., mass spectrum M⁺ 364 (hexathioanthracene C₁₄H₂₆S₆ requires M⁺ 364).

The crude hexathioanthracene was extracted continuously with hot dimethylformamide for 24 hr. The dimethylformamide extract, on removal of solvent, yielded a dark brown tar which was not identified. The residue from the extraction consisted of hexathioanthracene (2.23 g., 30.2%) with a bright metallic lustre. This process was repeated with 1,2,4-trichlorobenzene. A portion of the purified material was sublimed (350°C., 0.1 mm. Hg) for 4 hrs. when sufficient sublimate was obtained for analysis.

Analysis a) Sample obtained after extraction with dimethylformamide and 1,2,4-trichlorobenzene:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Required</td>
<td>46.15</td>
<td>1.10</td>
<td>52.75</td>
</tr>
<tr>
<td>Found</td>
<td>44.86</td>
<td>1.22</td>
<td>48.63</td>
</tr>
</tbody>
</table>
b) Sample obtained on sublimation:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Required</td>
<td>46.15</td>
<td>1.10</td>
<td>52.75</td>
</tr>
<tr>
<td>Found</td>
<td>46.34</td>
<td>1.66</td>
<td>47.32</td>
</tr>
</tbody>
</table>

c) Residue from sublimation:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>44.40</td>
<td>1.11</td>
<td>48.41</td>
</tr>
</tbody>
</table>

**Mass spectra**

Mass spectra indicated that the sublimed sample contained an impurity that volatilised at 210°C, and the main component near 300°C, whereas the sample which had been extracted contained only the main component at 300°C. Accurate mass measurement for this latter sample gave \( M = 363.8636 \) (required 363.8637).

3) 5,6-Dioxo-5H-thieno[1,2,3-bcd]thiophen

1,8-Dichloroanthraquinone (5.54 g, 0.02 mol) and sodium sulphide nonahydrate (14.45 g, 0.06 mol) were heated in a boiling mixture of water (50 ml) and dimethylformamide (100 ml) for 2 hr. After being cooled, the mixture was poured into water (ca. 500 ml) and acidified with dilute hydrochloric acid whereupon a dark green solid, crude trithioanthrone, was precipitated.

Yield = 5.37 g (93.5%)

m.p. = 230-260°C

**Mass spectrum** \( \text{H}^+ 286 \) (C\(_{14}\)H\(_6\)O\(_3\) requires \( \text{H}^+ 286 \))

A portion of the crude product was chromatographed on alumina with hot benzene as eluant to give a dark brown solid which yielded dark brown needles with a green reflex on crystallization from 1,1,2-trichloroethane.

m.p. = 293-295°C

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Required</td>
<td>58.74</td>
<td>2.10</td>
<td>33.57</td>
</tr>
<tr>
<td>Found</td>
<td>58.74</td>
<td>2.13</td>
<td>33.49</td>
</tr>
</tbody>
</table>

4) 2,3,6,7-Tetrachloroanthra[1,2,3-bcd:5,6,7-1,2,3-bcd]thiophen

Anthracone (3.56 g, 0.02 mol) and sulphur monochloride (10.8 g, 0.08 mol) were heated in boiling 1,2,4-trichlorobenzene (ca. 50 ml) for 2 hr. The solution
went black shortly after the solvent started to boil. On cooling, pale yellow crystals (2.3g, m.p. = 113°C) were obtained which were shown (mass spectrum, i.r.) to be 9,10-dichloroanthracene.

The reaction was repeated and boiling continued for 15 hr. On cooling, dark green needles (0.84g) were obtained, m.p. = > 320°C. The green solid was extracted continuously with boiling dimethylformamide for 24 hr. The residue from the extraction consisted of purified product (0.61g, 6.2%) which was identified by mass spectrum (M=500) and analysis.

The same product was obtained from the reaction of 9,10-dichloroanthracene and sulphur monochloride in 1,2,4-trichlorobenzene.

\[
\begin{array}{ccc}
C & Cl & S \\
\text{C}_6\text{Cl}_4\text{S}_6 & \text{Requires} & 33.47 \ 28.29 \ 38.24 \\
\text{Found} & 34.32 \ 27.62 \ 38.53 \\
\end{array}
\]

5) Attempted Preparation of Anthra(1,9-bc;5,10-b'c')bis(dithiole)

a) Reaction of 1,5-Dichloroanthraquinone with Sodium Sulphide

Sodium sulphide nonahydrate (0.06 mol) was dissolved in water (ca. 50 ml) and added to a suspension of 1,5-dichloroanthraquinone (5.5g, 0.02 mol) in dimethylformamide (ca. 100 ml). The mixture was boiled for 2 hr. poured into water (ca. 500 ml), and acidified with dilute hydrochloric acid whereupon a brown solid (4.19g) was obtained. The solid was placed in a Soxhlet apparatus and continuously extracted with chloroform for 24 hr. This procedure yielded a brown solid (3.1g, 57%) which was identified, by mass and n.m.r. spectroscopy, as 1,5-dimercaptoanthraquinone and was used without further purification.

b) Recording of N.m.r. spectrum

A small amount of sodium hydride (ca. 50 mg) was dissolved in deuterium oxide (ca. 1 ml) and
1,5-dimercaptoanthraquinone (ca. 50 ng) was added thus producing a solution of the disodium salt of 1,5-dimercaptoanthraquinone in sodium deuteroxide.

c) Reaction with Phosphorus pentasulphide

1,5-Dimercaptoanthraquinone (1.36 g., 0.005 mole) and phosphorus pentasulphide (3.33 g., 0.015 mole) were heated in boiling pyridine (50 ml.) for 3 hr. The warm solution was poured into boiling water (ca. 250 ml.) and allowed to cool overnight. A small amount of a light brown solid (0.1 g.) was precipitated and was identified by mass spectrum as sulphur. The filtrate was divided into two equal portions one of which was acidified with hydrochloric acid and the other with perchloric acid. Brown solids were precipitated in both cases (0.6 g. and 0.7 g. respectively). The two compounds had identical i.r. spectra (allowing for the perchlorato anion peak at 1100 cm\(^{-1}\)), and very similar mass spectra which indicated that the \(\text{C}_1\text{H}_2\text{S}_3\) \((N = 302)\) unit was present. The analysis results indicated that the brown compounds did not contain the anthracene(1,9-bc:5,10-b'c') bis(dithioliylum) cation but were more likely to be the neutral compound in a very impure state, possibly contaminated with pyridine or some product derived therefrom.

Analysis

a) For presumed chloride salt:

\[
\text{C}_{14}\text{H}_6\text{Cl}_2\text{S}_4 \text{ Requires: } \begin{array}{c} 45.16 \ 18.82 \ 0 \ 3.41 \\ 44.63 \ 2.68 \ 0 \ 3.66 \ 3.01 \end{array}
\]

b) For presumed perchlorate salt:

\[
\text{C}_{14}\text{H}_6\text{Cl}_2\text{O}_8\text{S}_4 \text{ Requires: } \begin{array}{c} 33.60 \ 14.00 \ 0 \ 25.60 \\ 36.16 \ 2.53 \ 4.73 \ 3.35 \ 26.09 \end{array}
\]

c) Neutral compound:

\[
\text{C}_{14}\text{H}_6\text{S}_4 \text{ Requires: } \begin{array}{c} 55.63 \ 1.99 \ 42.38 \end{array}
\]
SECTION 3  Attempts to Prepare 1,2,5,6-Tetra thiopentalone—
3,4-dithione and Related Compounds

1,2,5,6-Tetra thiopentalone—3,4-dithione

a) From 4-Ethoxycarbonyl-5-amino-1,2-dithiole-3-thione

Prepared by the method of Gewald\(^{11}\).  
Yield = 8.1 g. (25%) from 16.8 g. ethyl cyanoacetate  
m.p. = 180-182°C. (lit. m.p. = 183-184°C.)

i) Reaction of the aminothiolethione with phosphorus pentasul phide

The dithiolethione (0.78 g.) and phosphorus pentasulphide (3.52 g.) (molar ratio 1:4.5) were heated in boiling pyridine (5 ml.) for 1 hr. The warm mixture was poured into boiling water (ca. 100 ml.). After being cooled, the solution was extracted with ether, basified, and again extracted with ether. Both etheral extracts yielded very small amounts of yellow oils which could not be identified.

ii) Reaction of the aminothiolethione with sodium sulphide nonahydrate

The aminothiolethione (1 g.) and sodium sulphide nonahydrate (3.5 g.) were heated in a boiling mixture of water (10 ml.) and dimethylformamide (30 ml.) for 1 hr. After being cooled, the solution was acidified with dilute hydrochloric acid and extracted with ether. Removal of the ether yielded a light brown solid which had no bands in the i.r.

iii) Diazotization of the aminothiolethione

The aminothiolethione (0.5 g.) was dissolved in a solution of sodium nitrite (0.16 g.) in 50% \(\text{H}_2\text{SO}_4\) sulphuric acid (15 ml.). Water (5 ml.) was added and the solution heated to boiling. After being cooled, the solution was neutralized with dilute sodium hydroxide solution and extracted with ether. On removal of the solvent a small amount of a yellow solid was obtained (no bands in i.r.).
b) From 1,1,1-Trichloro-2-methylpropan-2-ol

This reaction was based on the method described by Brown.

The chloro-alcohol (75g, 0.4 mole) and sulphur (110g, 3.4 mole) were heated in boiling dimethylformamide (600 ml) for 6 hr. during which time the refluxate changed from blue to colourless. After cooling, the solvent was evaporated under reduced pressure and the residue extracted with chloroform. The soluble portion was chromatographed on alumina using chloroform as eluant to give:

i) a brown band which gave a small amount of brown solid (0.4g) which had no bands in the i.r.

ii) a red-brown band which gave a brown tar with a very poorly defined i.r. spectrum.

Most of the original product was insoluble in chloroform but dissolved in hot water and, on filtering and cooling, gave red-brown crystals. These were redissolved in water and the solution acidified with dilute hydrochloric acid to give an orange solution which was extracted with ether. Removal of the ether yielded, after trituration with ethanol, red crystals (2.2g) which were identified by mass and n.m.r. spectra as 5-mercapto-1-methyl-1,2-dithiole-3-thione.

m.p. = 87-88°C. (lit. m.p. = 88-89°C.)

c) From Diethyl 1,3-dithiolan-2-ylidene malonate

The starting material was prepared by the method of Jonsen and Henriksen.

i) The malonate (1g) and phosphorus pentasulphide (4.3g, purified) (molar ratio 1:5) were heated in boiling xylene (5 ml) for 30 min. Chromatography on alumina with benzene as eluant gave a red-brown band which yielded a small amount of a brown tar which could not be crystallized.

ii) The above reaction was repeated using unpurified phosphorus pentasulphide in pyridine as solvent. Heating was continued for 1 hr. and the warm mixture poured into boiling
water (ca. 100 ml.). After being cooled the mixture was filtered yielding a pale yellow solid which was shown (i.r.) to be the starting material.

iii) The above reaction was repeated using unpurified phosphorus pentasulphide and 2,6-lutidine as solvent. Again starting material was recovered.

d) **Attempted Preparation of 4-Butoxycarbonyl-5-thioperoxy-1,2-dithiole-3-thione**

The procedure used was based on that of Brown.  

n-Butyl methacrylate (50 ml.) and sulphur (55 g.) were heated in boiling dimethylformamide (300 ml.) for 36 hr. during which time the refluxate changed from blue to colourless. Removal of the solvent yielded a black tar. A portion of this tar was dissolved in water. Acidification with dilute hydrochloric acid followed by extraction with ether again yielded a black tar.

e) **From Diethyl dimercaptanethylenemalonate**

The dimercapto-compound was prepared by the method of Gross and Topf (which yields the disodium salt as a yellow solid). Acidification of an aqueous solution of the salt yielded the dimercapto-compound as an unstable brown oil.

This oil, on reaction with phosphorus pentasulphide (purified or unpurified) in pyridine or xylene, either in the presence or in the absence of sulphur, gave, by standard procedures as described above, a variety of brown solids in very small yield all of which had poorly defined i.r. spectra.

**Indeno(1,2-c)-1,2-dithiol-1,3-dithione**

i) **2-Methylthio-1,3-dithiolonium methylsulphate**

Prepared by the method of Mayer and Schäfer from 1,3-dithiolen-2-thione.

ii) **2-(1,3-Dithiolon-2-ylidene)indeno-1,3-dione**

Prepared from 2-methylthio-1,3-
dithiolanium methylsulphate and indeno-1,3-dione by the
to ihod of Mayor and Schafafi113.

The crude product, a purple solid, was
dissolved in chloroform and a small amount of a yellow solid,
which was not identified, was removed by filtration. The red
solid obtained by removal of the chloroform was chromatographed
on alumina with benzene as eluant to yield a pale yellow band
which gave a pale yellow solid. Recrystallization from
ethanol gave colourless needles.
Yield = 1.08. from 1.468 indeno-1,3-dione
(40.3%)

\[
\text{Yield} = 1.08. \text{ from } 1.468 \text{ indeno-1,3-dione (40.3%)}
\]

\[
\text{m.p.} = 261-262^\circ C.
\]

\[
\begin{align*}
\text{C} & \quad \text{H} & \quad \text{S} \\
\text{Required} & \quad 58.07 & \quad 3.23 & \quad 25.80 \\
\text{Found} & \quad 58.14 & \quad 3.26 & \quad 25.97
\end{align*}
\]

iii) 2-(1,3-Dithiolon-2-yldione)indeno-1,3-dithione

The dione (1g.) and phosphorus pentasulphide (2.7g., unpurified) were heated in boiling xylene
(5 ml.) for 30 min. Chromatography of the product mixture
on alumina using hot chloroform as eluant produced a
greenish-yellow band which yielded a very dark green solid.
Recrystallization from 1,1,2-trichloroethane yielded very
dark green prisms.
Yield = 0.95. (80%)

\[
\text{m.p.} = 266-269^\circ C.
\]

\[
\begin{align*}
\text{C} & \quad \text{H} & \quad \text{S} \\
\text{Required} & \quad 51.43 & \quad 2.86 & \quad 45.71 \\
\text{Found} & \quad 51.81 & \quad 2.91 & \quad 45.51
\end{align*}
\]

iv) Attempted Removal of Ethylene-bridge from Dithione

Firstly, the dithione (0.1g.) was heated
in boiling 1,2,4-trichlorobenzene for 24 hr. On cooling the
starting material was recovered unchanged.
Secondly, the dithione (0.1g.) was
sublimed at 275^\circ C. (0.1 mm Hg) for 3 hr. A yellow solid (\ldots 0.25 g.)
was recovered from the cold portions of the apparatus. This
solid was identified as sulphur (mass spectrum). The residue
consisted of an insoluble black glass which was not identified.

**Phenalene(1,2-c)(1,2)dithiolo-7,8-dithione**

a) 2,3-Dihydro-1H-phenalene-1,3-dione

Prepared by the method of Errara. A mixture of naphthalic anhydride (50g.), diethyl malonate (100g.) and fused zinc chloride (50g.) was boiled for 5 hr. On cooling a brownish-yellow crystalline mass was formed. The solid obtained by filtration was dissolved in dilute potassium hydroxide solution and on acidification a yellow precipitate was produced. Recrystallization from glacial acetic acid gave yellow crystals which were identified by n.m.r. spectroscopy as the required product. The material was used without further purification.

Yield = 17g. (34%)

m.p. = 224-226°C.

b) 2-(1,3-Dithiolan-2-ylidene)-2,3-dihydro-1H-phenalene-1,3-dione

Prepared by the reaction of the diketo-compound with 2-methylthio-1,3-dithiolanium methyl sulphate using the general method of Mayor and Schafor. Yield = 2.55g. from 1.96g. of diketo-compound (85%).

m.p. = 221-222°C. (pale yellow needles from ethanol).

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.43</td>
<td>3.36</td>
<td>21.48</td>
</tr>
</tbody>
</table>

**c) Attempted Sulphurization of Above Compound**

Reaction of the above compound with phosphorus pentasulphide (3 mols., purified or unpurified) in boiling xylene, pyridine or 1,2,4-trichlorobenzene resulted in recovery of starting material in all cases. Use of 2,6-lutidine as solvent resulted in decomposition of the starting material as did direct fusion with phosphorus pentasulphide at 220°C.
1,2-Dithio-6,6-dimethyl-4,5,6,7-tetrahydroindane-3,4-dithione

a) 5,5-Dimethyl-2-(1,3-dithiolan-2-ylidene)cyclohexene-1,3-dione

Prepared by the method of Mayor and Schafer from dimedone and 2-methylthio-1,3-dithiolanium methosulphate.  
Yield = 2g. from 1.40g. of dimedone (83%).  
m.p. = 200°C. (lit. m.p. = 201-202°C.)

b) Attempted Sulphurization of Above Compound

The dione (1.21g., 0.005 mole) and phosphorus pentasulphide (3.33g., 0.015 mole) were heated in boiling xylene (10 ml.) for 15 min. The mixture rapidly went dark brown. After being cooled the solvent was removed to give a dark brown tar from which no identifiable products could be obtained.

4,6-Dimethyl-1,7-dithioxene-4,5,6,7-tetrahydro(1,2)dithiole (3,4-d)-pyrimidine-5-one

a) 1,3-Dimethyl barbituric acid

Prepared by the method of Clark—Lewis and Thompson from dimethyluracil and malonic acid.  
Yield = 31.6g. from 33g. dimethyluracil (57%).  
m.p. = 120-121°C. (lit. m.p. = 121-122°C.)

b) 1,3-Dimethyl-5-(1,3-dithiolan-2-ylidene)hexahydro-pyrimidine-2,4,6-trione

Prepared from 1,3-dimethyl barbituric acid and 2-methylthio-1,3-dithiolanium methosulphate by the general method of Mayor and Schafer.  
Yield = 1.57g. from 1.56g. of 1,3-dimethyl barbituric acid (61%).  
m.p. = 236-237°C. (white needles from ethanol).

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₉H₁₀N₂O₃S₂ Requires</td>
<td>41.86</td>
<td>3.86</td>
<td>10.86</td>
</tr>
<tr>
<td>Found</td>
<td>41.73</td>
<td>3.81</td>
<td>11.43</td>
</tr>
</tbody>
</table>
c) \(1,3\text{-dimethyl-5-(1,3\text{-dithiolan-2-ylidene})-2-thioxohexahydropyrimidine-4,6-dione}\)

The adduct (0.5 g.) and phosphorus pentasulphide (1.4 g.) were heated in boiling 1,2,4-trichlorobenzene (5 ml.) for 2 hr. After being cooled the dark brown precipitate was obtained by filtration, dried and placed in a Soxhlet apparatus and extracted with chloroform for 12 hr. The chloroform was removed under reduced pressure to give a dark brown solid which was recrystallized from 1,1,2-trichloroethane to give pale yellow plates of 1,3-dimethyl-5-(1,3-dithiolan-2-ylidene)-2-thioxohexahydropyrimidine-4,6-dione.

Yield = 0.35 g. (66%)

m.p. = 255-257°C.

\[
\begin{array}{cccc}
\text{C} & \text{H} & \text{N} & \text{S} \\
9.10 N_{2}O_{2}S_{3} & 39.41 & 3.65 & 10.22 & 35.03 \\
\text{Found} & 38.77 & 3.29 & 10.27 & 35.49
\end{array}
\]
SECTION 4 Attempted Preparation of Naphtho (1,8- od-5,4- b'c') bis(dithiole)

1) From 1,5-Dibromonaphthalene

a) 1,5-Dibromonaphthalene

Prepared from 1,5-diaminonaphthalene by the method of Hodgson and Whitworth.119

Yield = 1.3g. from 6g. diamine (12,)

m.p. = 130°C. (lit. m.p. = 131-132°C.)

b) 1,5-Dibromo-4,8-dinitronaphthalene

Concentrated sulphuric acid (10 ml.) was added slowly, with cooling and stirring, to concentrated nitric acid (10 ml.). When the addition was complete 1,5-dibromonaphthalene (1g.) was added slowly to the mixture which was then placed on a boiling water bath for 5 min. The mixture was cooled and the precipitated solid was obtained by filtration and washed free of acid with water. The n.m.r. and mass spectra of the product were consistent with it's being the required compound contaminated with small amounts of starting material and dibromomononitronaphthalene. The product was used without further purification.

Yield = 0.873.

m.p. = 133-141°C.

c) Reaction of 1,3-Dibromo-4,8-dinitronaphthalene with Phosphorus pentabromide

The naphthalene derivative (0.5g.) was heated to its melting point and phosphorus pentabromide (1.3g.) was added slowly. The temperature was maintained for 30 min. and the resulting brown mass was recrystallized from ethanol to give the starting material (0.42g.).

Repetition of the experiment at higher temperatures resulted in decomposition of the starting material and no identifiable products were obtained.

d) Attempted Thiocyanation of 1,5-Diaminonaphthalene

i) Method based on that of Kaufman

1,5-Diaminonaphthalene (5.5g.) was dissolved in the minimum amount of methanol (ca. 250 ml.) at
room temperature. Ammonium thiocyanate (10.5 g.) was added and the solution was cooled to 5°C. To the stirred solution was added dropwise a solution of bromine (2.2 ml.) in methanol (10 ml.). Stirring was continued for 1 hr. and the solution then poured into water (ca. 1 litre) whereupon a dark brown precipitate (0.8 g.) was produced. This material had no bands in the i.r. No identifiable products were obtained by acidification of the solution or by extraction with ether.

ii) Method based on that of Browster and Schroeder

1,5-Diaminonaphthalene (7.2 g.) and ammonium thiocyanate (8 g.) were dissolved in glacial acetic acid (ca. 120 ml.). To this solution was added, dropwise with stirring, a solution of bromine (2.6 ml.) in acetic acid (10 ml.) at such a rate that the temperature of the mixture did not exceed 20°C. Stirring was continued for 2 hr. after the addition was complete. The mixture was then poured into water (ca. 1 litre) and a very dark brown precipitate (5.3 g.) was obtained. This material had no bands in the i.r. and no identifiable product was obtained by Soxhlet extraction with chloroform.

2) From Naphthalene-1,5-dithiol

c) Naphthalene-1,5-disulphonyl chloride

Prepared by the method of Foldmann

Yield = 16.5 g. from 20 g. of disodium naphthalene-1,5-disulphonato (82,)

m.p. = 180-181°C. (lit. m.p. = 183°C.)

b) Naphthalene-1,5-dithiol

Prepared by the method of Harval and Caeser

Yield = 3.25 g. from 8 g. of naphthalene-1,5-disulphonyl chloride (69,)

m.p. = 118-120°C. (lit. m.p. = 118-121°C.)

c) Reaction between Naphthalene-1,5-dithiol and Sulphur dichloride

The procedure followed was that of Fohrer,
Glinka and Malcharok. On removal of the volatile components of the reaction mixture the starting material was recovered.

3) From Naphthazarin

Naphthazarin (1.90 g., 0.01 mole) and phosphorus pentasulphide (13.3 g., 0.06 mole, purified or unpurified) were heated in boiling pyridine (ca. 125 ml.) for 3 hr. The warm mixture was poured into boiling water (ca. 250 ml.). On cooling a pale yellow solid was precipitated which was shown to be sulphur (mass spectrum M^+256). Acidification of a portion of the aqueous solution with dilute hydrochloric acid resulted in precipitation of more sulphur. On being allowed to stand both the solutions deposited more sulphur but no other identifiable product could be obtained either by filtration or by extraction with ether. Similar results were obtained using xylene and carbon disulphide as reaction solvents.
N.M.R. SPECTRA

Also included in this table are melting points and analysis data not previously recorded.

<table>
<thead>
<tr>
<th>FORMULA</th>
<th>PROTONS</th>
<th>NO. OF PROTONS</th>
<th>( \gamma ) VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>[diagram]</td>
<td>a</td>
<td>1</td>
<td>1.87 (s)</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>2</td>
<td>7.39 (s)</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>9</td>
<td>9.08 (s)</td>
</tr>
</tbody>
</table>

| [diagram] | a | 9 | 8.49 (s) |
| | b | 3 | 7.69 (s) |

| [diagram] | a | 9 | 8.44 (s) |
| | b | 2 | 6.96 (s) |
| | c | 9 | 8.94 (s) |
\[ \begin{align*}
\text{CH}_3\text{CH}_2\text{CO}_2 & \quad \gamma 8.59 \text{ (t), 8.60 (t)} \\
\text{CH}_3\text{CH}_2\text{CO}_2 & \quad \gamma 5.61 \text{ (q), 5.62 (q)} \quad J_{cd} = 7 \text{ cps.}
\end{align*} \]

\[ \begin{align*}
\text{a, a'} & \quad 3, 3 \\
\text{b, b'} & \quad 2, 2 \\
\text{c, c'} & \quad 1, 1 \\
\text{d, d'} & \quad 1, 1 \\
\text{o, o'} & \quad 2, 2 \\
\text{c, c'} & \quad 3, 3 \\
\end{align*} \]
\[ \text{Formula 1: } S-S-S \text{ with } \text{Ph}^e \]

\[ \text{CO}_2\text{CH}_2\text{CH}_3 \]

\[
\begin{array}{ll}
a & 3 \quad \gamma 8.60 \text{ (t)} \quad J_{ab} = 7 \text{ cps.} \\
b & 2 \quad \gamma 5.60 \text{ (q)} \\
c & 1 \quad \gamma -0.18 \text{ (s)} \\
d & 1 \quad \gamma 0.33 \text{ (s)} \\
e & 2 \quad \gamma 2.09-2.20 \text{ (m) (ortho protons)} \\
 & 3 \quad \gamma 2.50-2.62 \text{ (m) (meta and para protons)} \\
\end{array}
\]

\[ \text{Formula 2: } S-S-S \text{ with } \text{Ph}^e \]

\[ \text{CH}_3\text{CH}_2\text{CO}_2 \]

\[
\begin{array}{ll}
a & 3 \quad \gamma 8.55 \text{ (t)} \quad J_{ab} = 7 \text{ cps.} \\
b & 2 \quad \gamma 5.66 \text{ (q)} \\
c & 1 \quad \gamma 1.49 \text{ (s)} \\
d & 1 \quad \gamma 1.62 \text{ (s)} \\
e & 2 \quad \gamma 2.08-2.20\text{(m)(ortho protons)} \\
 & 3 \quad \gamma 2.35-2.56\text{(m)(meta and para protons)} \\
\end{array}
\]
a 3  \( \gamma 9.15 \) (t)  \( J_{ab} = 6 \) cps.
b 2  \( \gamma 5.95 \) (q)
d 1  \( \gamma 1.52 \) (s)
c, o 4  \( \gamma 2.16 - 2.31 \) (m) (ortho protons)
    6  \( \gamma 2.52 - 2.72 \) (m) (meta and para protons)

a 3  \( \gamma 9.01 \) (t)  \( J_{ac,b} = 7 \) cps.
b 2  \( \gamma 5.95 \) (q)
d 1  \( \gamma 2.17 \) (s)
o, o 10  \( \gamma 2.36 - 2.80 \) (m)
\[
\begin{align*}
\text{a, b} & \quad 1,1 \\
& \quad \gamma_{2.92, 2.94} \ (d) \quad J_{ab} = 4 \ \text{cps.} \\
& \quad \gamma_{2.96, 2.98} \ (d) \\
\text{c, e} & \quad 2,2 \\
& \quad \gamma_{6.94} \ (t) \quad J_{cd} = J_{ce} = 7 \ \text{cps.} \\
& \quad \gamma_{7.06} \ (t) \\
\text{d} & \quad 2 \\
& \quad \gamma_{7.86} \ (quin) \\
\end{align*}
\]

\[
\begin{align*}
\text{a, b, c, d, e, f} & \quad 8-10 \\
& \quad \gamma_{6-9} \ (\text{complex multiplets}) \\
\text{g} & \quad 1 \\
& \quad \gamma_{2.78} \ (s) \\
\text{h} & \quad 2 \\
& \quad \gamma_{2.04, 2.18} \ (\text{m (ortho)}) \\
& \quad 3 \\
& \quad \gamma_{2.18, 2.64} \ (\text{m (meta and para)})
\end{align*}
\]
a, d 4  \( \gamma 7.30-7.50 \) (m)
b, c 4  \( \gamma 8.02-8.19 \) (m)
c 1  \( \gamma 1.80 \) (s)
f 2  \( \gamma 2.06-2.20 \) (ortho protons)
3  \( \gamma 2.52-2.68 \) (meta and para protons)

m.p. = 186-187°C. (from ethyl acetate)
(lit. m.p. = 183-186°C.)

a, c' 3,3  \( \gamma 6.19 \) (s)
d, e 1,1  \{ \( \gamma 1.74,1.76 \) (d), 3.15, 3.17 (d)
\}
\( J_{de} \) or \( J_{d,e} \) = 2 cps.
\{ \( \gamma 1.81 \) (s); 2.98 (s)
\}
b, c, z, b', c', f' 18 complex aromatic envelopes.
m.p. = 175-176°C.
(lit. m.p. = 177°C.)

\[
\begin{align*}
\text{m.p.} & = 185-186°C. \text{ (from ethyl acetate) (lit. m.p. = 186°C.)} \\
a & \quad 3 \quad \gamma 6.12(s) \\
b & \quad 2 \quad \gamma 2.98, 3.07 (d) \quad J_{bc} = 9 \text{ cps.} \\
c & \quad 2 \quad \gamma 2.12, 2.21 (d) \\
d, o & \quad 2 \quad \gamma 1.81 (s) \\
f & \quad 2 \quad \gamma 2.08-2.21 (a) \text{ (ortho protons)} \\
3 & \quad \gamma 2.49-2.59 (a) \text{ (meta and para protons)}
\end{align*}
\]
m.p. = 215-216°C. (orange needles from ethyl acetate)

C₁₆H₁₁NS₃  Requires  61.34  3.52  4.47  30.68
Found      61.05  3.25  4.52  30.93

No n.m.r. spectrum, (identified by rearrangement to the corresponding thiathiophthen and by elemental analysis).

m.p. = 154-155°C. (red needles with a green reflex from ethyl acetate).

C₁₆H₁₁NS₃  Requires  61.34  3.52  4.47  30.68
Found      61.02  3.23  4.30  29.25

a  3  γ 2.47-2.72 (m) (meta and para protons)
b  1  γ 1.72 (s)
c  1  γ 1.13 (s)
d  1  γ 1.26-1.36 (m)
e  1  γ 2.12-2.25 (m)
f  1  γ 1.89-2.01 (m)
g  1  γ 2.47-2.72 (m)
m.p. = 208-210°C. (from ethyl acetate)  
(lit. m.p. = 209-211°C.)

No n.m.r. spectrum - material insufficiently soluble in deuterochloroform.

\[
\begin{align*}
\text{a} & : 2 \quad 2.57, 2.66 \text{ (d) } J_{ab} = 9 \text{ cps.} \\
\text{b} & : 2 \quad 1.99, 2.08 \text{ (d)} \\
\text{c, d} & : 2 \quad 1.73 \text{ (s)} \\
\text{e} & : 2 \quad 2.12-2.23 \text{ (m) (ortho protons)} \\
& : 3 \quad 2.56-2.57 \text{ (m) (meta and para protons)}
\end{align*}
\]

\[
\begin{align*}
\text{m.p.} &= 144-145^\circ C. \quad \text{(brown needles with green reflex from ethyl acetate)}
\end{align*}
\]

\[
\begin{align*}
\text{C}_{23}\text{H}_{16}\text{S}_3 & \quad \text{Requires} \\
\text{C} & = 71.13 \quad 4.12 \quad 24.75 \\
\text{S} & = 71.32 \quad 4.28 \quad 24.89 \\
\text{multiplets at } & \gamma 2.06-2.20 \text{ and} \\
\gamma 2.54-2.78. \\
\text{c} & : 1 \quad \gamma 1.79 \text{ (s)}
\end{align*}
\]
m.p. = 187-188°C. (lit\textsuperscript{10} m.p. = 186-187°C.)

m.p. = 151-152°C. (brown needles from ethyl acetate).
(lit\textsuperscript{11} m.p. = 158°C.)

c, b, d 22 2.36-2.81 (m)

a', b', d' 3,3 7.62(s); 7.66(s)

c, c'
m.p. = 161-163°C.
(rod plates from ethyl acetate)
(lit. m.p. = 156°C.)

a 2 $^\gamma$ 2.08-2.21 (m) (ortho protons)
b 1 $^\gamma$ 1.87 (s)
c 3 $^\gamma$ 7.54 (s)
d 5 $^\gamma$ 2.52-2.65 (m)

m.p. = 130-131°C. (rod needles from ethyl acetate)

C₅₀H₃₈S₄

C
H
S

Required 60.3% 3.91 35.75
Found 59.98 3.94 36.75

$^\gamma$ 3.12 (s); 3.16 (s)
$^\gamma$ 2.38-2.30 (m)
$^\gamma$ 7.49 (s); 7.51 (s)
m.p. = 178 - 179°C (bright red plates from ethyl acetate)

\[
\text{C}_{18}H_{14}S_4
\]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Required</td>
<td>60.34</td>
<td>3.91</td>
<td>35.75</td>
</tr>
<tr>
<td>Found</td>
<td>59.88</td>
<td>3.70</td>
<td>37.16</td>
</tr>
</tbody>
</table>

a, b, c 11 \( \gamma 2.34 - 2.77 \) (m)
d 3 \( \gamma 7.47 \) (s)

m.p. = 181 - 182°C (bright red plates from ethyl acetate)

\[
\text{C}_{16}H_{18}S_3
\]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Required</td>
<td>62.75</td>
<td>5.88</td>
<td>31.28</td>
</tr>
<tr>
<td>Found</td>
<td>63.19</td>
<td>5.78</td>
<td>31.28</td>
</tr>
</tbody>
</table>

a 2 \( \gamma 2.12 - 2.23 \) (m) (ortho protons)
3 \( \gamma 2.53 - 2.68 \) (m) (meta and para protons)
b 1 \( \gamma 1.96 \) (s)
c 3 \( \gamma 7.40 \) (s)
d 9 \( \gamma 8.49 \) (s)
No analysis data — material non-crystalline.

a 2 $\gamma$ 2.07-2.19 (m) (ortho protons)

b 1 $\gamma$ 1.69 (s)

c 2 $\gamma$ 6.73 (s)

d 9 $\gamma$ 9.01 (s)

e 9 $\gamma$ 8.48 (s)

m.p. = 143-144°C (orange plates from ethyl acetate).

C$_{14}$H$_{12}$S$_3$

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>61.27</td>
<td>4.41</td>
<td>34.63</td>
</tr>
<tr>
<td>Requi</td>
<td>60.87</td>
<td>4.35</td>
<td>34.79</td>
</tr>
</tbody>
</table>

a 1 $\gamma$ 2.73 (s)

b 5 $\gamma$ 2.36-2.64 (m)

c, e 4 $\gamma$ 6.83-7.12 (m)

d 2 $\gamma$ 7.81 (quintet) $J_{de}$ and $J_{cd}$ $\approx$ 6 cps.
No analysis data - material non-crystalline, identified by rearrangement to the thiothiophthon.

\[
\begin{align*}
\text{a, b, c, o} & \quad 15 \quad \gamma 2.17-3.42 (m) \\
\text{a', b', c', o'} & \quad 15 \quad \gamma 6.20 (s); 6.28 (s) \\
d, d' & \quad 3,3
\end{align*}
\]

\[
\text{c' }
\]

\[
\text{n.p. = 129-130°C.} \\
\text{(lit. m.p. = 130-131°C.)}
\]

\[
\begin{align*}
a & \quad 5 \quad \gamma 2.40-2.72 (m) \\
b & \quad 1 \quad \gamma 1.13 (s) \\
c & \quad 1 \quad \gamma 2.53, 2.55, 2.61, 2.63 (q) \\
J_{cd} = 8 \text{ cps}; J_{co} = 2 \text{ cps.}
d, o, f & \quad 3 \quad \gamma 2.03-2.26 (m)
\end{align*}
\]
m.p. = 146-147°C. (bright red plates from ethyl acetate).

\[
C_{25}H_{10}O_3S\]

Required 67.26 4.04 21.53

Found 66.73 4.03 21.00

\[\begin{array}{c}
\text{a, c, o} \\
\text{b} \\
\text{d}
\end{array}\]

γ 2.23 - 2.92 (m)

γ 1.95 (s)

γ 6.21 (s)

---

m.p. = 138-139°C. (brown needles from ethyl acetate).

\[
C_{15}H_{11}S_3\]

Required 62.07 4.83 33.11

Found 62.23 4.81 32.85

\[\begin{array}{c}
\text{a} \\
\text{b} \\
\text{c} \\
\text{d} \\
\text{e}
\end{array}\]

γ 2.92 (s)

γ 2.36 - 2.66 (m)

γ 6.93 (t) \(J_{cc} = 6 \text{ cps.}\)

γ 7.18 - 7.38 (m)

γ 7.86 - 8.30 (m)
m.p. = 171–172°C (brown plates from ethyl acetate).

\[
\begin{array}{c|c|c|c}
\text{C}_{16}\text{H}_{16}\text{S}_{3} & \text{Required} & 63.16 & 5.26 & 31.58 \\
\text{Found} & 63.31 & 5.20 & 30.88 \\
\hline
\text{a} & 3 & \gamma 7.61 (s) \\
\text{b} & 2 & \gamma 2.75, 2.82 (d); J_{bc} = 7 \text{cps} \\
\text{c} & 2 & \gamma 2.48, 2.55 (d) \\
\text{d} & 1 & \gamma 2.75 (s) \\
\text{o} & 2 & \gamma 7.16–7.36 (m) \\
\text{f} & 2 & \gamma 6.91 (t); J_{fg} = 6 \text{cps} \\
\text{g} & 4 & \gamma 7.86–8.26 (m) \\
\end{array}
\]

m.p. = 178–179°C (bright red plates from ethyl acetate).

\[
\begin{array}{c|c|c|c}
\text{C}_{16}\text{H}_{16}\text{S}_{3} & \text{Required} & 63.16 & 5.26 & 31.58 \\
\text{Found} & 63.06 & 5.02 & 31.68 \\
\hline
\text{a} & 3 & \gamma 7.61 (s) \\
\text{b} & 2 & \gamma 2.74, 2.82 (d); J_{bc} = 8 \text{cps} \\
\text{c} & 2 & \gamma 2.20, 2.28 (d) \\
\text{d} & 1 & \gamma 1.97 (s) \\
\text{o,f} & 4 & \gamma 6.96–7.18 (m) \\
\text{g} & 4 & \gamma 8.00–8.16 (m) \\
\end{array}
\]
m.p. = 168-169°C. (bright red plates with a green reflex from ethyl acetate).

\[
\begin{array}{ccc}
\text{C}_{17}\text{H}_{20}\text{S}_3 & \text{Requires} & 63.76 \quad 6.11 \quad 30.00 \\
& \text{Found} & 63.70 \quad 6.05 \quad 30.14 \\
\text{a} & 3 & \gamma 7.35 (s) \\
\text{b} & 2 & \gamma 2.75, 2.83 (d); J_{bc} = 8 \text{ cps.} \\
\text{c} & 2 & \gamma 2.18, 2.26 (d) \\
\text{d} & 1 & \gamma 1.93 (s) \\
\text{e} & 3 & \gamma 7.51 (s) \\
\text{f} & 9 & \gamma 8.46 (s)
\end{array}
\]

m.p. = 152-153°C. (bright red plates with a green reflex from ethyl acetate).

\[
\begin{array}{ccc}
\text{C}_{21}\text{H}_{27}\text{S}_3 & \text{Requires} & 67.01 \quad 7.45 \quad 25.54 \\
& \text{Found} & 67.18 \quad 7.24 \quad 25.72 \\
\text{a} & 3 & \gamma 7.62 (s) \\
\text{b} & 2 & \gamma 2.76, 2.83 (d); J_{bc} = 7 \text{ cps.} \\
\text{c} & 2 & \gamma 2.19, 2.26 (d) \\
\text{d} & 1 & \gamma 1.69 (s) \\
\text{e} & 2 & \gamma 6.71 (s) \\
\text{f} & 9 & \gamma 8.99 (s) \\
\text{g} & 9 & \gamma 8.42 (s)
\end{array}
\]
<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
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</tr>
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<tr>
<td></td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>2</td>
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<td>3</td>
</tr>
<tr>
<td>( \tau )</td>
<td>1.19 (s)</td>
<td>2.55 (s)</td>
<td>1.95 (s)</td>
<td>2.31, 2.40 (d), ( J_{\text{dc}} = 9 ) cps.</td>
<td></td>
<td>6.19 (s)</td>
</tr>
</tbody>
</table>

(Spectrum recorded in hot 1,1,2-trichloroethane).
a  2  \( \gamma \ 2.15, 2.16, 2.27, 2.28 \) (q)
b  2  \( \gamma \ 2.70 \) (t)
c  2  \( \gamma \ 2.23, 2.21, 2.35, 2.36 \) (q)

\( J_{ab} = 12 \) cps.
\( J_{ac} = 1 \) cps.
\( J_{bc} = 12 \) cps.

(Spectrum recorded in deuterium oxide).

c  4  \( \gamma \ 6.53 \) (s)
b, c  4  \( \gamma \ 2.12 - 2.49 \) (m)
a. 4 \( \gamma 7.51 \) (s)
b,c 4 \( \gamma 2.12 \text{--} 2.51 \) (m)

(C.A.T. spectrum in deuterochloroform)

\[ \begin{align*}
a & \quad 1 \quad \gamma 2.30 \text{ (s)} \\
b & \quad 2 \quad \gamma 0.88, 0.89, 1.01, 1.02 \text{ (q)} \\
c & \quad 2 \quad \gamma 1.99 \text{ (t)} \\
d & \quad 2 \quad \gamma 1.26, 1.27, 1.39, 1.40 \text{ (q)} \\
\end{align*} \]

\( J_{bc} = 8 \text{ cps.} \)
\( J_{ca} = 8 \text{ cps.} \)
\( J_{bd} < 1 \text{ cps.} \)

(Spectrum recorded in trifluoroacetic acid).
\[
\begin{align*}
\text{Compound 1:} & \\
\text{a} & = 4 \quad \gamma 6.40 \text{ (s)} \\
\text{b, d} & = 4 \quad \gamma 2.00-2.24 \text{ (m)} \\
\text{c} & = 2 \quad \gamma 2.62 \text{ (t)}; J_{bc} \approx J_{cd} \approx 8 \text{ cps}.
\end{align*}
\]

\[
\begin{align*}
\text{Compound 2:} & \\
\text{a} & = \text{Me} \quad \gamma 6.61 \text{ (s)} \\
\text{b} & = \text{Me} \quad \gamma 6.49 \text{ (s)}
\end{align*}
\]

\[
\begin{align*}
\text{Compound 3:} & \\
\text{a} & = \text{Me} \quad \gamma 6.26 \text{ (s)} \\
\text{b} & = \text{Me} \quad \gamma 6.53 \text{ (s)}
\end{align*}
\]
\( O_2N \text{ Br} \)

\[
\begin{align*}
\text{a} & \quad 2 \quad \gamma 1.93, 2.01 \text{ (d)} \\
\text{b} & \quad 2 \quad \gamma 2.25, 2.33 \text{ (d)} \\
J_{ab} & = 8 \text{ opa.}
\end{align*}
\]
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