A STUDY OF

THE PREPARATION & REACTIONS OF SOME ORGANIC SULPHIDES,

WITH SPECIAL REFERENCE TO

THE CONVERSION OF DITHIOCARBALKYL DISULPHIDES INTO THE CORRESPONDING MONOSULPHIDES

A STUDY OF THE PREPARATION AND REACTIONS OF SOME ORGANIC SULPHIDES, WITH SPECIAL REFERENCE TO THE CONVERSION OF DITHIOCARBALKYL DISULPHIDES INTO THE CORRESPONDING MONOSULPHIDES.

THESIS

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BY

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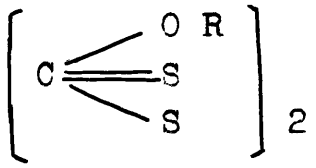
I INTRODUCTION

The object of the present investigation was, in part, to find more satisfactory methods for the preparation of organic disulphides, in particular for the preparation of the acid disulphides derived from the alkyl esters of di thio carbonic acid. There are described in the literature a number of methods for the preparation of organic disulphides of the acid type, but none of these can be applied to the preparation, in a pure state, of such disulphides as those obtainable by the oxidation of the higher aliphatic alkali xanthates, which, on account of their physical properties and unstable nature, cannot be purified by ordinary methods.

The main object of the present investigation was the study of the chemical properties of acid disulphides, in particular their behaviour towards alkali cyanides, which convert them into the corresponding monosulphides by the removal of one atom of sulphur. It was proposed at first to confine the study of the action of alkali cyanides on acid disulphides to their action on di thio carbalkyl disulphides of the general formula:

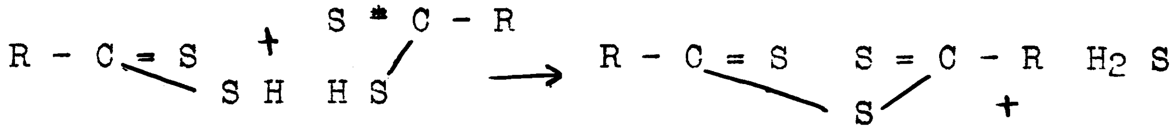


It was soon found, however, that a more promising line of attack for determining the mechanism of the desulphurizing action of alkali cyanides on acid disulphides was to study the desulphurization of tetra substituted thiuram disulphides. This modification of the original program is justified by the fact that the latter show the same behaviour towards alkali cyanides as the di thio carbalkyl disulphides or dixanthogens. Hence it is permissible to assume that the mechanism of the reaction is the same in each case.

Since many of the compounds dealt with in this thesis belong to classes of sulphur compounds to which but little space is devoted in text-books, and which are usually described in the literature under specific names, it will perhaps avoid confusion to indicate here the classification that has been adopted.

1. Thio anhydrides.

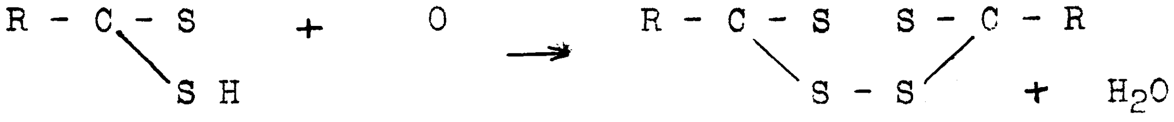
This term will be used to designate collectively the acid monosulphides derived from thiol acids by the removal of hydrogen sulphide from two moles of the acid.



where R may be a monovalent oxy alkyl, amino alkyl phenyl or aromatic radical.

2. Thio acid disulphides.

This term will be used to designate, as a class, the compounds derived from di thio acids, such as xanthic, di thio carbamic or di thio carboxylic acids, by oxidation.



$$\begin{array}{l} R-C-S \quad + \quad O \longrightarrow R-C-S \quad S-C-R \\ \qquad \diagdown SH \qquad\qquad\qquad\qquad \diagdown S-S \diagup \quad + \quad H_2O \end{array}$$

3. Thio acid thio cyanates.

This term will be applied to that class of compounds obtained from derivatives of thio carbonyl chlorides by the action of metallic thio cyanates.

$$\begin{array}{l} R-C-S \quad + \quad MSCN \longrightarrow R-C-S \quad + \quad MCl \\ \qquad \diagdown Cl \qquad\qquad\qquad\qquad \diagdown SCN \end{array}$$

II HISTORICAL

Preparation of thio acid disulphides.

There are described in the literature numerous methods for the oxidation of organic compounds containing a thiol group to disulphides. The use of most of these methods is limited to the oxidation of compounds of the R.SH type, that is, mercaptans, to their disulphides, RSSR, and only a few can be used for the oxidation of compounds of the RCSSH type to the corresponding disulphides, on account of the unstability of the free di thio acids, in particular xanthic and di thio carbamic acids.

The oxidizing agent most commonly used up to the present time is iodine, either in alcoholic or aqueous potassium iodide solution. Its use for the oxidation of metallic xanthates to dixanthogens was first described by Desains (1) and Debus (2). Except in the few cases where the dixanthogen is a solid, and can be purified by recrystallization, iodine cannot be used to prepare pure dixanthogens.

Copper sulphate, in aqueous solution, is another oxidizing agent which is commonly used. (3). The main disadvantage of using copper sulphate is, as can be seen by the following equation, only half of the xanthate is converted to the dixanthogen, the other half being lost through the formation of cuprous xanthate.

$$Cu\ SO_4 + ROCS.SK \rightarrow (ROCS.S)_2 + K_2SO_4$$

$$ROCS.S\ Cu$$

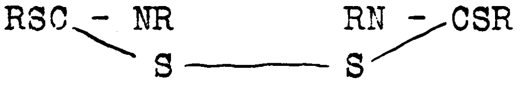
Chlorine has also been used as an oxidizing agent (4), but gives poor yields and impure products on account of side reactions, such as formation of hydrochloric acid which then decomposes some of the xanthate.

Desulphurization of thio acid disulphides to the corresponding thio anhydrides.

J. von Braun and F. Stechele (5) were the first to observe that tetra substituted thiuram disulphides of the type $(R_2NCS.S)_2$ were desulphurized by the action of potassium or di alkyl ammonium cyanides in alcoholic solution, to the corresponding thiuram monosulphide.

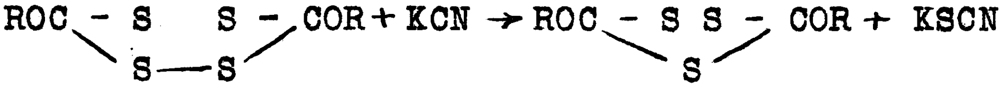
$$(R\ NCS.S)_2 + KCN \rightarrow (R\ NCS)_2\ S + KSCN$$

They showed that the thione sulphur atoms cannot be the point of attack of the cyanide, for disulphides of the general structure,



can be partly desulphurized by the same agent. They offer the view that desulphurization might take place in two stages, first reduction of the thiuram disulphide to the free acid, then conversion of the free acid to the anhydride by the removal of H_2S, but do not give any evidence in support of this view.

Von Braun and Stechele were led to the study of the action of alkali cyanides on thiuram disulphides by the observation that the colourless tetramethyl thiuram disulphide, obtained by the action of cyanogen bromide on dimethyl-ammonium di-methyl di-thio-carbamate in cold alcoholic solution, gradually changed over to a deep yellow compound when left for some time in contact with the mother liquor, or if the solution is warmed. The yellow compound was identified as tetra methyl thiuram monosulphide, and the conversion of the dimethyl ammonium cyanide formed in the first part of the reaction into the corresponding thiocyanate indicated that the cyanide was the desulphurizing agent. This was later confirmed experimentally by acting on tetra methyl thiuram disulphide with KCN in alcoholic solution. Von Braun and Stechele report in the same paper that normal disulphides, such as benzyl disulphide, are not desulphurized by alkali cyanides, also that isothiuram disulphides, although readily acted on by cyanides, only give in a very small yield a product which appears to be the isothiuram monosulphide, the main products obtained being decomposition products of the disulphide. They also attempted to prepare the monosulphide from di phenyl carbamyl disulphide and also from the acid disulphide derived from benzoic and cinnamic acids but without success. That alkali cyanides had a desulphurizing action on the acid disulphides of the type $(ROCS.S)_2$ (dixanthogens), was shown in the course of some work done in this laboratory under the direction of Dr.G.S. Whitby by Mr.H.Greenberg (6). They have shown that the reaction is analogous to that between cyanides and tetra substituted thiuram disulphides.



$$\begin{array}{l}\mathrm{ROC - S \qquad S - COR + KCN \rightarrow ROC - S\ \ S - COR + KSCN}\\ \qquad \diagdown\ \mathrm{S{-}S}\ \diagup \qquad\qquad\qquad\qquad\qquad \diagdown\ \mathrm{S}\ \diagup\end{array}$$

Desulphurization in this case, however, occurs somewhat more readily than in the case of the thiuram compound, probably on account of the much greater solubility of the dixanthogens in the solvents used.

It may be of interest to give here other examples of the desulphurizing action of alkali cyanides, for it is probable that the mechanism of the reaction in many of these is analogous to that between alkali cyanides and thio and disulphides.

It is well known that alkali cyanides in aqueous solution are converted into thio cyanates by the action of sulphur even at room temperature (7). The reaction takes place more rapidly on warming (8). Sodium or potassium polysulphides are readily desulphurized by alkali cyanides in aqueous solution)9), also thiosulphates (10) and tetra thionates (11), the latter being reduced to sulphites. Gutmann (12) found that thio sulphonates such as $C_6H_5S.SO_2Na$ are desulphurized by alkali cyanides to sulphonates.

$$R.S.SO_2Na + KCN \rightarrow RSO_2Na + KSCN$$

An entirely different result is obtained, however, if an organic thio sulphate, such as $C_6H_5CH_2S.SO_3Na$, is treated with an alkali cyanide. Footner (13) observed that if benzyl thio sulphate, for instance is treated with NaCN in aqueous solution, benzyl thio cyanate and sodium sulphite are formed,

$$RS.SO_3Na + NaCN \rightarrow RSCN + Na_2SO_3$$

Formation of thio anhydrides by other than desulphurization methods.

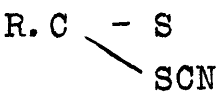
Thio anhydrides of xanthic acids were first prepared by the action of acid chlorides on metallic xanthates. Welde (14) prepared the first member of that series by the action of ethyl chlor carbonate on potassium ethyl xanthate. He believed that the following equation represented the reaction:

$C_2H_5OCS.SK + C_2H_5OCO.Cl \rightarrow C_2H_5CS.S.CS.OC_2H_5 + C_2H_5OCO.OK + KCl$

Other acid chlorides were later found to give the same reaction. Wilcox (15) used phosgene and acetyl chloride for preparing ethyl monoxanthogen. Tschugaeff (16) used ethyl chlor carbonate and benzoyl chloride for preparing menthyl monoxanthogen. It will be shown in the theoretical part that Welde's view is not correct, and also that the mechanism of the action of acetyl and benzoyl chlorides on xanthates is the same as that of ethyl chlor carbonate.

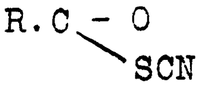
<u>Formation and chemical properties of acid thio cyanates and acid iso thio cyanates.</u>

The thio acid thio cyanates isolated in the course of this work which have been identified as the intermediate compounds in the desulphurization of thio acid disulphides to the corresponding monosulphides, belong to a hitherto unknown series of sulphur compounds of the general type.



$R.C(=S)SCN$

The corresponding oxyacid thio cyanates however,



$R.C(=O)SCN$

have been known for some time. The latter differ markedly in some of their chemical properties from the thio compounds. Under certain conditions, however, the new thio acyl thiocyanates give the same characteristic reactions as the oxy acyl thiocyanates. From this it would appear that these two classes of compounds have the same constitution, and since the question as to the structure of the oxy compounds has not been definitely solved yet, it will be of interest to give here an account of the work reported in the literature on the oxy acyl thiocyanates. Much evidence has been accumulated in support of the view that these compounds offer an example of a peculiar kind of tautomerism which is characterized by their power to react either in the thiocyanate or in the iso thiocyanate or thiocarbamidic form, according to the conditions under which reaction takes place. This fact was recognized by Miquel (17) who was the first to prepare thio cyanates of the acidic type by heating lead thiocyanate with acid chlorides in benzene solution. He prepared acetyl, butyryl, benzoyl and salicyl thio cyanates in solution, and isolated two of these, acetyl and benzoyl. Miquel considered these compounds as true thiocyanates, not as thio carbimides. That is, he assigned to them the formula R.Co.SCN instead of RCO.NCS and considered as 'abnormal' such reactions as that which takes place with aniline:

$$R.CO.NCS + C_6H_5NH_2 \rightarrow RCO.NH \cdot CSNH - C_6H_5$$

because the formation of an acyl phenyl thio urea under these conditions can only be explained by assuming that the thiocyanate reacts in the iso or thio carbamidic form. Dixon later showed (18) that acid thiocyanates, at least insofar as their behaviour towards armoatic bases is concerned, are true thio carbimides, and that consequently, Miquel's reaction was not to be regarded as an abnormal one. Dixon based his view on a more thorough study of the action of aromatic bases on the acid thiocyanates as prepared by Miquel, (loc.cit) and on a new series of acid thio cyanates, ROCO.SCN which he obtained by the action of chlor carbonates on lead thio cyanate. He found that $C_2H_5OCO.SCN$, prepared from ehtyl chlor carbonate and lead thiocyanate in benzene reacts with aniline to form a ~~ab~~ carboxy ethyl phenyl thio carbamide. Consequently, this acid thio cyanate also must be regarded as existing under the iso form,

$$C_2H_5O\ CO.NCS + C_6H_5NH_2 \rightarrow C_2H_5O\ CO.NHCS.NH.C_6H_5$$

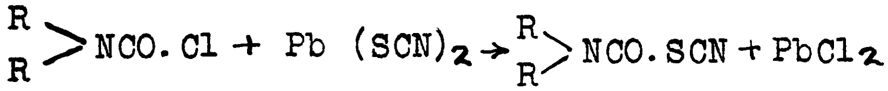
Dixon describes in the same paper the action of alcohols on the new acid thio cyanates, and found that in this case also the latter undergo the thio carbamidic reaction.

By the action of methyl alcohol on the ethyl compound, he obtained a substituted ~~M~~Urethane,

$$C_2H_5O\ CO.NCS + CH_3OH \rightarrow C_2H_5O.CO.NHCS.OCH_3$$

In the above work Dixon did not isolate the ethyl thio cyan carbonate, but used a benzene solution of the compound obtained by refluxing for a short time lead thio cyanate with a benzene solution of ethyl chlor carbonate, then filtering the solution from lead chloride. He actually isolated the compound later (19) and determined its boiling point.

A few years later Dixon (20) reported that the action of lead thiocyanate on di substituted carbamyl chlorides gives rise to compounds which show the same general reactions with aromatic bases and alcohols as the acid thio cyanates then known. The method he used ~~for~~ to prepare~~d~~ these carbamyl thio cyanates was to heat the carbamyl chloride with excess of lead thio cyanate in benzene.

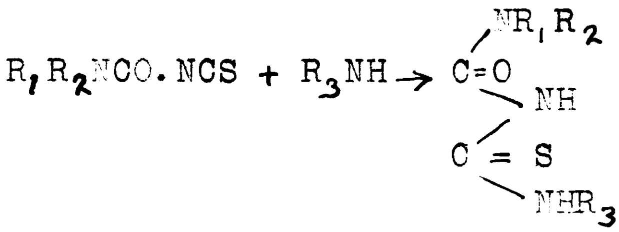


$$\begin{matrix}R\\R\end{matrix}\!>NCO.Cl + Pb\ (SCN)_2 \rightarrow \begin{matrix}R\\R\end{matrix}\!>NCO.SCN + PbCl_2$$

The excess lead thio cyanate and the lead chloride were then filtered off, and the benzene solution of carbamyl thiocyanate thus obtained used directly without further treatment. Dixon states that the above reaction between carbamyl chlorides and metallic thio cyanates cannot be carried out in alcohol, because the thiocyanate first formed changes over directly into the thio carbimide, which then reacts with the alcohol to form urethane derivatives,

$$R_2NCO.SCN \rightarrow R_2NCO.NCS + R_1OH \longrightarrow R_2NCO.NHCS.OR_1$$

Dixon prepared the methyl phenyl,ethyl phenyl and benzyl phenyl carbamyl thio cyanates, and found that all of these, when mixed in benzene solution with primary aromatic amines, reacted readily to form tri-substituted thio biuret.



$$R_1R_2NCO.NCS + R_3NH \rightarrow \begin{array}{l} \quad NR_1R_2 \\ C=O \\ \quad NH \\ C=S \\ \quad NHR_3 \end{array}$$

In these experiments the carbamyl thiocyanates were used in benzene solution, as obtained from the action of lead thio cyanate on carbamyl chlorides, and Dixon states that all attempts at isolating the thiocyanates failed, due apparently to the fact that these are very unstable, except in solution.

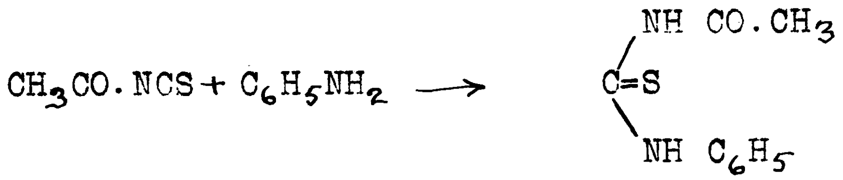
It will be noted that at this stage of the work on acid thio cyanates, it was a generally accepted view that these compounds were true thio carbimides, and incapable of existing as normal thio cyanates. This view was based mainly on their behaviour towards primary aromatic bases, the reaction being generally carried out at the boiling point of benzene. A chance observation made by Dixon,(21) however, showed that the temperature at which the reaction takes place between a given thio cyanate and a given base is a very important factor in determining the nature of the reaction. He observed that if acetyl thio cyanate and aniline are caused to react at low temperature, appreciable amounts of aniline thio cyanate and acetanilide are formed, while at the boiling point of benzene, acetyl phenyl thio carbamide is the main product. Hawthorne took up the problem at this point (22) and determined quantitatively the reaction products of acetyl thio cyanate and aniline at temperature ranging from -12° to 120°. He found that at -12°, aniline hydro thio cyanate and acetanilide formed 94% of the total products obtained, sonsequently at this temperature the acetyl compound behaves as a true thio cyanate. At 120°, the aniline hydro thio cyanate only formed 2.5% of the total products obtained, these consisting mainly of acetyl phenyl thio urea, hence at high temperature the acetyl compound no longer behaves as a thio cyanate but as a thio carbimide.

The two reactions are:

1) Thio cyanic, at low temperature,

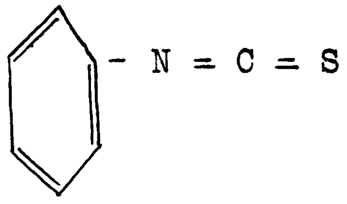
$$CH_3CO.SCN + 2C_6H_5NH_2 \rightarrow CH_3CONH\ C_6H_5 + C_6H_5NH + HSCN$$

2) Thio carbimidic, at high temperature,



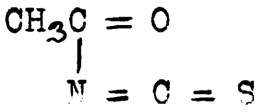
$$CH_3CO.NCS + C_6H_5NH_2 \longrightarrow C(=S)(NH\,CO.CH_3)(NH\,C_6H_5)$$

The same author in a later paper (23) gives the values for molecular refraction obtained from observations on a highly purified sample of acetyl thio cyanate, and concludes from the close agreement between the values observed and the calculated values for CH CO.NCS, that acetyl thio cyanate is a true thio carbimide. They also observed that the molecular refraction of the compound does not vary with temperature, from which it follows that isomeric change of the SCN group does not take place under these circumstances. It must be pointed out that the calculated value for the molecular refraction of $CH_3CO.NCS$ was obtained by Hawthorne by adding to the value for the group CH_3CO-, the mean of the molecular refraction of the group NCS obtained from observations on ethyl, allyl and benzyl thiocarbimides. This does not seem very logical, since, it is known that the system $= C = S$ in conjugation witha double bond gives abnormally high values for refraction; this is very apparent in phenyl thio carbimide:



$$C_6H_5 - N = C = S \qquad (24)$$

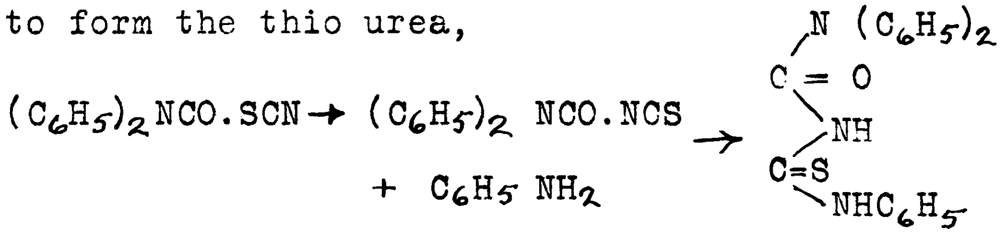
and conjugation occurs in acetyl thio cyanate, if it is given the thio carbamidic form,



$$\begin{array}{l} CH_3C = O \\ \quad\;\; | \\ \quad\;\; N = C = S \end{array}$$

so that one would not expect a normal value for the NCS group under these conditions.

Johnson and Levi (25) were the first to obtain any direct evidence as to the existence of two distinct isomeric forms of an acid thio cyanate. They prepared diphenyl carbamyl thiocyanate by the action of KSCN on the carbamyl chloride in boiling alcohol. They believed that the compound thus obtained was a true thio cyanate, for it did not react with aniline. They observed, however, that on heating the compound for one hour at 138° to 141°, a product was obtained which reacted readily with aniline to give a·b· di phenyl carbamyl phenyl thio urea. This they considered as strong evidence that the thio cyanate first obtained had undergone isomeric change into the thio carbimide under the influence of heat, the latter then reacting with aniline to form the thio urea,



$(C_6H_5)_2NCO.SCN \rightarrow (C_6H_5)_2\,NCO.NCS + C_6H_5\,NH_2 \rightarrow$

Subsequently to the publication of the above paper by

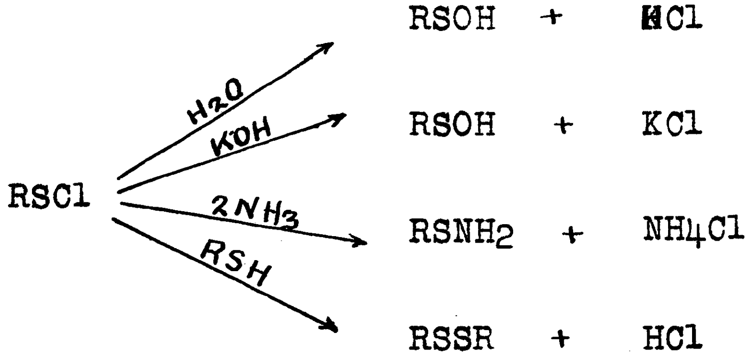
Johnson and Levi, Dixon and Taylor (26) took up the question again. They prepared in a highly purified form carboxy methyl and carboxy ethyl thio cyanates, and determined the molecular refraction of these two compounds. They found a close agreement between the observed value and that calculated for ROCO.NCS, but did not take into account the fact that the presence of a conjugated system of double bonds in such a structure would be expected to produce exaltation. Dixon and Taylor report in the same paper that in the presence of aqueous alkalis such acid thio cyanates as acetyl, benzoyl, carboxy methyl and carboxy ethyl react almost exclusively in the normal form.

There is a new series of organic thio cyanates, the first members of which were prepared recently by Lecher and Wittmer (27) that can be considered as acid thio cyanates, Lecher's thio cyanates, which he calls 'thio rhodanides' have the general structure RS.SCN, hence these, as the acid thio cyanates, consist of an .SCN radical attached to an electro negative group. The first thio rhodamide prepared by Lecher was the nitro phenyl one, by the action of thio cyanogen on the mercaptan.

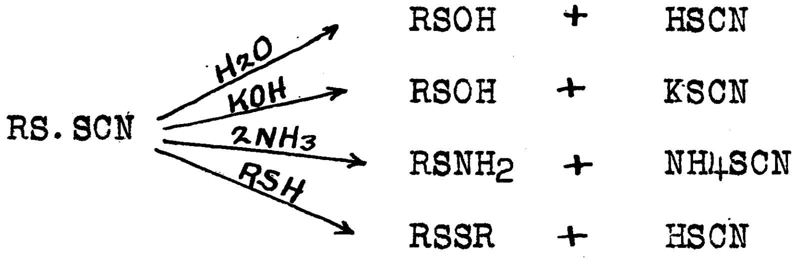
$$NO_2C_6H_4SH + (SCN)_2 \rightarrow NO_2C_6H_4S.SCN + HSCN$$

Lecher later prepared the ethyl, phenyl and B naphthyl thio rhodamides by the same method (28).

In his first paper on thio-rhodamides (29), Lecher points out the close analogy between these compounds and the aryl sulphur chlorides first prepared by Zincke (30), and gives as examples, the following reactions, in which the .SCN group of the thio rhodanides show the same reactivity and properties as the .Cl atom in the aryl sulphur chlorides. The latter react in the following manner with water, alcoholic KOH, alcoholic NH_3 and mercaptans,



Under the same conditions thio-rhodanides give the same products.



Another reaction common to both the aryl sulphur chlorides and aryl sulphur thiocyanates is mentioned by the same author in a later paper (31). With H_2S in ether, both give rise to trisulphides.

$$2RSCl + H_2S \longrightarrow RSSSR + 2HCl$$

$$2RS.SCN + H_2S \longrightarrow RSSSR + 2HSCN$$

It is claimed by Lecher that the above reactions show conclusively that the compounds he prepared are not to be regarded as aryl cyanogen sulphides with homopolar union between the sulphur atoms, but as aryl sulphur thiocyanates, with heteropolar union between those two atoms, as between the Cl and the S atoms in the chlorides. In support of this view the author gives the example of free 'rhodan' which Söderbäck (32) considered to be of the type NCS.SCN, and which the latter called 'compound halogen', on account of its marked halogen-like character in most of its reactions. In free 'rhodan' the halogen-like valence doubtless proceeds from the sulphur atoms, since in all halogen-like reactions of the compound derivatives are formed with the grouping .SCN. Consequently the .SCN group can retain its halogen-like charater in such a configuration as RS.SCN.

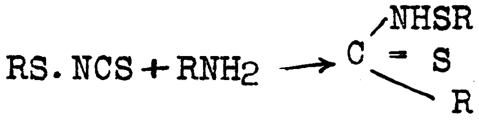
Lecher established the constitution of the organic sulphur thiocyanates and showed that these contain an .SCN group by the following reactions: He prepared o'nitrophenyl sulphur thiocyanate by the action of KSCN on o'nitrophenyl sulphur chloride.

$$1.2\ NO_2C_6H_4SCl + KSCN \rightarrow 1.2\ NO_2C_6H_4S.SCN + KCl$$

The thiocyanate obtained by this method is identical with that obtained by the action of free rhodanm$(.SCN)_2$ on the mercaptan. He also points out that in their reaction with ammonia or primary amines, these compounds behave as thiocyanates and not as isothiocyanates.

$$RS.SCN + 2RNH_2 \rightarrow RS.NHR + RNH_2 \text{——} .HSCN$$

If these compounds contained an .NCS instead of an .SCN group, one would expect,



$$RS.NCS + RNH_2 \longrightarrow C\begin{array}{l}\diagup NHSR\\ = S\\ \diagdown R\end{array}$$

A consideration of the results of later investigations by the same author brings out very clearly the great similarity between, on the one hand, thio cyanogen, either in the free state or in combination, and, on the other hand, the halogens. He determined the molecular weight of free rhodan, and found it to correspond to the formula NCS.SCN. From that he concludes that the marked electron affinity of free rhodan and its halogen like character make it apparent that the bond~~s~~ between the S atoms in that compound is similar in energy value to the interatomic bonds in elementary halogens. The same author subseqnently put forward the view that rhodan, as judged from the stability of some of its derivatives, would be placed between Br and I.

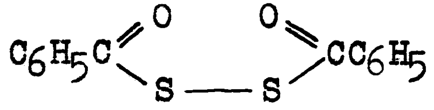
It is interesting to note that this position corresponds to that given to the same compound by Bjerrum and Kirschner (33) on electro-chemical grounds.

General properties and structure of organic disulphides.

The stability and chemical properties of organic disulphides are, as one would expect, dependent on the nature of the substitu~~y~~ent groups. E. Fromm has shown however, (34), that the configuration of the molecules itself has a marked effect on the chemical behaviour of these compounds. He divides organic disulphides into two classes. 1) Disulphides with adjacent single bonds, such as benzyl disulphides,

$C_6H_5CH_2S\text{-}SCH_2C_6H_5$

2) Disulphides with adjacent doube bonds, such as benzoyl disulphide,



$C_6H_5C(=O)S\text{—}SC(=O)C_6H_5$

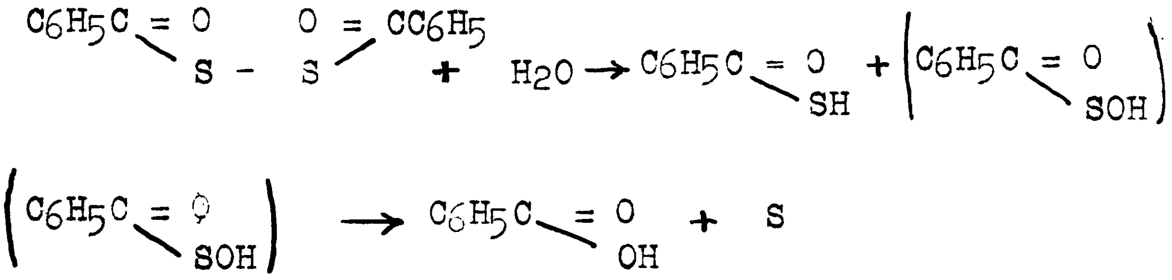
All disulphides are readily hydrolysed by alkalies, but those of the second class more readily than those of the first class. Also the products of hydrolysis are not the same. With benzyl disulphide, for instance, the reaction is,

$$(C_6H_5CH_2S)_2 + H_2O \rightarrow C_6H_5CH_2SH + (C_6H_5CH_2SOH)$$

The peracid, which is formed simultaneously with the mercaptan, breaks into mercaptan and active oxygen, the latter then oxidizing some of the mercaptan to benzoic and thio benzoic acids,

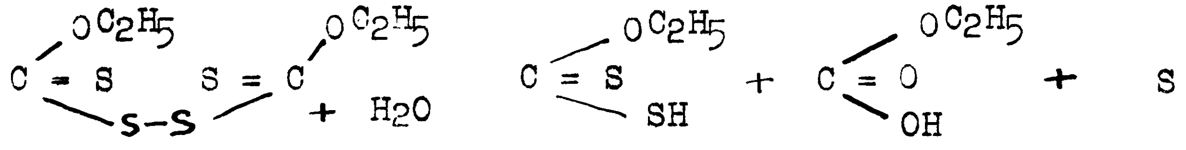
$$(C_6H_5CH_2SOH) \longrightarrow C_6H_5CH_2SH + (O)$$

With the disulphides of the second glass, the first stage of the reaction is the same, but the peracid formed breaks down into the corresponding oxygen acid and elementary sulphur. To take benzoyl disulphides as an example,



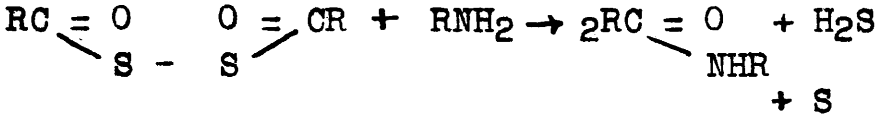
Fromm states that the splitting up of sulphur under these conditions is so generally established, that its formation can be taken as an indication of the presence of adjacent double bonds.

Another example is the hydrolysis of ethyl dixanthogen (35),



Thio benzoyl disulphide also yields sulphur when boiled with KOH (36).

The same sharp distinction exists between the two classes of organic disulphides with respect to their behaviour towards organic bases or ammonia. Disulphides of the first class, such as alkyl or aryl disulphides, are not decomposed by the action of nitrogenous bases, such as ammonia or primary amines, while the disulphides of the second class, such as acid disulphides, are readily decomposed by those substances, amides being formed,



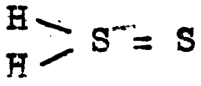
$$RC(=O)-S-S-C(=O)CR + RNH_2 \rightarrow 2RC(=O)NHR + H_2S + S$$

Structure of organic polysulphides.

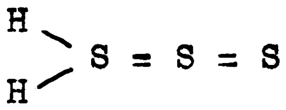
There has been much speculation as to the mode of union between the sulphur atoms in polysulphides, Schone (37), considered the latter as sulphur derivatives of sulphuric acids, and Mendelejeff held the same view. There is, however, much evidence against such a structure. Kuster (38) states, for instance, that one would expect such perthiosulphuric acids to be very strong acids, and this is not the case with hydrogen polysulphides.

There are at present two main views as to the structure of poly sulphides. According to the first, polysulphides correspond in structure to the straight chain formula. This idea was first put forward by Frankland, and later by Blanksma (39(and is supported by the following facts; the substitution of H by HS produces a constant deepening in colour, and H_2S_3 is readily converted to H_2S_2 by heating. Also, as Holmberg points out (40), the readiness with which mercaptans are oxidized to disulphies and disulphides reduced back to mercaptans, is to be regarded as strong evidence in favour of the straight chain structure.

According to the second view, polysulphides contain one or more tetravalent sulphur atoms. The structure of hydrogen di- and trisulphide, for instance, would be,



and



This view was first put forward by Spring and Demarteau (41) and later slightly modified by Kuster (loc.cit) who claimed that it explained the readiness with which monosulphides take up sulphur in solution to form polysulphides.

III THEORETICAL

I. OXIDATION OF XANTHATES TO DIXANTHOGENS

Action of nitrous acid on xanthates in acid solutions.

Much time was spent at the beginning of this work in a search for satisfactory oxidizing agents for the preparation of dixanthogens. The first oxidizing agent which gave promising results was nitrous acid. Its use was suggested by the fact that it oxidizes HI to I_2 and H_2O.

$$2HI + 2HONO \rightarrow I_2 + 2H_2O + 2NO$$

A similar action on xanthic acid would yield a dixanthogen.

$$2ROCS.SH + 2HONO \rightarrow (ROCS.S)_2 + 2H_2O + 2NO$$

This was found to be the case. The use of nitrous acid as an oxidizing zinc agent is limited, however, to the oxidation of those xanthic acids which are sufficiently stable in the presence of water in the free state, such as ethyl and isopropyl xanthic acids. This is shown by the variations in the yields obtained from different xanthates. By the action of nitrous acid on ethyl xanthic acid, an 87% yield of ethyl dixanthogen was obtained; with isopropyl and n-butyl xanthic acid, 80% yields of dixanthogen were obtained. With the higher alcohols, such as iso amyl and benzyl, the use of nitrous acid gives poor yields of the dixanthogens, also the products obtained are contaminated, the alcohols formed by the decomposition of the free xanthic acids dissolving in the dixanthogens, from which theycannot be completely extracted.

In the above experiments with nitrous acid, the procedure followed was essentially to add the required amount of 25% sulphuric acid to a solution containing equimolecular quantities of the alkali xanthate and sodium nitrite. It was found later, however, that hydrochloric acid of the same concentration gave better yields, a 97% yield of dixanthogen being obtained from ethyl xanthic acid, and an 87% yield from isopropyl xanthic acid. This seems to indicate that xanthic acids are more stable in aqueous hydrochloric than in aqueous sulphuric acids, unless hydrochloric acid itself takes part to some extent in the oxidation process, through the formation of nitrosyl chloride,

$$HCl + HONO \rightarrow NOCl + H_2O$$

$$2ROCS.SH + NOCl \rightarrow (ROCS.S)_2 + HCl + NO$$

Stanek has shown that nitrosyl chloride can be prepared by the action of aqueous HCl on sodium nitrite (42) while nitrosyl sulphate is not formed under the same conditions from sulphuric acid. It is very unlikely, however, that HCl would be oxidized to NOCl in the presence of free xanthic acid, because the latter undergoes oxidation far more readily than HCl itself. Consequently the reaction can be regarded as taking place according to the following equation, as already indicated.

$2ROCSSH + 2HONO \rightarrow (ROCS.S)_2 + 2H_2O + 2NO$

In view of the fact that the chemical properties of di substituted dithiocarbamates are, in many respects, analogous to those of the xanthates, it was thought interesting to determine the action of nitrous acid on the former.

On treating an aqueous solution of sodium di ethyl dithiocarbamate containing an equimolecular quantity of sodium nitrite with the required amount of hydrochloric acid, a 51% yield of tetra ethyl thiuram disulphide was obtained. Hence dithiocarbamic acid also can be oxidized to the disulphide by nitrous acid,

$2R_2NCS.SH + 2HONO \rightarrow (R_2NCS.S)_2 + 2H_2O + 2NO$

the lower yield obtained in this case being obviously due to the greater unstability of the free dithio acid.

Action of cyanogen bromide on alkali xanthates.

The oxidizing property of cyanogen bromide on salts of di substituted dithiocarbamic acids was first noted by von Braun (43), who obtained tetramethylthiuram disulphide by the action of cyanogen bromide on dimethyl ammonium dimethyldithiocarbamate in alcoholic solution at low temperature. It was thought that the action of cyanogen bromide on alkali xanthates would give dixanthogens under the same conditions. It was found, however, that monoxanthogens were almost exclusively obtained. The reason for this becomes evident if one compares the behaviour of tetrasubstituted thiuram disulphides with that of dixanthogens towards cyanides. The first are only slowly desulphurized by cyanides in cold alcohol, where as the second are very readily acted on by cyanides under the same conditions. Consequently the reaction, in the case of the xanthates, does not stop at the dixanthogen stage, for the cyanide which is formed simultaneously with the oxidation product immediately converts the latter to the monoxanthogen. The two reactions can be represented by the following equations:

$$2\mathrm{ROCS.SK} + \mathrm{CNBr} \rightarrow (\mathrm{ROCS.S})_2 + \mathrm{KCN} + \mathrm{KBr}$$

$$(\mathrm{ROCS.S})_2 + \mathrm{KCN} \rightarrow (\mathrm{ROCS})_2\mathrm{S} + \mathrm{KSCN}$$

It was later found,however, that the reaction could be stopped at the first stage by using as reaction media solvents in which either the dixanthogen or the alkali cyanide are insoluble, such as water, dry ether, or benzene. If water is used, the dixanthogen first formed precipitates out, and is not acted on by the cyanide, while if benzene is used, the alkali cyanide, being insoluble in that solvent, has no effect on the dixanthogen.

Aqueous cyanogen bromide appears to be very specific~~i~~ in its oxidizing action on xanthates, and its use has made it possible to prepare directly in a pure state xanthogens such as those derived from the higher aliphatic alcohols, which are relatively unstable liquids that cannot be purified by ordinary methods. The results obtained in the preparation of b-phenyl ethyl dixanthogen by the oxidation of the corresponding sodium xanthate with I_2 and CNBr can be given as an example, of the relative merits of the two methods. The above dixanthogen was prepared in the early part of this work by the action of an aqueous I_2- KI solution on an aqueous solution of the corresponding sodium xanthate, and obtained as an oil which even on cooling in CO_2-acetone, did not crystallize. It was expected, however, that this product should be a solid, and consequently, after having obtained good results in other preparations with CNBr, the same compound was prepared again, using CNBr, the reaction being carried out in water. As a result the dixanthogen was now obtained in the form of a well defined crystalline solid, melting at 49.5°-50°.

The action of cyanogen bromide on xanthates can be represented by the same equation that von Braun used to represent its action on dithiocarbamates (loc.cit.)

$$\begin{array}{c} \mathrm{ROCS.SM} \\ \mathrm{ROCS.SM} \end{array} + \begin{array}{c} \mathrm{CN} \\ | \\ \mathrm{Br} \end{array} \longrightarrow \begin{array}{c} \mathrm{ROCS.S} \\ | \\ \mathrm{ROCS.S} \end{array} + \begin{array}{c} \mathrm{MCN} \\ \mathrm{MBr} \end{array}$$

The above equation does represent the initial and final products present in the solution, when the reaction is carried out in water, but is very probably misleading as to the mechanism of the reaction. In the above reaction, the cyanogen group plays the same role as the halogen atom in the oxidation process, but it has been determined in a separate experiment, that cyanogen itself has no action on an aqueous solution of a sodium xanthate. The oxidizing action of cyanogen bromide can readily be explained, however, by assuming that water plays a part in the reaction, the hydrolysis of CNBr to HOBr and HCN being the first step, and HOBr being the actual oxidizing agent. Nef has shown that CNBr hydrolyses in the manner indicated (44),

$$\mathrm{CNBr} + \mathrm{HOH} \longrightarrow \mathrm{HOBr} + \mathrm{HCN}$$

$$\begin{array}{c}\mathrm{ROCS.SM}\\ \\ \mathrm{ROCS.SM}\end{array} + \begin{array}{c}\mathrm{OH}\\ |\\ \mathrm{Br}\end{array} \longrightarrow \begin{array}{c}\mathrm{ROCS.S}\\ \quad|\\ \mathrm{ROCS.S}\end{array} + \begin{array}{c}\mathrm{MOH}\\ \\ \mathrm{MBr}\end{array}$$

$$\mathrm{HCN} + \mathrm{MOH} \longrightarrow \mathrm{MCN} + \mathrm{HOH}$$

Strong evidence in support of the above view has been obtained from the fact that by the action of cyanogen bromide on metallic dithiocarbamates in the absence of water, products are obtained which are not oxidation, but substitution products, the reaction being in this case,

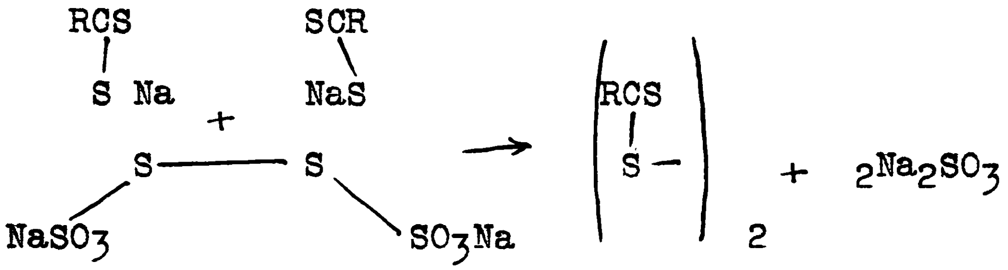
$$\mathrm{R_2NCS.SM} + \mathrm{BrCN} \rightarrow \mathrm{R_2NCS.SCN} + \mathrm{MBr}$$

Action of sodium tetrathionate on alkali xanthates.

Footner (45) has reported that he obtained in almost quantitative yields the corresponding disulphide by the action of sodium tetrathionate on an aqueous solution of sodium 6.methoxy m tolyl mercaptan. He also applied the method to benzyl and dichlorphenyl mercaptans with equally good results.

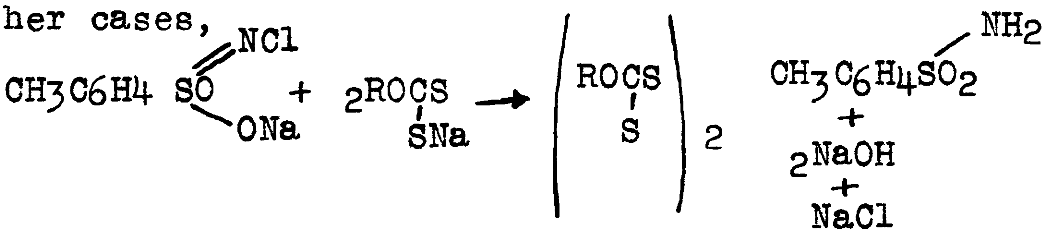
Sodium tetrathionate being a mild oxidizing agent, neutral in reaction, and water soluble, it was thought that it might have, on alkali xanthates, the same specific oxidizing action that Footner observed it to have in alkali mercaptides. That was found to be the case, and the yields obtained with xanthates have been found to be as good as those obtained by Footner with mercaptans, and the small heat of the reaction makes it possible to carry out the oxidation at room temperature without affecting the yield. As examples of the excellent results obtained with this compound, the preparations of methyl and benzyl dixanthogen may be mentioned. The former is described in the literature as an oil by Desains (46) who prepared it by the action of iodine on sodium methyl xanthate, and by Ragg (47) who obtained it by the action of copper sulphate on the same salt. It was obtained as a crystalline solid melting at 23-23.5° by the action of sodium tetrathionate on potassium methyl xanthate. Benzyl dixanthogen was also obtained as an liquid by Ragg, (loc.cit.) using copper sulphate. With tetrathionate the compound is obtained as a crystalline solid melting at 54°. Sodium tetrathionate has also been used with good results for the oxidation of dithionaphthaic and dithio benzoic acid.

The oxidation of dithio acids by sodium tetrathionate takes place according to the following equation:



Action of chloramine T on alkali xanthates.

The above compound is capable of oxidizing two moles of alkali xanthate to the corresponding dixanthogen, in neutral aqueous solution. The yield is very good and a pure product is obtained. This result was to be expected in view of the great similarity between the activity of the Cl in sodium tolylsulphochlor acid and in hypochlorous acid. The reaction is probably the same as that indicated by Schiemann (48) in other cases,



Action of nitrosyl chloride on xanthates.

Nitrosyl chloride was prepared by the method described by Stanek (loc.cit.) by the action of concentrated hydrochloric acid on sodium nitrite at 0°. The NOCl formed was extracted with chloroform, and the extract washed with cold saturated NaCl solution to remove free acid. By the addition of sodium isopropyl xanthate to an excess of NOCl in chloroform about a 40% yield of isopropyl dixanthogen was obtained.

Action of benzene sulphonyl chloride on xanthates.

This oxidizing agent was used by von Braun (49) for the oxidation of dithiocarbamates. It was found to have the same action on xanthates, ethyl dixanthogen being obtained in good yield by acting on sodium ethyl xanthate with the sulphonyl chloride in ether.

Action of cyanogen on xanthates.

This oxidizing agent gave unexpected results, It was believed at first that, since one half mole of cyanogen bromide is capable of oxidizing two moles of sodium xanthate, the CN group in the CNBr molecule played the same part as the Br atom in the oxidation process. The following experiment proved that that is not the case. On passing an excess of cyanogen gas through an aqueous solution of sodium xanthate, no appreciable action takes place. The obvious explanation of this is that the electron affinity of the CN group is less than that of the  $\underset{\text{S-}}{\text{ROCS}}$ group, and that consequently, it cannot displace the latter from its salts.

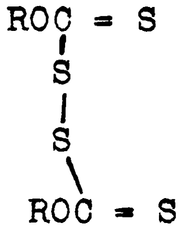
If this is the case, one would expect that the reverse reaction should take place, that is, it should be possible to oxidize NaCN by the action of a dixanthogen. This is actually what happens when a dixanthogen is allowed to act on sodium cyanide, the (ROC(S)S) group of the dixanthogen displaces the (.CN) group from its salt, a sodium xanthate and an acid thiocyanate being formed. This point however will be taken up again in the following chapter in connection with the desulphurization of disulphides.

II.DESULPHURIZATION OF THIO ACID DISULPHIDES BY THE ACTION OF ALKALI CYANIDES

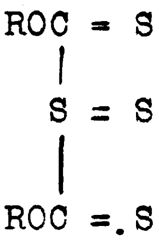
The mechanism of the action of alkali cyanides on di-substituted thiuram disulphides, whereby one atom of sulphur is removed from the chain and the corresponding monosulphide formed, was the subject of some speculation on the part of von Braun (50), who states that the lack of any analogy makes it difficult to form a plausible idea as to the nature of the reaction. The above author did not make any attempt to determine the mechanism of the reaction, but offered the view that the desulphurization process might take place in two stages; first, reduction of the disulphide to the acid, then formation of the thio anhydrides by the removal of H_2S from two moles of the acid.

There is another view of the mechanism of the same reaction, which was put forward more recently by Greenberg (51). The latter view is based on the assumption that disulphides exist in two tautomeric forms, which may be represented as follows:

A

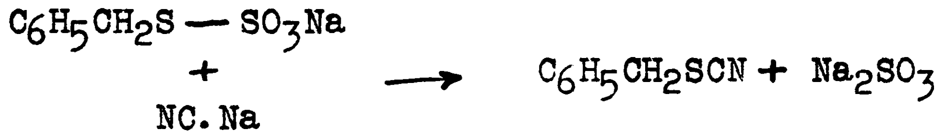


B



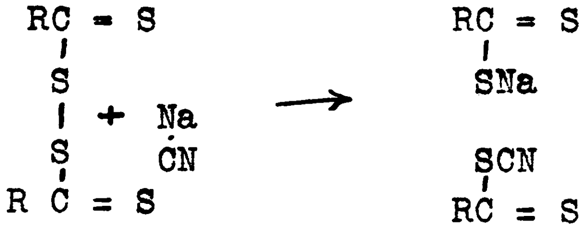
Of these two, the B form would be the one susceptible to the action of the cyanide, it being also assumed that the sulphur atom forming the side chain is loosely bound, and consequently easily removed. This view, however, does not explain why alkyl and aryl disulphides are not desulphurized by cyanides.

On reviewing the literature on the action of cyanides on organic sulphur compounds, it was noted that in a paper published recently (52), Footner and Smiles, obtained benzyl thio cyanate by the action of sodium cyanide on benzyl thio sulphate.



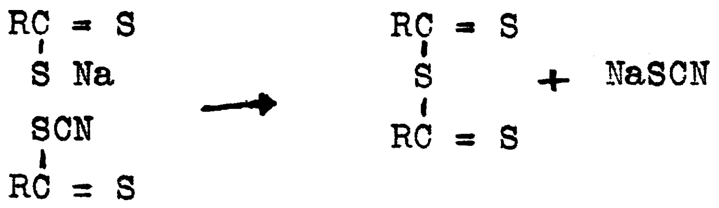
$$\begin{array}{c} C_6H_5CH_2S - SO_3Na \\ + \\ NC.Na \end{array} \longrightarrow C_6H_5CH_2SCN + Na_2SO_3$$

Although the disulphide bond in thiosulphates is of a somewhat different character from that of the corresponding bond in acid disulphides, there is some similarity between the two particularly in their behaviour towards hydrolysing and reducing agents. Consequently it was believed that sodium cyanide might react with thio acid disulphides in the same manner as on organic thio sulphates. In this case, one would have,



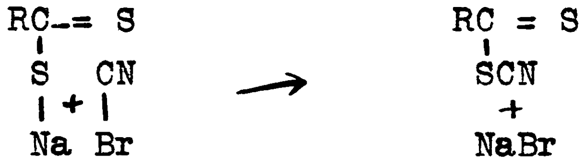
$$\begin{array}{l} RC = S \\ \;| \\ \;S \\ \;| \\ \;S \\ \;| \\ RC = S \end{array} + \begin{array}{c} Na \\ CN \end{array} \longrightarrow \begin{array}{l} RC = S \\ \;| \\ \;SNa \\ \\ \;SCN \\ \;| \\ RC = S \end{array}$$

and the formation of the thio anhydride would result from the interaction of the sodium salt with the acid thiocyanate, as follows,



$$\begin{array}{l} RC = S \\ \ | \\ \ S\ \ Na \\ \ SCN \\ \ | \\ RC = S \end{array} \longrightarrow \begin{array}{l} RC = S \\ \ | \\ \ S \\ \ | \\ RC = S \end{array} + NaSCN$$

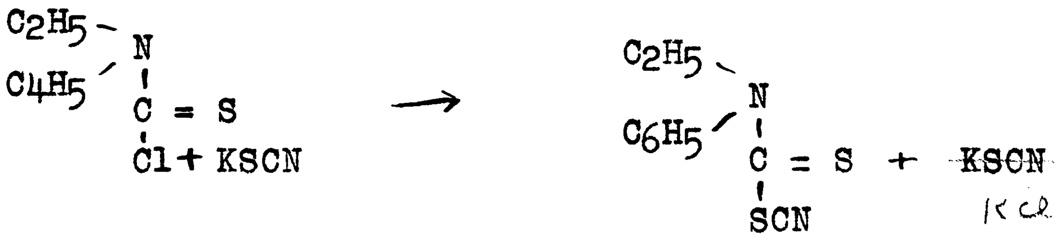
In order to determine whether the above scheme was correct, it was first sought to isolate the thio acid thiocyanate, The first attempts in this direction were made by acting on sodium xanthates with cyanogen bromide. It was thought that, in non aqueous solvents, the CNBr would react in the following manner:



$$\begin{array}{l} RC = S \\ \ | \\ \ S\ \ \ CN \\ \ |\ +\ | \\ Na\ \ Br \end{array} \longrightarrow \begin{array}{c} RC = S \\ | \\ SCN \\ + \\ NaBr \end{array}$$

Ether,benzene and chloroform were used successively as reaction media. Only in the case of chloroform was any indication obtained that a thiocyanate was formed, but the latter could not be isolated.

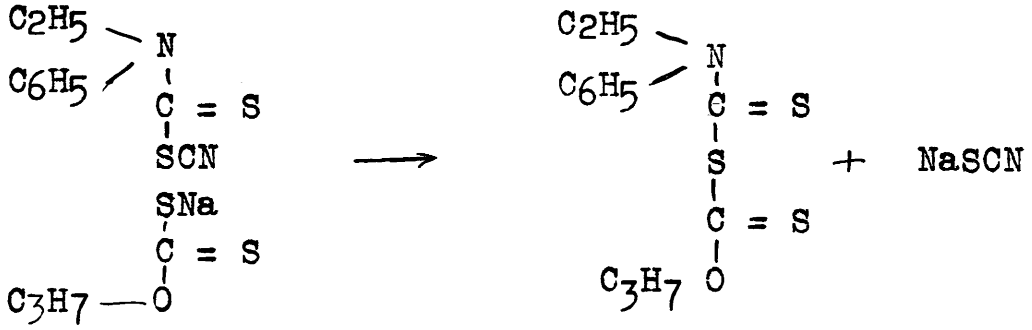
After these unseccessful attempts to prepare a thio acid thiocyanate by the action of CNBr on sodium xanthates, the first member of an analogous new series of compounds was finally obtained by the action of potassium thiocyanate on ethyl phenyl thio carbamyl chloride.



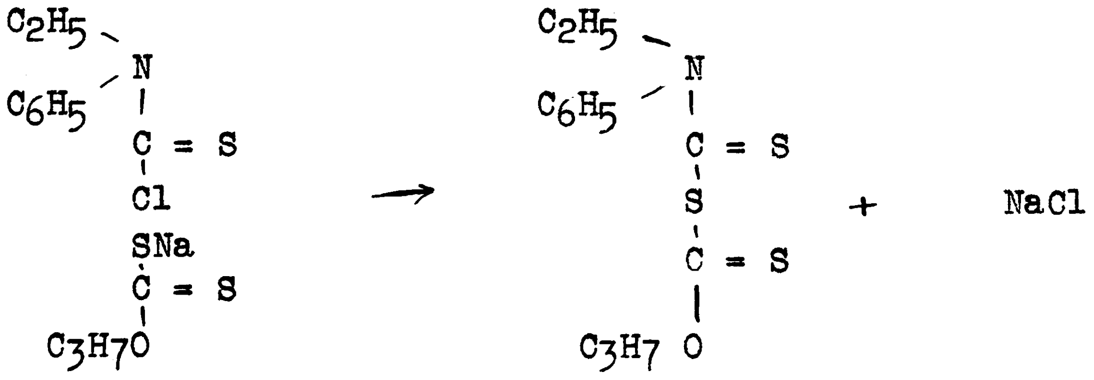
$$\begin{array}{l} C_2H_5 \diagdown \\ \qquad\quad N \\ C_4H_5 \diagup\ | \\ \qquad\quad C = S \\ \qquad\quad | \\ \qquad\quad Cl + KSCN \end{array} \longrightarrow \begin{array}{l} C_2H_5 \diagdown \\ \qquad\quad N \\ C_6H_5 \diagup\ | \\ \qquad\quad C = S + \cancel{KSCN} \\ \qquad\quad | \qquad\qquad KCl \\ \qquad\quad SCN \end{array}$$

The thiocyanate being obtained as a well defined crystalline solid.

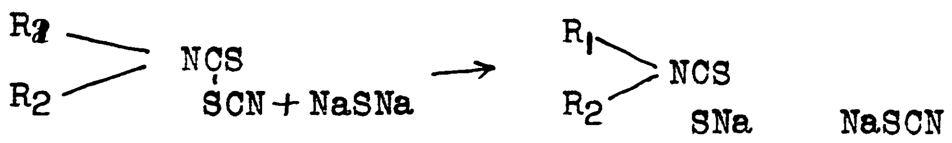
Now, in order to determine whether this type of compound will react with the alkali salts of dithio acids to form thio anhydrides, the acid thiocyanate obtained as above was allowed to act on sodium isopropyl xanthate, whereby a yellow crystalline solid was obtained. The product thus formed was identified as the mixed anhydride derived from emthyl phenyl dithio carbamic and isopropyl xanthic acids, according to the following reaction,



The identity of the product obtained in the preceding reaction was established by the fact that the same product was obtained by the action of ethyl phenyl thio carbamyl chloride on sodium isopropyl xanthate.



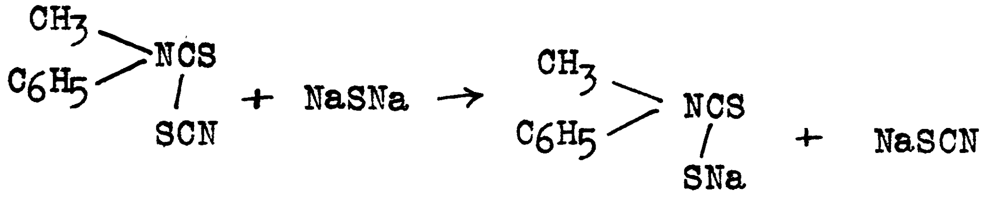
It was thought, however, since such mixed anhydrides are new compounds, and are not described in the literature, that a more rigid proof would be obtained by determining the action of a thio acid thiocyanate on the sodium salt of the same acid, in order to obtain a symmetrical thio anhydride. This had not been done before because, on the one hand, although sodium xanthates are easily obtained, all attempts to prepare the corresponding acid thiocyanates had failed, and on the other hand, although methyl phenyl and ethyl phenyl thio carbamyl thiocyanates had been isolated, there is no satisfactory procedure described in the literature for the preparation of the corresponding sodium dithiocarbamates. This difficulty was overcome later, when it was found that sodium aryl alkyl dithiocarbamates could be conveniently prepared by the action of sodium sulphide on the corresponding thiocarbamyl thiocyanates in alcohol.



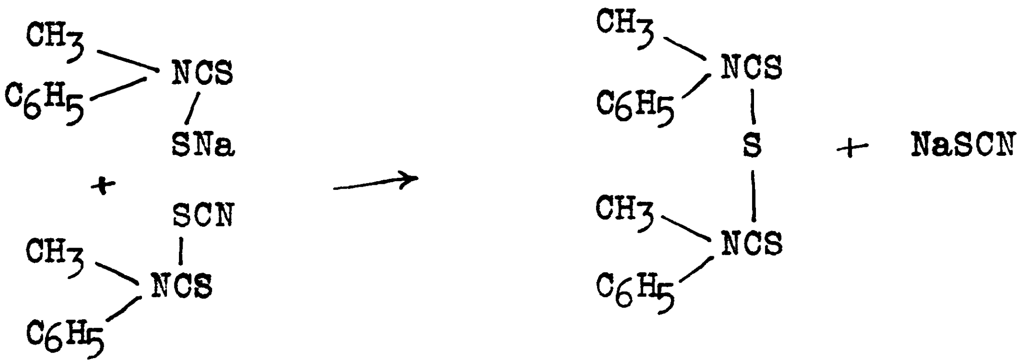
$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>NCS\cdot SCN + NaSNa \longrightarrow \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>NCS\cdot SNa \quad NaSCN$$

Consequently, the following experiment was carried out. A solution of sodium methyl phenyl dithiocarbamate was prepared by the action of sodium sulphide on the corresponding thio acid thiocyanate in alcohol. To a measured fraction of the sodium dithiocarbamate solution thus obtained was added an equivalent amount of methyl phenyl thiocarbamyl thiocyanate. The product isolated from this reaction was identified as methyl phenyl thiuram monosulphide, melting at 149°, and a yield of 90.5% was obtained as calculated from the following equations:

I.

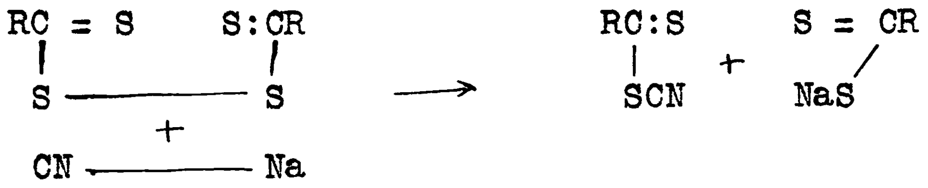


II.



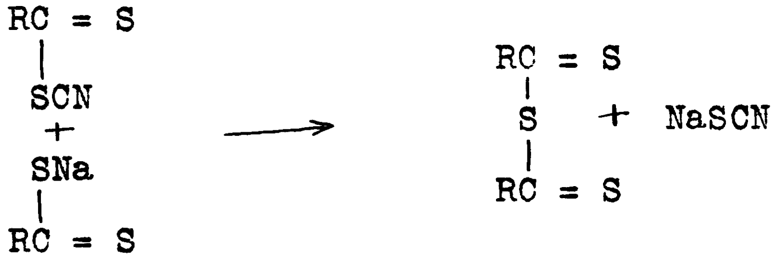
Now, in order to establish that the solution obtained by the action of sodium sulphide on the thiocyanate actually contained sodium methyl phenyl dithiocarbamate, the remainder of it was diluted with water, this gave a clear solution, showing all the carbamyl thiocyanate had been reduced, and then treated with an aqueous solution of cyanogen bromide. The white precipitate obtained on the addition of the bromide was re-crystallized from chloroform-alcohol, and identified as methyl phenyl thiuram disulphide. The yield of the latter was 89%, based on the amount of carbamyl thiocyanate originally used.

The above experiment shows conclusively that if acid disulphides can undergo what may be termed 'cyanic hydrolysis' in the following manner:



$$\begin{array}{lcl} RC=S & & S{:}CR\\ | & & /\\ S & \underline{\qquad\qquad} & S\\ & + & \\ CN & \underline{\qquad\qquad} & Na\end{array} \longrightarrow \begin{array}{l}RC{:}S\\ |\\ SCN\end{array} + \begin{array}{l}S=CR\\ /\\ NaS\end{array}$$

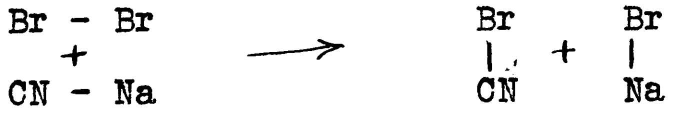
The products formed would immediately interact to form the thio anhydride with the elimination of sodium thiocyanate, as follows:



$$\begin{array}{l} RC=S\\ |\\ SCN\\ +\\ SNa\\ |\\ RC=S\end{array} \longrightarrow \begin{array}{l}RC=S\\ |\\ S\\ |\\ RC=S\end{array} + NaSCN$$

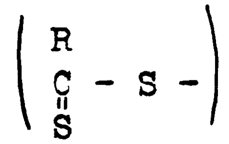
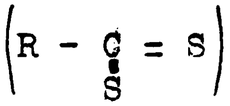
Direct experimental evidence of the formation of thio acid thicyanates by the action of alkali cyanides on acid disulphides would be very difficult, on account of the readiness with which these react with the sodium salt simultaneously formed. The following considerations will show, however, that 'cyanic hydrolysis' must be expected to take place.

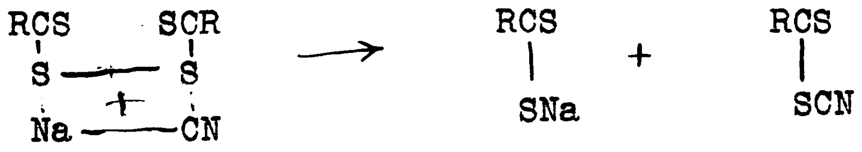
When bromine and sodium cyanide are allowed to react in molecular proportion, cyanide bromide is formed,



$$\begin{array}{c}Br - Br\\ +\\ CN - Na\end{array} \longrightarrow \begin{array}{c}Br\\ |\\ CN\end{array} + \begin{array}{c}Br\\ |\\ Na\end{array}$$

The displacement of the CN group from its salt by Br is

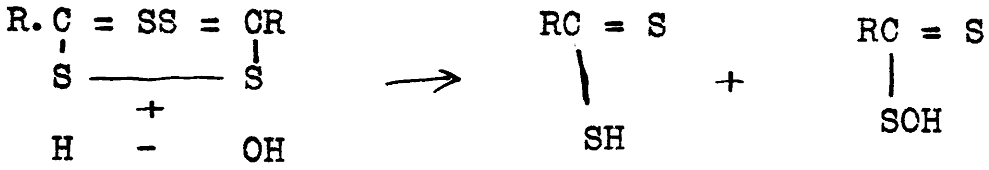
Obviously due to the fact that the latter has a greater electron affinity than the former, or in other words, Br is negative to CN. But it has been shown that, with respect to electron affinity, or electronegative character, the  $\left(\begin{array}{l} R \\ C - S - \\ \| \\ S \end{array}\right)$ group is in the same position relatively to the CN group, as Br itself is to the latter, for $(CN)_2$ will not displace the  $\left(R - \underset{\overset{\|}{S}}{C} = S\right)$ group from its salt, this is somewhat to be expected in view of the fact that dithio acids are strong acids. Consequently, one would expect the same reaction between the thio acid disulphides and sodium cyanide as in the case of Br_2,



$$\begin{array}{ccc} RCS & & SCR \\ | & & | \\ S & \text{——} & S \\ & + & \\ Na & \text{——} & CN \end{array} \longrightarrow \begin{array}{c} RCS \\ | \\ SNa \end{array} + \begin{array}{c} RCS \\ | \\ SCN \end{array}$$

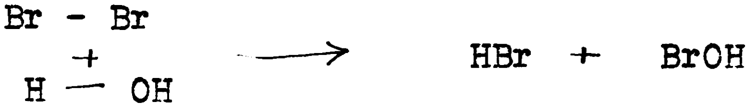
It will be noticed that, in the above reaction, the disulphide molecule behaves very much like a molecule of a halogen. This also is to be expected from the strong electron affinity of the constituent groups. Other examples of the halogen like character of the  $R\underset{\overset{\|}{S}}{C}S-$ group will be given later, there is one reaction, however, which may be mentioned here, that is the hydrolysis of acid disulphides as compared to the hydrolysis of halogens.

With disulphides we have, as Fromm has shown, (p.22)



$$\begin{matrix} R.C = SS = CR \\ | \qquad\quad | \\ S \text{———} S \\ + \\ H \;-\; OH \end{matrix} \longrightarrow \begin{matrix} RC = S \\ \backslash \\ SH \end{matrix} + \begin{matrix} RC = S \\ | \\ SOH \end{matrix}$$

Similarly with halogens:

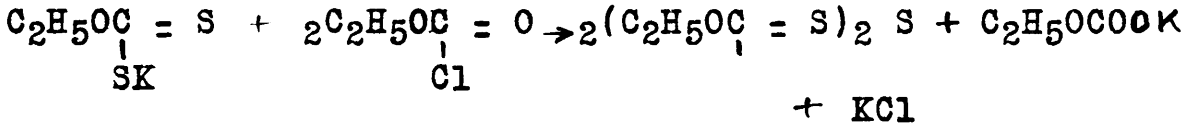


$$\begin{matrix} Br - Br \\ + \\ H - OH \end{matrix} \longrightarrow HBr + BrOH$$

The application of the above relations to the case of the normal organic disulphides RS.SR, explains very clearly, as will be shown in a later chapter, why alkali cyanides have no action on these.

III. FORMATION OF THIO ANHYDRIDES BY OTHER THAN DESULPHURIZATION METHODS

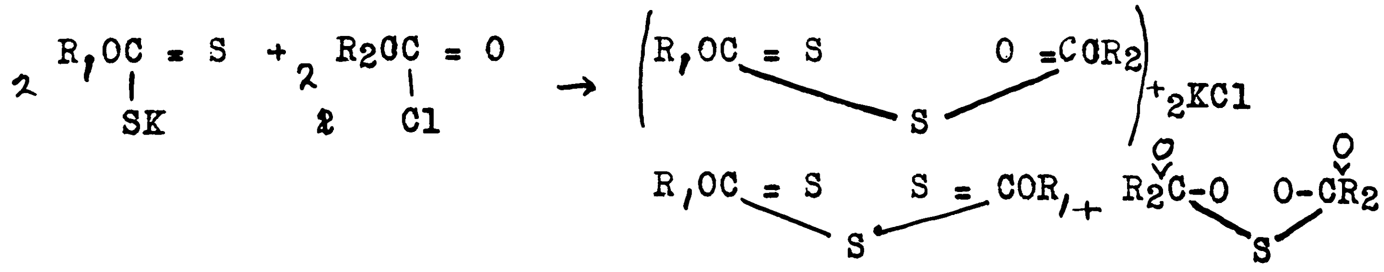
It is by means of the action of acid chlorides on alkali xanthates that thio anhydrides of dithio acids were first prepared. The first member of this class of organic sulphides was obtained by Welde (53) from the action of ethyl chlorcarbonate on potassium ethyl xanthate. Welde claimed that the thio anhydride of xanthic acid, (commondly called monoxanthogen), was formed according to the following reaction:



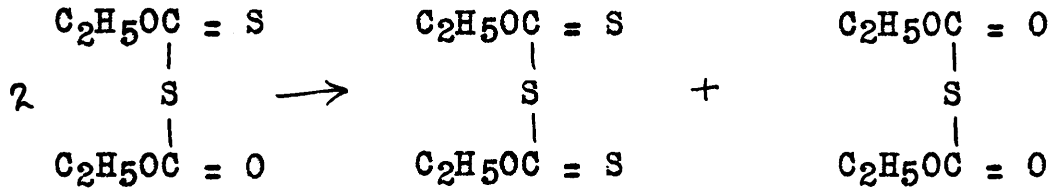
$$\underset{SK}{C_2H_5OC} = S + 2\underset{Cl}{C_2H_5OC} = O \rightarrow 2(C_2H_5OC = S)_2\,S + C_2H_5OCOOK + KCl$$

It is difficult to see how the reaction could take such a course, for it involves the replacement of the doubly linked oxygen atom in a $C_2H_5OC = O$ group by an atom of sulphur.

More recently Willcox (54) offered an alternative view as to the mechanism of the formation of monoxanthogens by the action of acid chlorides on xanthates. The latter believed that the asymmetrical anhydride formed in the first stage of the reaction, breaks down into a mixture of monoxanthogen and thio acid anhydride as follows:



In order to determine the correctness of the above view, Willcox studied the heat decomposition of the mixed thio anhydride of acetic acid and ethyl xanthic acids, but failed to isolate any monoxanthogen from the products obtained. A subsequent experiment with the mixed thio anhydride of ethyl xanthic and ethyl carbonic acids gave positive results, but the yield of monoxanthogen obtained was lower than that calculated from the following equation:

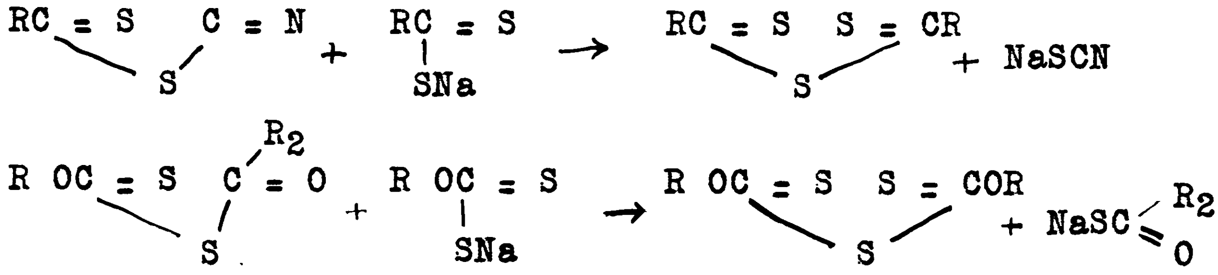


$$2\begin{array}{c} C_2H_5OC = S \\ | \\ S \\ | \\ C_2H_5OC = O \end{array} \longrightarrow \begin{array}{c} C_2H_5OC = S \\ | \\ S \\ | \\ C_2H_5OC = S \end{array} + \begin{array}{c} C_2H_5OC = O \\ | \\ S \\ | \\ C_2H_5OC = O \end{array}$$

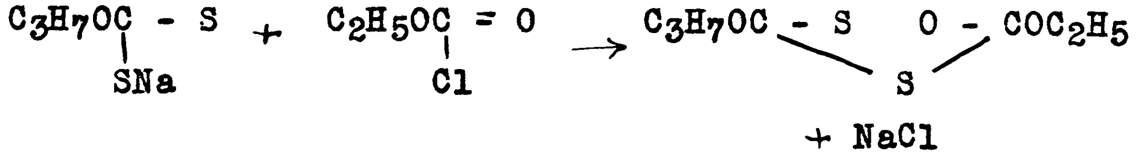
and, further, the formation of monoxanthogen could only be brought about by heating the mixed anhydride. The main objection to the above scheme is that the formation of monoxanthogen, by the action of ethyl chlorcarbonate on sodium ethyl xanthate for instance, takes place at room temperature. It is also significant that the particular anhydride which Willcox converted partly to monoxanthogen by heat was described later by Holmberg (55) who isolated it in a pure condition, and describes it as a relatively stable compound, boiling at 149° under 50 mm. pressure.

One of the reactions described in the preceding chapter suggested a simpler view as to the mechanism of reaction in question.

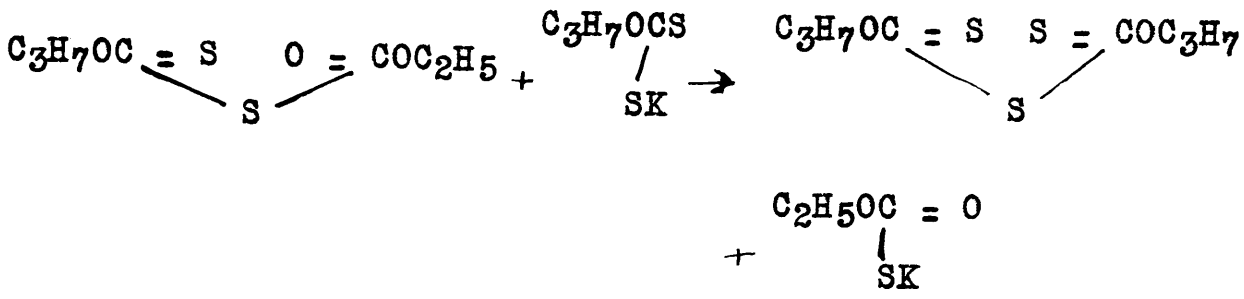
The thio acid thiocyanates which have been first described can be regarded as mixed thio anhydrides of dithiocarbamic and thiocyanic acids, and since these react with another mole of sodium dithiocarbamate to form a symmetrical thio anhydride, it was thought that the mixed thio anhydrides obtained by the action of acid chlorides on xanthates might react in a similar manner with another mole of xanthate to form a symmetrical anhydride:



In order to test the above view, the mixed thio anhydride of isopropyl xanthic and ethyl carbonic acids was prepared by the action of ethyl chlorcarbonate on sodium isopropyl xanthate in dry acetone at -5°,

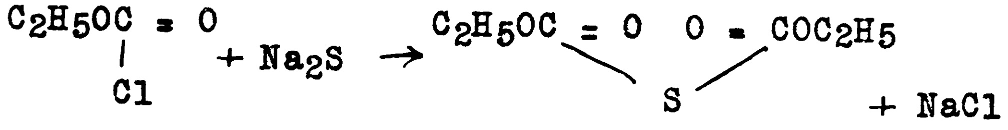


The mixed anhydride was obtained in 98.5% yield as a pale yellow oil. On adding one mole of the anhydride to an alcoholic solution of an equivalent amount of sodium isopropyl xanthate, an intense yellow colour was immediately produced, and, after the solution had stood for some time at room temperature, the monoxanthogen started to crystallize out. The amount of isopropyl monoxanthogen obtained corresponded to a yield of 69.1%, as calculated from the following equation:



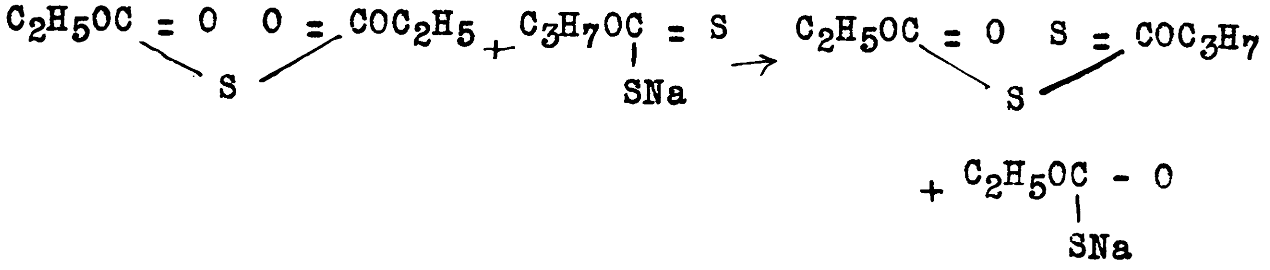
$$C_3H_7OC(=S)\text{–}S\text{–}(O=)COC_2H_5 + C_3H_7OCS\text{–}SK \rightarrow C_3H_7OC(=S)\text{–}S\text{–}(S=)COC_3H_7 + C_2H_5OC(=O)\text{–}SK$$

The yield of monoxanthogen obtained clearly indicates that its formation cannot be due to the decomposition of the mixed anhydride alone, as Willcox believed. More conclusive evidence that the reaction takes place in the manner indicated was obtained in the following experiment. The thio anhydride of ethyl thiol carbamic acid was prepared according to Holmberg's method (55), by the action of sodium sulphide on ethyl chlorcarbonate,

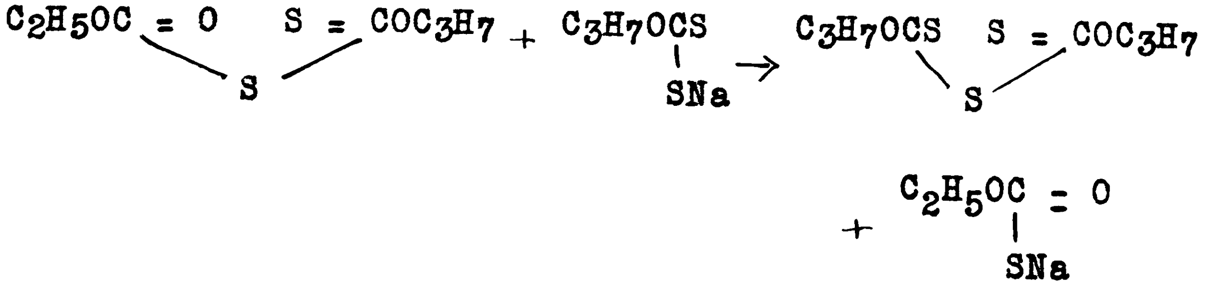


$$C_2H_5OC(=O)\text{–}Cl + Na_2S \rightarrow C_2H_5OC(=O)\text{–}S\text{–}(O=)COC_2H_5 + NaCl$$

By acting on this anhydride with sodium isopropyl xanthate in alcohol, a 34.5% yield of monoxanthogen was obtained. The reaction in this case may be considered as taking place in two steps:



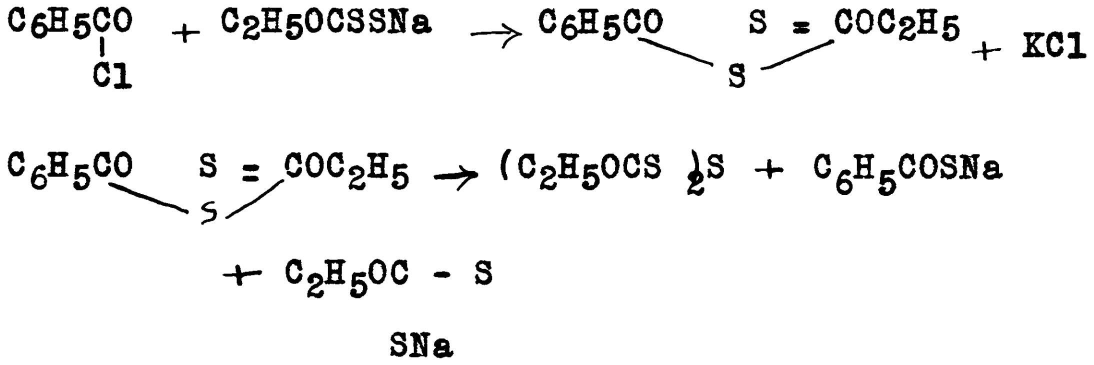
$$C_2H_5OC(=O)\text{–}S\text{–}(O=)COC_2H_5 + C_3H_7OC(=S)\text{–}SNa \rightarrow C_2H_5OC(=O)\text{–}S\text{–}(S=)COC_3H_7 + C_2H_5OC(-O)\text{–}SNa$$



$$C_2H_5OC(=O)\text{–}S\text{–}(S=)COC_3H_7 + C_3H_7OCS\text{–}SNa \rightarrow C_3H_7OCS\text{–}S\text{–}(S=)COC_3H_7 + C_2H_5OC(=O)\text{–}SNa$$

Since the anhydride used in this experiment did not contain the $\mathrm{RO}\underset{\mathrm{S}}{\underset{|}{\mathrm{C}}} = \mathrm{S}$ group, the monoxanthogen obtained must have come from the sodium salt.

It was next attempted to detect the sodium salt of thiol carbonic acid, which, if the above equation is correct, is formed simultaneously with the monoxanthogen. This was done by adding an oxidizing agent to the mother liquor from which the monoxanthogen was obtained in order to convert any $\mathrm{C_2H_5O}\underset{\mathrm{SNa}}{\underset{|}{\mathrm{C}}} = \mathrm{O}$ present into the corresponding disulphide, $\left(\mathrm{C_2H_5O}\underset{\mathrm{S}}{\underset{|}{\mathrm{C}}} = \mathrm{O}\right)_2$ which is a water insoluble oil. This did not give very definite results, for the addition of sodium tetrathionate to the mother liquor gave a liquid product which, after standing for some time, deposited crystals of isopropyl dixanthogen, and it was found impossible to remove the latter completely. Better results were obtained by using benzoyl chloride which, as Tschugaeff has shown (56), gives the same reaction with xanthates as acetyl chloride and ethyl chlor carbonate. The procedure followed was the same as with ethyl chlor carbonate. Two moles of sodium ethyl xanthate were added to an acetone solution of 1 mole of benzoyl chloride, The reaction product was precipitated with water, and separated from the solution. By the action of sodium tetrathionate on the mother liquor a solid product was obtained, melting at 127°. The correct melting point of benzoyl disulphide is 128°. It is significant that the percentage yields of ethyl monoxanthogen and benzoyl disulphides obtained in the above experiment, were about equal, as one would expect from the following equation:

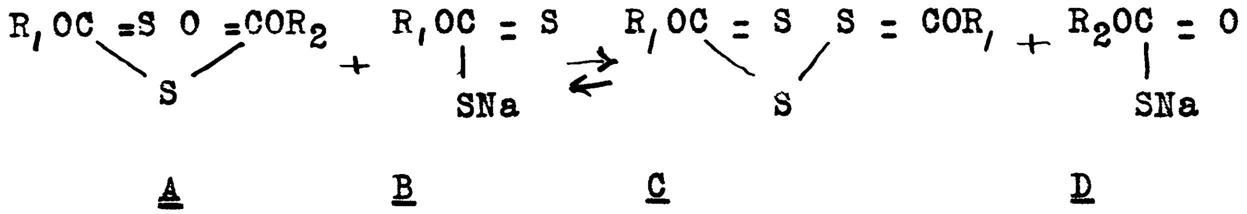


$$\underset{\mathrm{Cl}}{\mathrm{C_6H_5CO}} + \mathrm{C_2H_5OCSSNa} \rightarrow \mathrm{C_6H_5CO}\diagdown\underset{\mathrm{S}}{}\diagup\mathrm{S = COC_2H_5} + \mathrm{KCl}$$

$$\mathrm{C_6H_5CO}\diagdown\underset{\mathrm{S}}{}\diagup\mathrm{S = COC_2H_5} \rightarrow \mathrm{(C_2H_5OCS)_2S} + \mathrm{C_6H_5COSNa} + \underset{\mathrm{SNa}}{\mathrm{C_2H_5OC - S}}$$

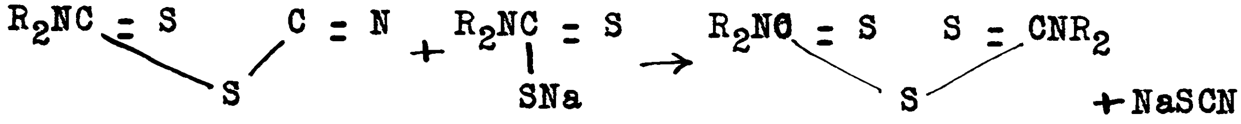
The identification of sodium thio benzoate as one of the reaction products, with the experimental facts already stated, showed fairly conclusively that the reaction takes place as indicated.

The reaction between mixed anhydrides and xanthates is a reversible one, as a consideration of the compounds involved will show.



$$\underset{\underline{A}}{\mathrm{R_1OC{=}S}\diagdown\underset{\mathrm{S}}{}\diagup\mathrm{O{=}COR_2}} + \underset{\underline{B}}{\underset{\mathrm{SNa}}{\mathrm{R_1OC = S}}} \rightleftarrows \underset{\underline{C}}{\mathrm{R_1OC = S}\diagdown\underset{\mathrm{S}}{}\diagup\mathrm{S = COR_1}} + \underset{\underline{D}}{\underset{\mathrm{SNa}}{\mathrm{R_2OC = O}}}$$

It is obvious that the same equilibrium mixture would be obtained if, instead of starting from equimolecular quantities of A and B, one started from the same relative amounts of C and D, the relative amounts of A and B present at equilibrium depending, in the above example, on the relative strength of the two acids, $\mathrm{R\ OC}\begin{smallmatrix}\nearrow \mathrm{S}\\ \searrow \mathrm{SH}\end{smallmatrix}$ and $\mathrm{R_2OC}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{SH}\end{smallmatrix}$. The same relation holds in the case of reaction between a thio carbamyl thiocyanate and the corresponding sodium dithiocarbamate.



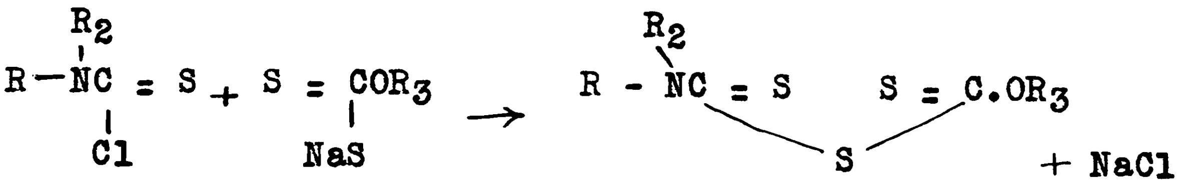
$$\mathrm{R_2NC{=}S}\diagdown_{\mathrm{S}}\diagup\mathrm{C{=}N} + \underset{\substack{|\\ \mathrm{SNa}}}{\mathrm{R_2NC}}\mathrm{{=}S} \rightarrow \mathrm{R_2NC{=}S}\diagdown_{\mathrm{S}}\diagup\mathrm{S{=}CNR_2} + \mathrm{NaSCN}$$

The reaction here goes almost quantitatively from left to right, because the dithiocarbamic acid is a very weak acid compared to thiocyanic.

It is probable that the yields of monoxanthogen obtained in the reaction between chlorcarbonates and xanthates would be lower than those observed, were it not for the fact that the decomposition of one of the products appears to favour the reactions from left to right.

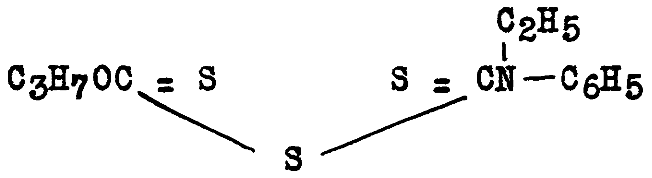
Mixed anhydrides of xanthic and dithiocarbamic acids.

Having occasion to prepare a number of di-substituted thiocarbamyl chlorides for the investigation of carbamyl thiocyanates, it was thought interesting to determine whether these chlorides would react with alkali xanthates, to give mixed thio anhydrides of xanthic and dithiocarbamic acids, as follows:

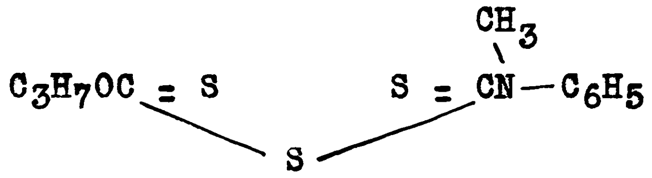


$$\mathrm{R{-}}\underset{\substack{|\\ \mathrm{Cl}}}{\overset{\substack{\mathrm{R_2}\\ |}}{\mathrm{N}}}\mathrm{C{=}S} + \mathrm{S{=}}\underset{\substack{|\\ \mathrm{NaS}}}{\mathrm{C}}\mathrm{OR_3} \rightarrow \mathrm{R-}\overset{\substack{\mathrm{R_2}\\ \diagdown}}{\mathrm{N}}\mathrm{C{=}S}\diagdown_{\mathrm{S}}\diagup\mathrm{S{=}C.OR_3} + \mathrm{NaCl}$$

Two members of this new series of thio anhydrides were prepared, one derived from isopropyl xanthic acid and ethyl phenyl dithiocarbamic acid.



and the corresponding methyl phenyl compound,



In order to remove the possibility of these compounds, as obtained, consisting of mixtures of the corresponding symmetrical anhydrides, they were recrystallized several times from glacial acetic, and also from ligroin. Repeated recrystallization did not cause any variation in the melting point.

It was noted that these asymmetrical thio anhydrides have melting points lower than that of isopropyl monoxanthogen.

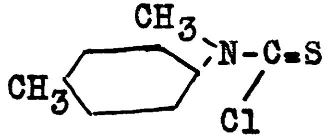
The ethyl phenyl compound melts at 40.5° - 41°, the methyl phenyl at 42°, while isopropyl monoxanthogen melts at 55°. Ethyl phenyl and methyl phenyl thiuram monosulphides have much higher melting points, 115° and 150° respectively. Lecher (57) observed the same effect in the case of mixed organic sulphides of the type R_1SSR_2. Ortho nitro phenyl disulphide, for instance, melts at 55°, while phenyl disulphide melts at 60°- 62°, and ortho dinitro phenyl disulphide melts at 198°.

IV. PREPARATION AND REACTIONS OF THIO ACID THIOCYANATES

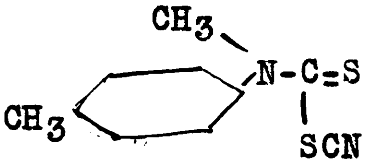
Preparation of thiocarbamyl thiocyanates.

The failure of the first attempts to isolate a thio acid thiocyanate by the action of cyanogen bromide on alkali xanthates was later found to be due to the presence of water, which favours the action of cyanogen bromide as an oxidizing agent. Even small amounts of water appear to be sufficient to prevent the formation of a thiocyanate by substitution, but this may be explained by the fact that the oxidation reaction is an ionic one, and consequently proceeds at a much faster rate than substitution, which is not ionic.

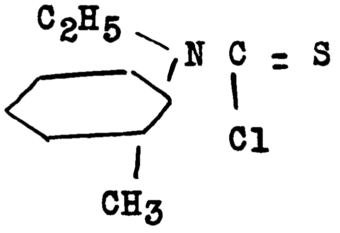
The action of the thio acid chlorides on KSCN was later found to be a very convenient method for the preparation of thio acid thiocyanates, and it is by this method that the first member of this new series was prepared, that is, ethyl phenyl thio carbamyl thiocyanate. Absolute alcohol has been found to be the best solvent to carry out the reaction, which takes place smoothly at room temperature. Methyl phenyl and methyl para tolyl thio carbamyl thiocyanates were prepared by the same method. An attempt was also made to prepare methyl ortho tolyl thio carbamyl thiocyanate, but not definite result was obtained. It is interesting to note that derivatives of methyl para and ethyl ortho tolyl dithiocarbamic acids are unknown, consequently it was hoped that after preparing without difficulty the thio carbamyl chloride and thiocyanate of the methyl para compound,



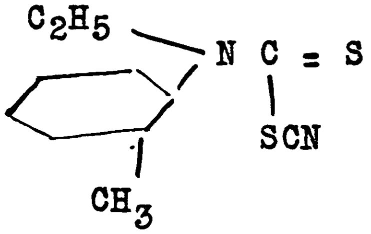
and



the corresponding derivatives of the ethyl ortho compound would also be obtained,

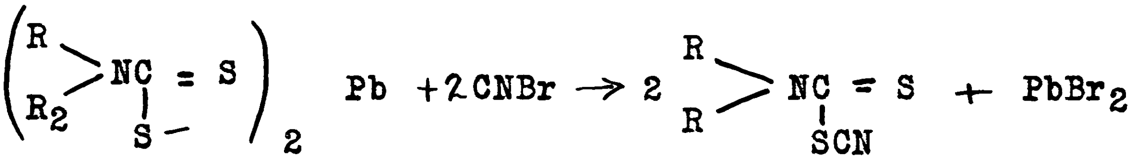


and



The thio carbamyl chloride was first prepared by the action of thio phosgene on ethyl ortho toluidine, and obtained as a stable crystalline compound. The action of potassium thiocyanate on this carbamyl chloride, however, gave an amorphous solid product which would not be recrystallized, and decomposed on standing, but which gave some of the characteristic reactions of carbamyl thiocyanates, such as the production of a yellow colour with sodium xanthate, and the formation of a deep red solution on warming with aqueous ferric chloride solution. Ortho or para substitution in the alkyl tolyl dithiocarbamic acids does not seem to affect the stability of the corresponding carbamyl chlorides, while ortho substitution renders the corresponding carbamyl thiocyanate unstable, the para substituted compound being stable. The same relation appears to hold with the ammonium dithiocarbamates of these amines, for, ammonium methyl para tolyl dithiocarbamate can be isolated, although it is very unstable, while the corresponding ethyl ortho tolyl compound will not form at all.

An alternative method by which di-substituted thiocarbamyl thiocyanates can be prepared was later found. This method is somewhat more convenient, for it does not require the preparation of the carbamyl chloride, and consequently does away with the use of thio phosgene. It consists in acting on the lead salt of the dithiocarbamic acid with cyanogen bromide in dry benzene. The reaction is,

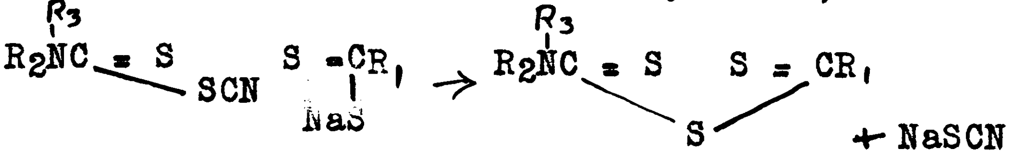


Methyl phenyl thio carbamyl thiocyanate was prepared in this manner in good yield.

Reaction of thio carbamyl thiocyanates.

The following characteristic reactions of thio carbamyl thiocyanates will show the close similarity between the reactivity of the .SCN group in these compounds and that of the chlorine in acid chlorides.

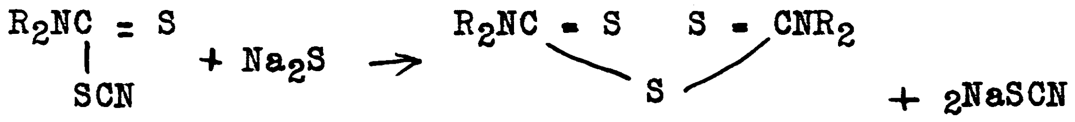
These thiocyanates react with alkali xanthates and dithiocarbamates to form thio anhydrides,



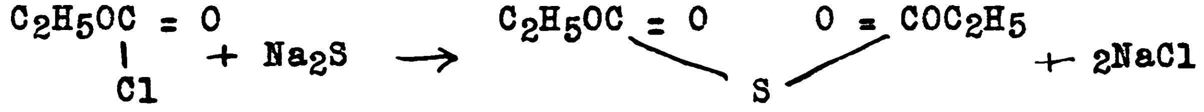
The reaction with the thio carbamyl chlorides is identical (58),

With sodium sulphide, the nature of the product obtained depends on the molecular prpportion of the sulphide used.

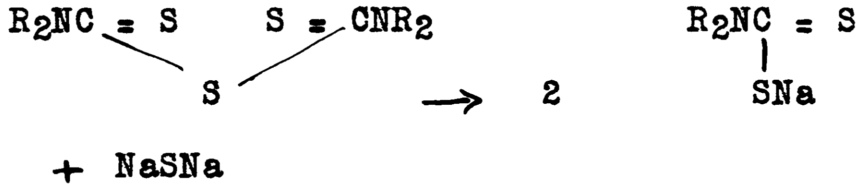
With one half mole of sodium sulphide, a thio anhydride is obtained.



Analogous reactions have been obtained with acid chlorides (59),

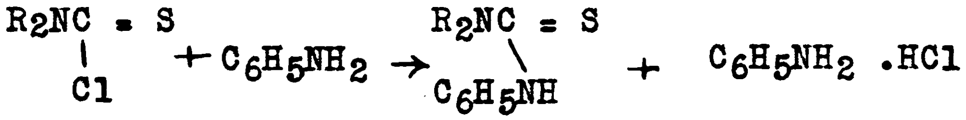


With one mole of sodium sulphide, the thio anhydride first formed is reduced to the sodium salt of the acid,



The above reaction has been found very useful for preparing, in solution, the sodium salts of aryl alkyl di-substituted dithiocarbamic acids. The reaction is practically quantitative. It appears that the reduction of the anhydride to the sodium salt of the acid takes place much more readily when the anhydride is formed in the presence of the sodium sulphide, because, in a separate experiment, ethyl phenyl thiuram monosulphide was refluxed 3 hours in alcohol with excess of sodium sulphide, and only a small fraction was converted to the sodium salt, the latter being identified by oxidation to the disulphide.

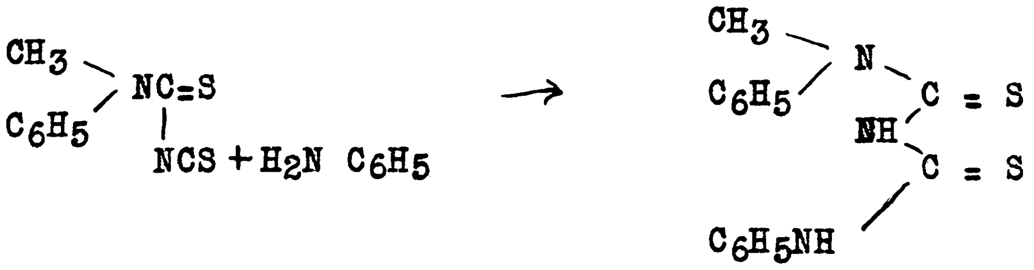
There is one reaction in which, under certain conditions, these thio carbamyl thio cyanates differ from the corresponding carbamyl chlorides, and that is with aniline. This distinction only appears when the thiocyanates have been converted by heating into the isomeric thio carbimides, for, at ordinary temperatures their reactions are the same, both reacting with the formation of a tri-substituted thio urea, aniline hydrochloride or aniline thiocyanate being also formed according to the carbamyl compound used,



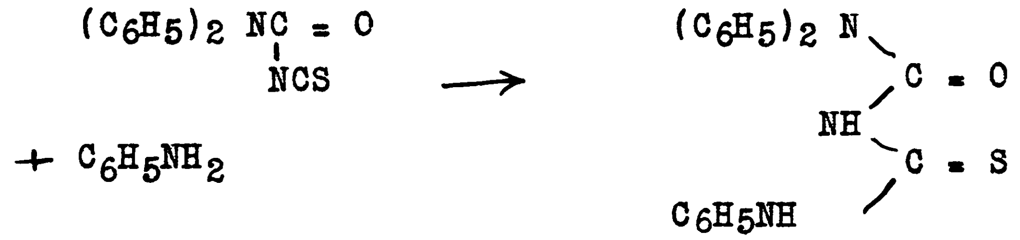
$$R_2N\underset{Cl}{C}=S + C_6H_5NH_2 \rightarrow \underset{C_6H_5NH}{R_2NC=S} + C_6H_5NH_2.HCl$$

$$R_2N\underset{SCN}{C}=S + 2 \text{ '' } \rightarrow \text{ '' } + C_6H_5NH_2.HSCN$$

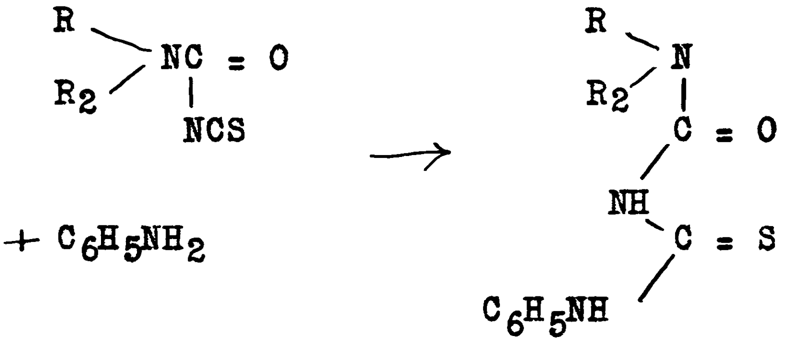
If the thio carbamyl thiocyanate is heated for some time at a temperature close to its melting point, it no longer reacts in the above manner, but adds on a mole of aniline to form a tri-substituted di thio biuret. With methyl phenyl thio carbamyl thiocyanate, for instance, the following reaction was obtained after first heating the thiocyanate at 110° for 10 minutes.



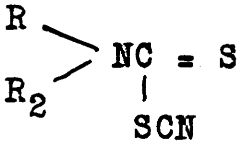
That an irreversible change in the constitution of these thio carbamyl thiocyanates takes place under the influence of heat is shown by the fact that on standing for some time at temperatures from 15° to 20° below their melting points, they are gradually converted into deep red oils, and it is the liquid products obtained in this manner which show the characteristic reactions of isothiocyanates. Such conversion of an acid thiocyanate into the corresponding iso form is not without analogy, for T.B.Johnson and Levi (60) observed the same behaviour on the part of diphenyl carbamyl thiocyanate, which does not react normally with aniline, as an iso thiocyanate, but which, on heating at 138°-140°, appears to be completely converted to the iso form, the latter then reacting with aniline, even at room temperature, to give the corresponding thio biuret.



The above example is the only one of a carbamyl thiocyanate existing under two distinct isomeric forms, Dixon, who prepared methyl phenyl, ethyl phenyl, and benzyl phenyl carbamyl thiocyanates in solution (61), states that all of these, as obtained, react with aromatic primary bases in the iso form, for tri-substituted thio biurets are the only products isolated from the reaction.



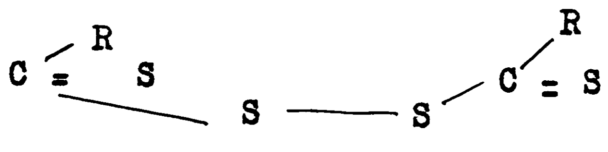
It must be noted that Dixon prepared these acid thiocyanates by the action of the carbamyl chlorides on lead thio cyanate in boiling benzene, and although Johnson and Levi, (loc.cit.) found that isomerization of the diphenyl compound occurred at 138°-140°, this is a special case, for the presence of the two phenyl group increases the positive character of the $R_2NC\overset{O}{<}$ group to such an extent, that the carbamyl chloride is not appreciably decomposed even by boiling water, and can be recrystallized from hot alcohol, while this is not the case with the aryl alkyl carbamyl chlorides, which are readily hydrolyzed by hot water, and react with warm alcohol; consequently one would expect the alkyl aryl carbamyl thiocyanates to be less stable than the diphenyl compound, and to undergo isomerization more readily, and it is probable that the alkyl aryl compounds prepared by Dixon in boiling benzene were completely converted to the iso form at that temperature. This seems to be borne out by the results obtained later by the same author (62), who observed that acid thiocyanate, prepared in warm acetone from potassium thiocyanate and the acid chloride, behaved almost exclusively as true thiocyanates towards bases at lower temperatures. The author, however did not attach any significance to the fact that these acid thiocyanates had been prepared at a lower temperature than those previously prepared in boiling benzene. When the new thio carbamyl thiocyanates described in this thesis were first isolated, there was some doubt as to what constitution should be ascribed to them, principally in view of the fact that the constitution of the known oxygen analogues has not yet been satisfactorily established. The above considerations on the work of Dixon and Johnson, however, show quite conclusively that they are true thiocyanates, and that their structure is represented by the formula:



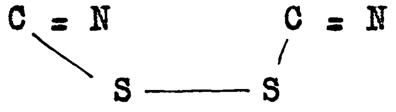
The pronounced analogy between the reavtions of these thiocyanates and the corresponding carbamyl chlorides is also strong evidence in support of the above structure.

<u>Structure of organic polysulphides.</u>

The 'cyanic' hydrolysis' of acid disulphides, which has been shown to be the intermediate step in the desulphurizing action of cyanides is strong evidence in support of a straight chain structure for these compounds.

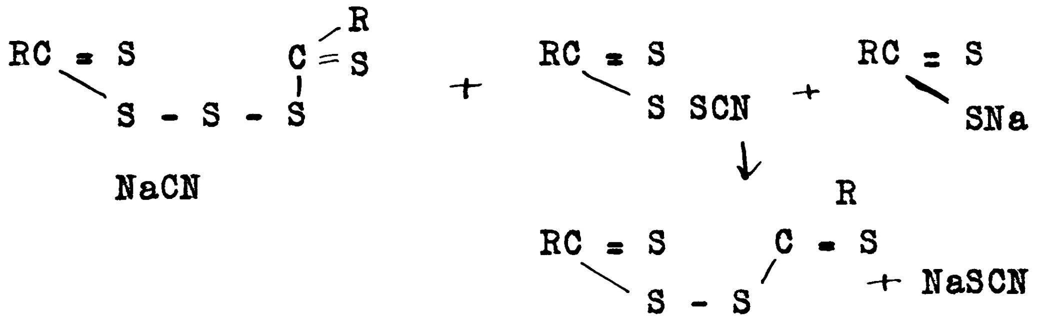


for the analogy between the acid disulphide molecules and the halogens in many reactions appear to show that the potential ion $(RC\begin{smallmatrix}{/\!\!/}S\\ \backslash S^{\cdot}\end{smallmatrix})$ remains intact in the disulphide. Further, Soderbäck's free rhodan (63), which can be considered as the simplest acid disulphide, has been shown to have a straight chain structure.



With regards to the acid tri and tetra sulphide, there is evidence to show that the mechanism of the desulphurizing action of cyanides on these is the same as with the disulphides and that, consequently, they also possess a straight chain structure.

The desulphurization of a trisulphide, for instance, would take place in two stages, the disulphide being formed first:



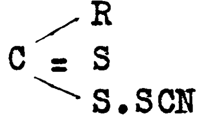
The disulphide being then acted on again by the cyanide, as shown before. That the compound which is here assumed to be the first intermediate product in the action of sodium cyanide on an acid trisulphide is capable of existence is shown by the fact that Lecher (64) has prepared a number of derivatives of the same type, by the action of free rhodan on mercaptans.

$$RSH + (SCN)_2 \longrightarrow RS.SCN + HSCN$$

and ~~who~~ observed, further, that these sulphur thiocyanates react with mercaptans to form disulphides,

$$RS.SCN + RSH \longrightarrow RSSR + HSCN$$

The latter is a reaction analogous to that assumed to take place between the acid sulphur thiocyanate,



$R{-}C({=}S){-}S.SCN$

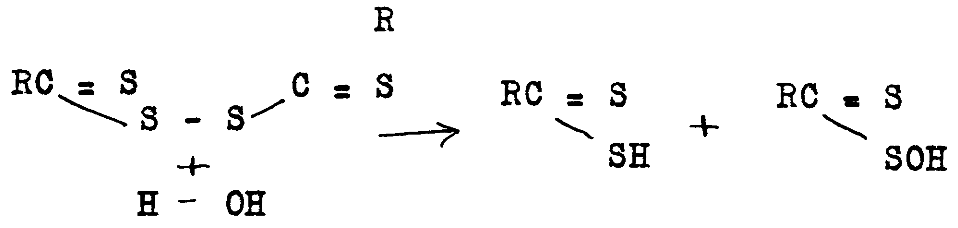
and the sodium salt of the dithio acid in the desulphurization of an acid trisulphide.

The reaction observed by Lecher between sulphur thiocyanates and mercaptans explain why trisulphides of the type RSSSR can be desulphurized by cyanides, for the products of 'cyanic hydrolysis' of this sulphide would immediately react to form a disulphide,

$$RS.SCN + RSNa \longrightarrow RSSR + NaSCN$$

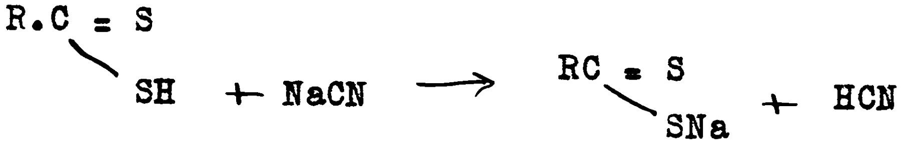
In the case of a disulphide of the type RSSR, it can be shwon that desulphurization by cyanides cannot take place, because 'cyanic hydrolysis' is not possible. 'Cyanic hydrolysis' undoubtedly proceeds in the following manner, the disulphide first undergoing true hydrolysis.

I.



The acid formed then reacts with the cyanide, being a stronger acid, (this is the case with all dithio acids), to form the sodium salt and hydrocyanic acid.

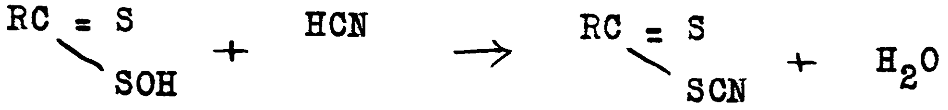
II.



$$R.C(=S)SH + NaCN \rightarrow RC(=S)SNa + HCN$$

The HCN being then oxidized by the per acid,

III.



$$RC(=S)SOH + HCN \rightarrow RC(=S)SCN + H_2O$$

Disulphides of the type RSSR are also hydrolysed,

$$RSSR + HOH \rightarrow RSH + RSOH$$

but the RSH formed would not react with sodium cyanide, at least to any appreciable extent, because mercaptans are much weaker acids than hydrocyanic acid, so that the reaction would not proceed any further. That HCN is a stronger acid than mercaptans was confirmed by experiment. Phenyl disulphide was obtained in good yield by oxidizing an aqueous solution of sodium thio phenol with cyanogen gas,

$$C_6H_5\ SNa + (CN)_2 \rightarrow C_6H_5SSC_6H_5 + NaCN$$

IV. EXPERIMENTAL

I. OXIDATION OF XANTHATES TO DIXANTHOGENS

Action of nitrous acid on xanthates in acid solution.

Ethyl dixanthogen.

A solution of 16 gr. potassium ethyl xanthate and 7.2 gr. sodium nitrite in 75 cc. of water was treated at 5° with 40 cc. of 25% sulphuric acid. The dixanthogen was obtained as a white solid, which, after one recrystallization from alcohol, melted at 32.5°, which is the correct melting point for ethyl dixanthogen. The yield was 10.5 gr. 87% of the theory.

The above experiment was repeated, using the equivalent amount of hydrochloric acid, instead of sulphuric. From 20 gr. of potassium ethyl xanthate and 10 gr. of sodium nitrite were obtained 14.6 gr. of ethyl dixanthogen, or 97% of theory. That the product was quite pure as obtained was shown by the melting point, 30.5°, this being only 2° below the melting point of pure ethyl dixanthogen.

Isopropyl dixanthogen.

This was obtained in the same manner as the ethyl compound. From 50 gr. of isopropyl xanthate and 20 gr. of sodium nitrite were obtained 30.1 gr. dixanthogen, 80% of theory, when using sulphuric acid, and 32.5 gr. or 87% of theory, when using hydrochloric acid.

n-Butyl dixanthogen.

This was obtained in 80% yield, using sulphuric acid.

Qualitative tests with iso amyl and benzyl were also carried out, but the products obtained in these experiments contained appreciable amounts of the corresponding alcohols, as was shown by extraction with methyl alcohol.

Tetra ethyl thiuram disulphide.

A solution of 43 gr. of sodium di ethyl dithio carbamate and 18 gr. of sodium nitrite in 100 cc. water was treated at 0° to 6° with 80 cc. of 25% hydrochloric acid. The product was obtained as a pure white solid, m.p.68.5° before recrystallization, and 71° after recrystallization from alcohol. The melting point of this product is given in the literature as 70.5°.

Action of cyanogen bromide on xanthates.

Action of cyanogen bromide on potassium ethyl xanthate in alcohol.

A solution of 10.5 gr. cyanogen bromide in 30 cc. 95% alcohol was added gradually to a cooled solution of 30 gr. potassium ethyl xanthate in 100 cc. of alcohol. The reaction mixture was stirred for one half hour at 5° after all the bromide had been added. The product was then precipitated by the addition of water, filtered off and recrystallized from alcohol, m.p.52.5°. The dixanthogen melts at 32°.

Action of cyanogen bromide on potassium isopropyl xanthate in water.

A solution of 5 gr. of cyanogen bromide in 25 cc. of water was added, without cooling, to a solution of 20 gr.

potassium isopropyl xanthate in 75 cc. of water. The product comes down directly as a pale yellow solid. This was filtered off, and, on recrystallization from alcohol, pure isopropyl dixanthogen is obtained, m.p. 57.5°-58.5°. The yield is practically quantitative.

The following dixanthogens, which are not described in the literature, have also been prepared by the action of cyanogen bromide on the corresponding sodium xanthate.

Glycol mono ethyl ether dixanthogen

An attempt was made to prepare the sodium glycolate by the action of metallic sodium on the alcohol. It appeared that some decomposition took place, for a dark coloured product was obtained on the addition of carbon disulphide. Better results were obtained on using carbonate free caustic soda, the latter, after pulverizing finely, was added gradually to a solution of excess carbon disulphide in twice the theoretical amount of the alcohol. The sodium xanthate which separated out was filtered off, and recrystallized from dry acetone.

Thirty grames of the recrystallized sodium xanthate were then oxidized by the addition of excess of freshly prepared sodium tetrathionate solution. The product, after washing and drying, was obtained as a pale yellow oil, N_D 1.5751 at 25°,

Analysis .2141 gr. subst. .5980 gr. $BaSO_4$

Calculated for $C_{10}H_{18}O_4S_4$ 'M.W. 3302) 38.84

Found 38.37

n. Hexyl di xanthogen

The sodium alcoholate was first prepared by the action of metallic sodium (15 gr.) on an excess of the alcohol (100 gr.) in 200 cc. of toluene. The reaction mixture was refluxed till all the sodium had reacted. An excess of carbon disulphide (70 gr.) was then added to the cooled sodium alcoholate solution. The sodium xanthate was filtered off, and washed free of alcohol with ether.

Forty grams of sodium hexyl xanthate, in 150 cc. of water, were treated with 10 gr. of cyanogen bromide, also in water. The liquid dixanthogen formed was separated, washed, and dried in vacuo. It is a pale yellow oil, with an odour faintly recalling that of the alcohol, and which boils with some decomposition, at 170°-175° at 3 mm.

N_D 1.5569 a t 25°.

Analysis: .2206 gr. subs. gave .5725 gr. $BaSO_4$

Calculated for $C_{14}H_{22}O_2S_4$ (M.W. 382.3) 36.21% S

Found 35.62

b.Phenyl ethyl dixanthogen

This compound was prepared in the same manner as the n.hexyl compound, using metallic sodium.

The dixanthogen was obtained as a white solid, which after recrystallization from glacial acetic acid, melted at 49.5°- 50°.

Analysis: .1439 gr.subst.gave .3394 gr.$BaSO_4$

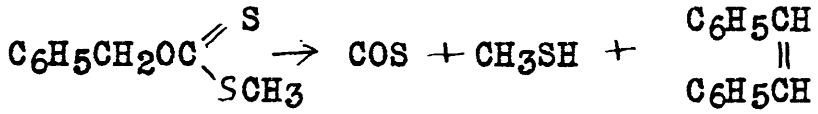
Calculated for $C_{18}H_{18}O_2S_4$ (M.W.398.3) 32.39%

Found 32.52

Heat decomposition of phenyl ethyl dixanthogen.

Nametkin (65) has reported obtaining stilbene by the heat decomposition of the methyl ester of benzyl xanthic acid, a method of dehydrating alcohols first used by Tschugaeff for the preparation of menthene (66).

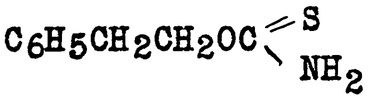
Dehydration, in the case of the methyl benzyl xanthate, takes place as follows,



$$C_6H_5CH_2OC{\overset{S}{\underset{SCH_3}{\lessgtr}}} \rightarrow COS + CH_3SH + \begin{matrix} C_6H_5CH \\ \| \\ C_6H_5CH \end{matrix}$$

Since dehydration in the case of phenyl ethyl alcohol can~~e~~ take place internally, one would expect styrene to be the main heat decomposition product of phenyl ethyl xanthates. That was found to be the case. From the distillation of 25 gr. phenyl ethyl dixanthogen at atmospheric pressure, 9.5 gr. of liquid products were obtained. After two fractionations, a 3 gr. fraction boiling at 142°-148° was obtained. This fraction was treated with slightly less than the required amount of bromine in glacial acetic acid, and 1.7 gr. of styrene dibromide were obtained, which, after recrystallization from acetic acid, melted at 73°-74°, which is the correct melting point for that compound.

Phenyl ethyl xanthogen amide



$$C_6H_5CH_2CH_2OC{\overset{S}{\underset{NH_2}{\lessgtr}}}$$

The above compound, which is not listed in the literature, was prepared by the action of alcoholic ammonia on the corresponding dixanthogen. It was obtained in the form of large lustrous plates from alcohol, melting at 79°.

Analysis: .1435 gr. gave .1931 gr. $BaSO_4$
Calculated for $C_9H_{11}ONS$ (M.W. 181) 17.62% S
Found 18.49

Action of sodium tetra thionate on xanthates.

Methyl dixanthogen

Thirty grams of pure potassium methyl xanthate in 150 cc. water were treated with an excess of aqueous sodium tetra thionate, the reaction being carried out at -5° to -3°. The dixanthogen was obtained directly in 98% yield. The product was recrystallized by dissolving it in methyl alcohol at room temperature till a saturated solution was obtained, then cooling the latter in an ice bath. The dixanthogen was then obtained in the form of small prisms, mp. 22.5°-23°.

Benzyl dixanthogen

To a solution of 29.1 gr. of sodium benzyl xanthate in 75 cc. water was added, with good stirring, a solution containing slightly more than the theoretical amount of sodium tetra thionate. The dixanthogen is obtained directly as a white solid. That the product, as obtained, is quite pure was shown by the melting point of the crude dixanthogen, 46°-49°, compared to that of a sample recrystallized from glacial acetic acid, 54°-54.5°,

Analysis: .2176 gr. subst. gave .5673 gr. $BaSO_4$
Calculated for $C_{16}H_{14}O_2S_4$ (M.W. 3665) 35.00% S
Found 35.82

Action of chloramine T on xanthates.

To a solution of 4 gr. of sodium isopropyl xanthate was added an aqueous solution containing an excess of the chloramine. The dixanthogen is obtained in practically quantitative yield, M.P. 58.5° after recrystallization from alcohol.

Action of nitrosyl chloride on xanthates.

Five grams of sodium isopropyl xanthate were added with stirring and cooling, to a chloroform solution of nitrosyl chloride. After letting stand for a few minutes, the chloroform solution was washed with water, then evaporated under reduced pressure, leaving as residue 2.1 gr. of pure isopropyl dixanthogen, M.P. 57.5°.

Action of benzene sulphochloride on xanthates .

Thirty two grams of potassium xanthate were gradually added to a solution of 8.6 gr. of benzene sulphochloride (.5 mole) in 100 cc. of dry ether. The reaction being carried out at -10°, the reaction mixture was then filtered from potassium chloride, and the ether evaporated off, leaving as residue an oil which would not be made to crystallize. The oil was dissolved in alcohol, and on cooling the solution in freezing mixture, 11.5 gr. of solid ethyl dixanthogen were obtained, M.P. 32°-32.5°.

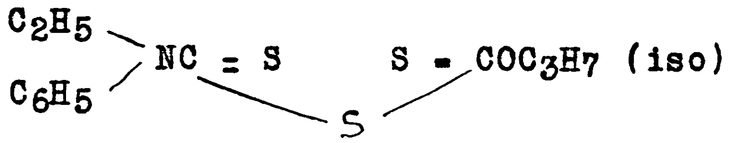
That the product was actually the dixanthogen was confirmed by converting a fraction of it to the corresponding monoxanthogen, by the action of potassium cyanide in alcohol.

Action of cyanogen on xanthates.

Cyanogen gas, prepared by the copper sulphate-potassium cyanide method, was bubbled through a solution of sodium isopropyl xanthate in alcohol. Except for the production of a red colour in the solution, no oxidation occurred. The same negative results were obtained on passing the gas through an aqueous solution of sodium cyclo pentamethylene dithiocarbamate.

DESULPHURIZATION OF THIO ACID DISULPHIDES BY ALKALI CYANIDES. (MECHANISM OF REACTION)

Action of ethyl phenyl thio carbamyl thio cyanate on sodium isopropyl xanthate.



Two grams of the thiocyanate and 1.75 gr. of sodium isopropyl xanthate, (slight excess), were dissolved separately in a few ccs. of absolute alcohol. On mixing the two solutions a yellow colour was produced after a few minutes. The reaction mixture was allowed to stand at room temperature for 2 hours. The addition of water to the solution precipitated an oil, which was extracted with ether. On evaporating off the ether, after washing, and drying the extract, the product was again obtained as an oil. As it was expected that the product would be a solid, it was purified by repeatedly dissolving it in alcohol, in which it was very soluble, then precipitating it with water. In this way about .5 gr. of a yellow solid was obtained which, after one recrystallization from glacial acetic, melted at 39.5°- 40°.

In order to confirm the identity of the above product, it was prepared by the action of ethyl phenyl carbamyl chloride on the same xanthate. Ten gr. of the carbamyl chloride and 8 gr. of sodium isopropyl xanthate were dissolved in 50 cc. of absolute alcohol, and the solution allowed to stand for about two hours at room temperature. The addition of water to the alcohol precipitated the product as an oil, The latter was extracted with ether, and, on evaporation of the latter, the mixed anhydride is obtained as a crystalline yellow solid, which after one recrystallization from lacial acetic, melted sharply at 41°. After repeated recrystallization from glacial acetic acid and also ligroin, the product still showed the same melting point. In mixing equal parts of this product and of the product obtained in the preceding experiment from carbamyl thiocyanate did decrease the m.p. of the latter product. The mixed anhydride~~s~~ is very soluble in alcohol, ether, and chloroform. It is a curious fact that its solubility in alcohol is much greater than that of isopropyl monoxanthogen itself.

Analysis: .1622 gr. subst. gave .3800 gr. $BaSO_4$

Calculated for $C_{13}H_{17}ONS_3$ (M.W. 299.2)	32.15% S
Found	32.18

.5268 gr. subst. gave .02552 gr. N

Calculated for $C_{13}H_{17}ONS_3$	4.70% N
Found	4.81

Action of methyl phenyl thio carbamyl thio cyanate on the corresponding sodium dithio carbamate.

An alcoholic solution of sodium methyl phenyl dithio carbamate was first prepared by the action of sodium sulphide (1.75 gr.) on an alcoholic solution of methyl phenyl thio carbamyl thio cyanate (1.50 gr.).

On adding the sodium cyanide, the solution soon turned yellow, the colour then gradually fading till the solution was almost colourless. The solution was allowed to stand till a drop of it, added to a few ccs. of water gave a clear solution, showing that all the thiocyanate had reacted. The solution was ~~then~~ made up to 45 cc. with alcohol, then divided into two fractions. To the first fraction, (24 cc). was added .8 gr. of methyl phenyl thio carbamyl thiocyanate. On adding the thiocyanate, the solution immediately assumed a deep yellow colour. The solution was warmed to about 35° to complete the reaction, and on cooling, a yellow crystalline precipitate was formed. The product was precipitated by the addition of an equal volume of water, filtered, and washed with water to remove potassium thiocyanate, the presence of which in the filtrate was shown by the deep red colour produced by adding a few drops of ferric chloride. After recrystallization from alcohol-chloroform, the product melted at 149.5°-150°, which is the correct melting point for sym-diphenyl dimethyl thiuram monosulphide. The identity of the product was confirmed by taking a mixed melting point with a pure sample of the monosulphide, on which no depression was observed.

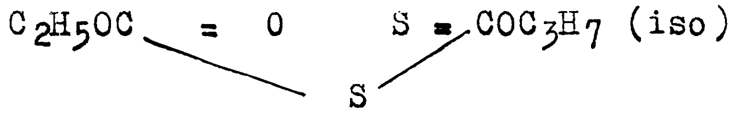
In order to prove that the alcoholic solution used in the above experiment actually contained sodium methyl phenyl dithiocarbamate, the remaining fraction (19 cc). was diluted with 50 cc. of water. To the clear solution thus obtained was added one gram of cyanogen bromide in water. A white precipitate was obtained directly which, after two recrystallizations from alcohol-chloroform, melted at 196°- 197°, showing it was sym. dimethyl diphenyl thiuram di~~mono~~sulphide.

The yield of thiuram monosulphide obtained in the first part of the experiment was 1.16 gr. or 90.5%, based on the .8 gr. of carbamyl thiocyanate used.

In the second part of the experiment, the yield of thiuram disulphide obtained was 0.49 gr., or 89%, based on 0.63 gr. of thiocyanate used.

FORMATION OF THIO ANHYDRIDES BY OTHER THEN DESULPHURIZATION METHODS

Preparation of mixed anhydrides from isopropyl xanthic acid and ethyl carbonic acids.



$$C_2H_5OC(=O)-S-C(=S)OC_3H_7 \text{ (iso)}$$

A solution of 16 gr. of ethyl chlorcarbonate in 40 cc. acetone was added gradually, with mechanical stirring, to a solution of 21 gr. of sodium isopropyl xanthate in 50 cc. of water, the reaction being carried out at -5°. There was only a very faint odour of the chlorcarbonate after one half hour stirring. The product was then precipitated by the addition of a large amount of water, separated, and dried under reduced pressure. Yield 30.4 gr. 98.5% of theory. The product is a very pale yellow oil.

N_D 1.5110 at 25.5°,

Action of sodium isopropyl xanthate on mixed anhydride obtained above.

Five grams of the thio anhydridenobtained above were added to an alcoholic solution of 5 gr. sodium isopropyl xanthate in 20 cc. alcohol, on the addition of the anhydride, the solution assumed a deep yellow colour. The solution was allowed to stand overnight, on which some of the monoxanthogen separated out. A small amount of water was added to precipitate the monoxanthogen completely, the latter was then filtered off, and recrystallized from alcohol, m.p. 55° to 55.5°, the yield obtained was 3.9 gr. or 69.1% based on the amount of mixed anhydride used.

The melting point observed here for isopropyl monoxanthogen is somewhat higher than the melting point observed on products prepared by desulphurization with cyanides. The former is probably more correct, for there is no possibility of the product obtained by that method being contaminated with the dixanthogen, while the product obtained by the cyanide method from the dixanthogen is probably always contaminated with small amounts of the latter.

Action of sodium isopropyl xanthate on the thio anhydride of ethyl thiol carbonic acid.

To a solution of 12.5 gr. sodium isopropyl xanthate in alcohol were added 14 gr. of the thio anhydride. After adding the latter, the solution gradually assumed a yellow colour, and, after standing for some hours, the isopropyl manoxanthogen started to crystallize out. On the addition of water, some oil was precipitated with the monoxanthogen, the water insoluble products were separated, and the oil removed from the solid monoxanthogen by adding a small amount of alcohol and filtering. The product, after one recrystallization from alcohol, showed the correct melting point for isopropyl monoxanthogen, 54.5° to 55°. The yield obtained was 3.25 gr. 34.5% of the theory.

Action of benzoyl chloride on potassium ethyl xanthate, and identification of potassium thio benzoate as a by-product in the reaction.

To 14 gr. of benzoyl chloride in 75 cc. of acetone were added gradually 36 gr. of potassium ethyl xanthate.

After the xanthate had been all added, the reaction mixture was warmed to35° to complete reaction. The water insoluble products were precipitated with water, and from these, after purification, were obtained 11 gr. of pure ethyl monoxanthogen. To the mother liquor was added a solution containing an excess of sodium tetrathionate, this caused the precipitation of an oil, which was extracted with ether; the ether extract was washed with water, dried with $CaCl_2$, then evaporated under reduced pressure. A deep coloured crystalline compound was obtained as residue, this was recrystallized a few times from alcohol, from which solvent it was finally obtained as a slightly coloured crystalline product, melting at 127°. On taking a mixed melting point with pure benzoyl disulphide, which melts at 128°, the m.p. of the product was not depressed.

PREPARATION AND REACTIONS OF THIO ACID THIOCYANATES

Preparation of ethyl phenyl thio carbamyl thiocyanate, $C_6H_5(C_2H_5)$ NCS SCN

Three grams of finely ground potassium thio cyanate were added to a solution of 5 gr. ethyl phenyl thio carbamyl in 25 cc. of absolute alcohol, and the mixture allowed to stand for two hours at room temperature with occasional shaking. The solution became turbid at first, due to the separation of potassium chloride, then gradually set to a semi solid mass of crystals. Water was then added to dissolve potassium salts and precipitate the thiocyanate, which was filtered off. The product is obtained in practically quantitative yield. It crystallizes from warm alcohol in shiny, colourless needles, melting at 75.5° - 76° to a bromine-red oil. It is quite soluble in warm alcohol, more so in ether, and very soluble in chloroform and benzene. The product assumes a pink colour after standing for a few days, and is gradually changed over to a clear red oil on standing for some weeks, the change being accelerated by exposure to light.

Analysis: .2146 gr.subst. gave .4413 gr. $BaSO_4$

Calculated for $C_{10}H_{10}N_2S_2$ (M.W. 222.1)	28.80% S
Found	28.25

Molecular weight determination,

.1646 gr.subst.in 17.8767 gr.C_6H_6(K 51.2) gave $T_1 - T_0$ 0.208°,

Calculated for $C_{10}H_{10}N_2S_2$	M.W. 222.1
Found	224

Methyl phenyl thio carbamyl thiocyanate,

$C_6H_5(CH_3)$ NCS. SCN

The above compound was obtained in the same manner as the ethyl phenyl compound just described.

It was obtained also from warm alcohol in the form of lustrous leaflets, melting at 114° to a deep red oil. It is not very soluble in alcohol, but it is very soluble in chloroform and benzene. It appears to be much more stable than the ethyl compound, for a sample which has been standing for two months shows no signs of discoloration or decomposition.

Analysis: .1223 gave .2696 gr. $BaSO_4$

Calculated for $C_9H_8N_2S_2$(M.W.208)	30.83% S
Found	30.30

Ethyl ortho tolyl thio carbamyl chloride.

$CH_3C_6H_4(C_2H_5)$ NCS.Cl

The above compound, which is not described in the literature was prepared by von Braun's method ( ), by the action of thio phosgene on the base in ether. The carbamyl chloride, after recrystallization from low boiling ligroin, was obtained in the form of small plates, melting at 69°.

Analysis: .1945 gr.subst.gave .1322 gr. AgCl

Calculated for $C_{10}H_{12}SCl$ (M.W.199.5)	16.61% Cl
Found	16.93

On acting with the above carbamyl chloride on potassium thiocyanate in absolute alcohol, an amorphous solid product was obtained, which could not be recrystallized, but which gave some of the characteristic reactions of thio carbamyl thiocyanates, such as production of a yellow colour with alcoholic sodium sulphide.

Methyl para tolyl thio carbamyl chloride.

$CH_3C_6H_4\ (CH_3)\ NCS.Cl$

This carbamyl chloride also is not described in the literature. It was prepared by the same method as the ethyl ortho compound described above, and obtained from low boiling ligroin in the form of leaflets, m.p. 53°-54°,

Methyl p.tolyl thio carbamyl thiocyanate.

p. $CH_3C_6H_4(CH_3)\ NCS.SCN$

Two and one half grams of the thio carbamyl chloride were treated with 2 gr. of potassium thiocyanate in absolute alcohol. After recrystallization from absolute alcohol, 2.1 gr. of pure thio cyanate were obtained as large shiny plates, melting at 116.5°. The compound appears to be as stable as the methyl phenyl one.

Analysis: .1323 gr. subst. gave .2791 gr. $BaSO_4$

Calculated for $C_{10}H_{11}N_2S_2$ (M.W.222) 29.00% S

Found 28.98

Preparation of methyl phenyl thio carbamyl thiocyanate by the action of cyanogen bromide in the corresponding lead dithiocarbamate.

A solution of 11.5 gr. of cyanogen bromide in benzene was dried carefully by letting stand over calcium chloride for a day. To the filtered solution were then added 30 gr. of dry lead methyl phenyl dithiocarbamate. After standing for four days the reaction mixture was filtered, and, on evaporation of the solvent, 7.5 gr. of methyl phenyl thiocarbamyl thiocyanate were obtained which, after one recrystallization from alcohol, melted correctly at 113.5°.

Conversion of methyl phenyl thio carbamyl thiocyanate to the iso form, and reaction of the latter with aniline.

One gram of the above thiocyanate was heated in a test tube immersed in an oil bath at 100-110° for 10 minutes. The heating was interrupted when the compound had changed to a dark red oil, and bubbles of a gas started to form. This liquid product was dissolved in benzene, and .45 gr. of aniline added. The solution was then allowed to evaporate spontaneously and the solid residue recrystallized from alcohol, upon which about .5 gr. of a light red product was obtained, melting at 123°.

Analysis: .0905 gr.subst. gave .1360 gr. $BaSO_4$

Calculated for $C_{15}H_{15}N_3S_2$ (M.W. 301.1) 21.30

Found 20.66

That the above compound is a dithio biuret is shown by the fact that it is soluble in aqueous alkalies.

Some new thio anhydrides

The following thio anhydrides have been prepared in the course of the work described in this thesis, and, since they are not described in the literature, a short account of them is given here,

Monoxanthogen from mono ethylene glycol mono ethyl ether

$C_2H_5OCH_2CH_2OCS.SCS.OCH_2CH_2OC_2H_5$

This compound was prepared by the action of potassium cyanide on the corresponding dixanthogen. It was obtained as a reddish yellow oil,

N_D 1.5561, at 25°

n.Hexyl mono xanthogen

$C_6H_{13}OCS.SCS.OC_6H_{13}$

This compound was prepared by the action of cyanogen bromide, one half mole, on the corresponding sodium xanthate in alcohol. Five grams of cyanogen bromide and 18 gr. of sodium n.hexyl xanthate in 75 cc. alcohol were allowed to stand for one and one half hours at room temperature. The monoxanthogen was the precipitated with water, washed, and dried. The yield is almost quantitative,

N_D 1.5410 at 25°

Analysis: .1532 gr. subst. gave .4133 gr. $BaSO_4$

Calculated for $C_{14}H_{26}O_2S_3$ (M.W.322.2)	29.80% S
Found	30.48

Benzyl mono xanthogen,

$C_6H_5CH_2OCS.SCS.OCH_2C_6H_5$

Five grams cyanogen bromide and 23 gr. sodium benzyl xanthate in 80 cc. of 80% alcohol
After stirring one one hour in an ice bath, the product was precipitated with water, extracted with ether, and, after evaporating off the ether, recrystallized from glacial acetic. The product is obtained in the form of small pale yellow crystals. m.p. 82.5°-83°.

Analysis: .1249 gr. subst. gave .2543 gr. $BaSO_4$

Calculated for $C_{16}H_{14}O_2S_3$ (M.W.167)	28.80% S
Found	28.00

The same product, m.p. 82° was obtained later by the action of ethyl chlor carbamate on sodium benzyl xanthate. Its purification in the latter case, however, was more difficult on account of the formation of liquid by-products.

Methyl p.tolyl thiuram monosulphide,

$(p.CH_3C_6H_4(CH_3)NCS)_2\ S$

To a solution of 1.6 gr. of the thiocyanate in alcohol were added 1.8 gr. of finely ground sodium sulphide. The solution turned yellow on the addition of the sulphide, but gradually becomes colourless again. When a drop of the solution no longer gave a precipitate on adding to water, 1.45 gr. of methyl p.tolyl thio carbamyl chloride dissolved in a few ccs. of absolute alcohol in the cold, were added. The solution becomes deep yellow again on the addition of the chloride, and a yellow crystalline precipitate begins to form after a few minutes. After standing for one half hour, an equal volume of water was added and the solution filtered. On recrystallization from alcohol chloroform, methyl p.tolyl thiuram monosulphide is obtained as small plates, melting at 143.5°-144°.

V. SUMMARY

1. Nitrous acid has been found a convenient agent for the oxidation of ethyl and isopropyl xanthates to the corresponding xanthogens.

Cyanogen bromide and sodium tetrathionate, in aqueous solution, have a very specific oxidizing action on alkali xanthates, these being smoothly converted to dixanthogens without the formation of by-products. Cyanogen bromide can be used with equally good results for the oxidation of di-sulstituted dithiocarbamates to thiuram disulphides, in aqueous solution, no monosulphide being obtained under these conditions.

2. The mechanism of the desulphurizing action of alkali cyanides on acid disulphides has been determined, and the 'cyanic hydrolysis' through which desulphurization takes place was defined.

The products of the 'cyanic hydrolysis of acid disulphides have been isolated, one of these being identified as belonging to a hitherto unknown series of organic sulphur compounds, the thio acid thiocyanates.

3. The formation of monoxanthogens by the action of acid chlorides on alkali xanthates has been shown to take place in two stages: first, the formation of a mixed thio anhydride, followed by the action of the alkali xanthate on the latter. The low yields always obtained in the reaction have been shown to be due to the fact that in the second

stage, the reaction is a reversible one.

4. Two methods for the preparation of the new thio carbamyl thiocyanates are described, one of which does not involve the use of thiophosgene, the thiocyanates being prepared directly from the dithiocarbamates. The structure of the new thio carbamyl thiocyanates has been established by showing the existence of two distinct isomers, one of which reacts with aniline as a thiocyanate; this is the form in which the compounds are isolated, and the other, obtained by isomerization of the normal thiocyanate by heat, reacts with aniline as an isothiocyanate with the formation of dithiobiuret.

5. The following sulphur compounds, which are not described in the literature, have been isolated and identified.

Mono xanthogen from ethylene glycol mono ethyl ether,
$(C_2H_5O(CH_2)_2OCS)_2S$ liquid

Dixanthogen from ethylene glycol mono ethyl ether,
$(C_2H_5O(CH_2)_2OCS.S)_2$ liquid

Mixed anhydrides of ethyl carbonic and isopropyl xanthic acids,
$C_2H_5OCO.SCS.OC_2H_7$(iso) liquid

n.Hexyl mono xanthogen,
$(C_6H_{13}OCS)_2S$ liquid

n.Hexyl dixanthogen
$(C_6H_{13}OCS.S)_2$ liquid

Benzyl mono xanthogen

$(C_6H_5CH_2OCS)_2S$ m.p.82.5°

B.Phenyl ethyl di xanthogen

$(C_6H_5CH_2CH_2OCS.S)_2$ m.p.49.5°-50°

B.Phenyl ethyl xanthogenamide

$C_6H_5CH_2CH_2OCS.NH_2$ m.p.79°

Mixed thio anhydride from methyl phenyl carbamic and isopropyl xanthic acids.

$C_6H_5(CH_3)$ NCS.SCS.OC_3H_7(iso) m.p.42°

Mixed thio anhydride from phenyl ethyl dithiocarbamic and isopropyl xanthic acids

$C_6H_5(C_2H_5)$ NCS.SCS.OC_3H_7(iso) m.p.41°

Methyl phenyl thio carbamyl thiocyanate

$C_6H_5(CH_3)$ NCS.SCN m.p.113.5°-114°

Ethyl phenyl thio carbamyl thiocyanate

$C_6H_5(C_2H_5)$ NCS.SCN m.p.75.5°

Methyl p.tolyl thio carbamyl thiocyanate

p.$CH_3C_6H_4(CH_3)$ NCS.SCN m.p.116.5°

Methyl p.tolyl thio carbamyl chloride

p.$CH_3C_6H_4(CH_3)$ NCS.Cl m.p.53°-54°

Ethyl o.tolyl thio carbamyl chloride

o.$CH_3C_6H_4(C_2H_5)$NCs.Cl m.p.69°

Methyl phenyl phenyl dithio biuret

a,b,$C_6H_5(CH_3)$ NCS.NH CS.NH C_6H_5 m.p.123°

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