## LVIII.—*Constitution of the Salts of* s-*Alkylthiocarbamides.*

By JOHN TAYLOR.

COMPOUNDS of thiocarbamide with alkyl haloids were first described by Claus (*Ber.*, 1874, **7**, 236; 1875, **8**, 41; *Annalen*, 1875, **179**, 145). The work was reviewed and extended by Bernthsen and Klinger (*Ber.*, 1878, **11**, 492; 1879, **12**, 575), who showed that the alkyl group was linked to the sulphur atom of thiocarbamide, formulating the substance thus, $NH_2 \cdot C(:NH) \cdot S \cdot R, HX$; the compound with benzyl chloride was further examined by E. A. Werner (T., 1890, **57**, 283). Other investigators have examined the additive products of alkyl haloids with substituted thiocarbamides.

An additive compound of thiocarbamide and ethyl oxalate has been described by Nencki (*Ber.*, 1874, **7**, 780).

Werner (*loc. cit.*) transformed thiocarbamide benzyl chloride * to sulphate by the use of sulphuric acid, $CSN_2H_4, C_6H_5 \cdot CH_2Cl \xrightarrow{H_2SO_4}$ $(CSN_2H_4)_2(C_6H_5 \cdot CH_2)_2SO_4$. He also records the transformation of thiocarbamide allyl bromide to sulphate by heating its alcoholic solution with silver sulphate,

$$CSN_2H_4, C_3H_5Br \xrightarrow{Ag_2SO_4} (CSN_2H_4)_2(C_3H_5)_2SO_4.$$
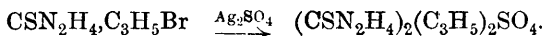
Arndt (*Annalen*, 1911, **384**, 331) prepared several salts of ψ-thioureas by combining them with various acids. He, however, was content with preparing the salts, and gave no indication of their structure:

$$NH_2 \cdot C(:NH) \cdot SR + HX \longrightarrow NH_2 \cdot C(:NH) \cdot SR, HX.$$
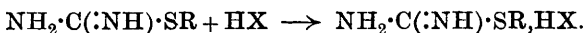
The present investigation seeks to extend the range of additive compounds, to suggest a structure indicating the position of the acidic group, and to show that compounds similar to the direct additive products may be prepared by indirect means.

It has now been found that thiocarbamide unites additively with alkyl sulphates, nitrates, and thiocyanates. These additive products were obtained by heating together, in alcoholic solution, thiocarbamide and a slight excess of the required ester.

Methyl esters combined most readily; next in order came benzyl esters, and lastly ethyl esters. This order is the same as holds in the case of combination of thiocarbamide with the alkyl haloids. It is probable that this order corresponds with the order of ease
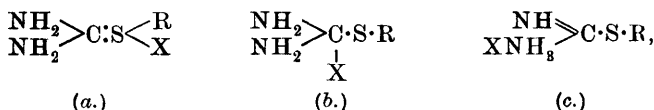
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* This nomenclature is used instead of the more cumbrous "the chloride of benzyl-ψ-thiourea" or "the additive compound of benzyl chloride with thiocarbamide."

of hydrolysis of the esters. In the case of the thiocyanates, it certainly corresponds with the order of ease of transformation of thiocyanate to thiocarbimide. In conformity with this view, it may be added that allyl thiocyanate, the most easily transformed of all the thiocyanates, combines completely, in the cold, on long contact with thiocarbamide, whilst phenyl thiocyanate, which shows no tendency towards transforming to thiocarbimide, gave no indication of combination even when boiled with thiocarbamide.

Substances similar to the additive products may be obtained by indirect means; thus the same compound was obtained by (a) combining benzyl chloride with thiocarbamide, and (b) the action of barium chloride on thiocarbamide benzyl sulphate. Compounds with methyl thiocyanate and nitrate obtained by these methods were also identical.

Since esters of organic acids failed to combine directly with thiocarbamide, advantage was taken of the method of double decomposition to obtain them indirectly. Their general sparing solubility in water served to render their isolation quite easy. For example, thiocarbamide methyl salicylate was precipitated on mixing aqueous solutions of sodium salicylate and thiocarbamide methyl sulphate. Under no condition that was tried could methyl salicylate be made to combine directly with thiocarbamide.

When direct addition of an ester to thiocarbamide takes place, the alkyl group becomes linked to sulphur. The acyl group may enter any one of three possible positions:

$$\begin{array}{ccc} \mathrm{NH_2}{>}\mathrm{C{:}S}{<}^{\mathrm{R}}_{\mathrm{X}} & \mathrm{NH_2}{>}\mathrm{C{\cdot}S{\cdot}R} & \mathrm{NH}{>}\mathrm{C{\cdot}S{\cdot}R,} \\ \mathrm{NH_2} & \mathrm{NH_2}\underset{\mathrm{X}}{|} & \mathrm{XNH_3} \\ (a.) & (b.) & (c.) \end{array}$$

which for convenience may be designated (a) sulphonium, (b) carbonium, and (c) ammonium compounds.

These additive products all behave like salts of a strong base. All are more or less readily soluble in water. Their solutions are neutral to litmus, give picrates on the addition of picric acid, and respond to the usual tests for the acidic ion. As a rule, organic compounds which have these acid groups directly linked to carbon are not at all freely ionised; thus ethyl potassium sulphate, ethyl oxalate, and ethyl thiocyanate do not respond to the ordinary tests for the acid radicles. This universal and strong ionisation of the additive products points to the improbability of the carbonium form (b).

Two observations point to the improbability of the ammonium form. First, thiocarbamide benzyl nitrite may be recrystallised from boiling water. Compounds which contain a nitrite group

directly linked to nitrogen are well known to be unstable. It seems unlikely that the compound $NO_2 \cdot NH_3 \cdot C(:NH) \cdot S \cdot R$ could be stable enough to be recrystallised from boiling water. Secondly, solutions of thiocarbamide methyl thiocyanate and of thiocarbamide benzyl thiocyanate, were evaporated repeatedly to dryness, and the substances fused without any noticeable change in properties. Amine thiocyanates when heated undergo transformation to thiocarbamides, $NH_3Ph \cdot SCN \longrightarrow NHPh \cdot CS \cdot NH_2$, $NH_4SCN \longrightarrow NH_2 \cdot CS \cdot NH_2$. A compound of the type $R \cdot S \cdot C(:NH) \cdot NH_3 \cdot SCN$ should yield with ease $R \cdot S \cdot C(:NH) \cdot NH \cdot CS \cdot NH_2$, which, in turn, would give hydrogen sulphide to an alkaline solution of a lead salt. The thiocyanates mentioned above gave after such treatment no trace of lead sulphide when heated with an alkaline solution of lead acetate. Hence in these products, which were obtained either by direct addition or by double decomposition, the acidic group does not form an ammonium compound.
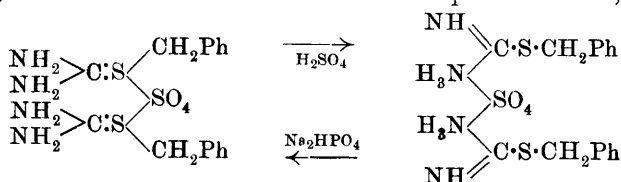
The only remaining possibility is the sulphonium linking. Here both alkyl and acyl groups unite directly with sulphur, thus: $(NH_2)_2CS + RX \longrightarrow (NH_2)_2C:SRX$. This view of the grouping is not opposed to any of the observed facts.

Sulphonium compounds are well known, and are either well-marked bases or salts. Their properties are very similar to those of the thiocarbamide additive products. Both are crystalline and soluble in water. Their solutions are highly ionised, and hence new salts may be prepared by double decomposition, consequently there is nothing improbable in the idea that these compounds are sulphonium salts.

Werner (T., 1912, **101**, 2184) considers it probable that thiocarbamide, under the influence of strongly ionised acids, gives an ammonium compound, $XNH_3 \cdot C(:NH) \cdot S \cdot R$. In this connexion, interesting observations were made with benzyl additive compounds, and it seems possible that with these both ammonium and sulphonium forms of compounds with strong acids may exist. Two distinct thiocarbamide benzyl sulphates were obtained, one, already described by Werner (*loc. cit.*), by heating together thiocarbamide benzyl chloride and sulphuric acid, and the other by heating an alcoholic solution of thiocarbamide benzyl chloride with silver sulphate. The two forms give identical analytical figures for "sulphate," but show many differences. Werner's sulphate melts at 144—145,* is exceedingly readily soluble in alcohol, and crystallises from its alcoholic solution in stout rhombs. The compound from silver sulphate melts at 180—181°, is sparingly soluble in alcohol, and crystallises from this solution in long needles. Each

* Werner gives 132—133°.

may be transformed into the other, Werner's to the sulphate of higher melting point by boiling with a feebly alkaline substance, such as a trace of sodium phosphate, or even by recrystallising from boiling water; the substance of higher melting point to Werner's sulphate, by heating with excess of dilute sulphuric acid. Werner's sulphate was also prepared by dissolving benzyl-ψ-thiourea in excess of dilute sulphuric acid and by heating thiocarbamide sulphate, CSN_2H_4,H_2SO_4, with benzyl alcohol. In every case, therefore, free sulphuric acid was present when Werner's sulphate was prepared. It seems probable that there are two isomeric compounds differing from one another in the point of attachment of the acid group, free acid determining the ammonium form, whilst feeble alkali determines the sulphonium form, thus:

$$
\begin{array}{c}
NH_2 \\
NH_2
\end{array}\!\!\!>\!\!C\!:\!S\!<\!\!\!\begin{array}{c}CH_2Ph \\ SO_4\end{array} \quad \xrightarrow{H_2SO_4} \quad
\begin{array}{c}NH \\ H_3N\end{array}\!\!\!>\!\!\!\begin{array}{c}C\cdot S\cdot CH_2Ph \\ SO_4\end{array}
$$

$$
\begin{array}{c}
NH_2 \\
NH_2
\end{array}\!\!\!>\!\!C\!:\!S\!<\!\!\!\begin{array}{c}\ \\ CH_2Ph\end{array} \quad \xleftarrow{Na_2HPO_4} \quad
\begin{array}{c}H_3N \\ NH\end{array}\!\!\!>\!\!\!\begin{array}{c}C\cdot S\cdot CH_2Ph\end{array}
$$

This transformation is effected by the use of "strong" acids only. Thiocarbamide benzyl acetate was recovered unchanged after recrystallisation from acetic acid. Werner also states (*loc. cit.*) that acetic acid has little or no power to change the configuration of thiocarbamide. A similar negative result was obtained with the thiocyanate and thiocyanic acid.

The electrical conductivities of equally concentrated aqueous solutions of the two forms of thiocarbamide benzyl sulphate were compared. At about 1·5 per cent. concentration, the solution of the ammonium form, which is the more readily soluble, conducted electricity 3·2 times as readily as the second solution. This great difference in conductivity points to differences in structure. Moreover the ammonium forms melt at a lower temperature than the corresponding sulphonium forms.

There are similarly two modifications of thiocarbamide benzyl chloride, namely, a form of higher melting point produced by direct combination of the constituents in a non-ionising solvent, such as acetone, melting at 174°, and a form of lower melting point (148°) produced from the first by twice recrystallising it from hydrochloric acid, in which it is sparingly soluble. The transformation to sulphonium form is less easy than with the sulphate, but it may be accomplished by boiling the alcoholic solution with sodium phosphate—the aqueous solution is not affected by this treatment—and then keeping the resulting crystals in the steam-oven for a few hours.
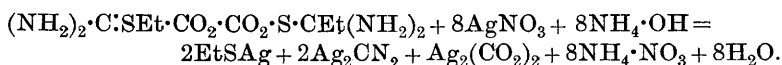
Indications of two nitrates were observed. Thus, benzyl-ψ-thio-urea dissolved in nitric acid gave, first, flattened needles melting at 118°; the mother liquors from these gave a much smaller crop of nearly square plates melting at 92°. Recrystallisation from alcohol converted these to the sulphonium form melting at 118°.

No indications of two thiocyanates were observed.

The existence of sulphonium and of ammonium forms appears to be confined to the benzyl derivatives. The thiocarbamide compounds of methyl nitrate and of methyl sulphate were recovered unchanged after recrystallisation from their respective acids.

It is noteworthy that when a salt is produced by double decomposition, the product is nearly always of sulphonium form, whether the original material is sulphonium or ammonium. Thus the products of double decomposition of "sulphonium" and of "ammonium" thiocarbamide benzyl sulphate with barium nitrate were identical, melting at 118°. The same sulphate of higher melting point was prepared by the interaction of silver sulphate and either the "ammonium" or "sulphonium" forms of thiocarbamide benzyl chloride.

An interesting isomeride of Nencki's thiocarbamide ethyl oxalate was obtained by heating an alcoholic solution of thiocarbamide ethiodide with silver oxalate. Nencki's product may be regarded as a molecular compound of ethyl oxalate with thiocarbamide, whilst the new compound may be described as the oxalate of ethyl-ψ-thiourea, $(NH_2)_2C\colon SEt\cdot CO_2\cdot CO_2\cdot S\cdot CEt(NH_2)_2$, or an ionic compound of the above-mentioned substances. The differences between the two are quite sharp, and are such as would be expected between a molecular compound of thiocarbamide with non-ionised ethyl oxalate and a highly ionised oxalate of a sulphonium base. The former does not yield calcium oxalate until after hydrolysis with alkali hydroxide, nor does it give a picrate; the latter readily gives, in aqueous solution, both calcium oxalate and a picrate. The former yields metallic sulphide with an alkaline solution of a lead salt and with ammoniacal silver nitrate. The latter under similar treatment yields metallic mercaptide and cyanamide,

$$(NH_2)_2\cdot C\colon SEt\cdot CO_2\cdot CO_2\cdot S\cdot CEt(NH_2)_2 + 8AgNO_3 + 8NH_4\cdot OH =$$
$$2EtSAg + 2Ag_2CN_2 + Ag_2(CO_2)_2 + 8NH_4\cdot NO_3 + 8H_2O.$$

A sharp difference in fusibility was noted between the two substances, Nencki's melting at 158°, whilst the other melts at 188°.

This sharp difference in properties between the two oxalates serves to indicate the course of the reaction between salts of thiocarbamide and other compounds. It was suggested by Dixon and Taylor (T., 1916, **109**, 1245) that when thiocarbamide hydro-

chloride reacted with acetaldehyde, it was probable that the acid first migrated from thiocarbamide to acetaldehyde, and that the acid compound of the acetaldehyde in turn united with free thiocarbamide, but no direct proof could be given.

It is now found that when the thiocarbamide oxalate is heated with ethyl alcohol, Nencki's compound results. Clearly ethyl oxalate is first formed and this afterwards unites with thiocarbamide. Therefore the acid migrates from thiocarbamide to alcohol in this case, and presumably to acetaldehyde in the preceding case.

A somewhat similar indication was observed with thiocarbamide nitrate. When this compound was heated with methyl alcohol or with benzyl alcohol, reduction of the nitric acid occurred exactly as if the acid had been heated with alcohol without having been freed from nitrous acid by heating with carbamide. It is evident that the hold of thiocarbamide for acid is very feeble.

EXPERIMENTAL.

Thiocarbamide and Sulphates.

Methyl Sulphate.—Thiocarbamide and methyl sulphate were heated together on a water-bath without any solvent. After a few minutes a vigorous reaction took place, which was moderated by cooling. The product, a brownish-orange paste, was heated with alcohol, when a white powder of microcrystalline needles was left undissolved. This powder was readily soluble in water. The aqueous solution gave all the reactions for a sulphate. When it was heated with sodium hydroxide, methyl mercaptan was liberated. Alkaline solution of lead acetate gave a yellow precipitate of lead mercaptide, but no lead sulphide. Ammoniacal solution of silver nitrate gave at first a white precipitate, which on heating turned yellow. Silver mercaptide and silver cyanamide were formed, but no silver sulphide.

The substance was apparently the sulphate of methyl-ψ-thiourea, $(CSN_2H_4)_2Me_2SO_4$. Analysis:

0·317 gave 0·255 $BaSO_4$. $SO_4 = 33·14$.

$C_{11}H_{14}O_4N_{11}S_3$ requires $SO_4 = 33·71$ per cent.

A similar product was obtained by heating thiocarbamide sulphate with methyl alcohol. Thiocarbamide was dissolved in half its weight of sulphuric acid, and to this was added excess of methyl alcohol. After short heating on a water-bath, a yellow, amorphous powder formed which was rejected, and the heating of the solution continued until no silver sulphide was formed on adding ammoniacal silver nitrate solution to a drop of the liquid.

D D 2

On cooling, thin plates separated, which behaved in all respects like the direct additive product. Each decomposed at 235°. Each gave a bright yellow picrate (m. p. 221°) which may be recrystallised easily from hot water.

The latter method of preparing the substance affords a convenient method of producing material as starting point for obtaining other derivatives of methyl-ψ-thiourea.

Ethyl Sulphate.—This substance reacted with thiocarbamide under similar conditions and in just the same way as methyl sulphate, except that heating had to be continued for a much longer time.

The sulphate, $(CSN_2H_4)_2Et_2SO_4$, crystallises in tufts of white needles melting and decomposing at 202°. Its picrate melts at 186°. Analysis:

0·302 gave 0·226 $BaSO_4$. $SO_4 = 30·86$.

$C_6H_{18}O_4N_4S_3$ requires $SO_4 = 31·22$ per cent.

An exactly similar product was obtained, but only in small yield, by allowing thiocarbamide sulphate and ethyl alcohol to remain together in the cold for three or four days.

Benzyl Sulphate.—An alcoholic solution of thiocarbamide benzyl chloride was heated on a water-bath for a few hours with silver sulphate. The filtrate gave white, silky needles free from chloride which melted and decomposed at 180—181°. These were somewhat sparingly soluble in alcohol and readily so in water. The aqueous solution gave the usual tests for sulphate and for ψ-thiourea. The picrate from this substance melted at 183°, as does the picrate from thiocarbamide benzyl chloride described by Werner (*loc. cit.*).

The same sulphate was obtained when either the " ammonium " or " sulphonium " form of thiocarbamide benzyl chloride was employed as starting point:

0·249 gave 0·132 $BaSO_4$. $SO_4 = 21·84$.

$C_{16}H_{22}O_4N_4S_3$ requires $SO_4 = 22·32$ per cent.

The " ammonium " form was obtained when thiocarbamide sulphate was heated with benzyl alcohol on a water-bath for half an hour, and the whole allowed to remain for a day. The resulting creamy paste was filtered and the residue crystallised from alcohol. The product melted at 143—144°, and agreed in all respects with Werner's sulphate.

This same form of the sulphate was also prepared by dissolving benzyl-ψ-thiourea in excess of hot dilute sulphuric acid. On cooling the solution, crystals melting at 143° separated (see Arndt, *loc. cit.*).

The specific conductivities of solutions of " ammonium " and of

" sulphonium " thiocarbamide benzyl sulphate were measured in a cell the constant of which was 0·105.

With a solution of 2·5 grams in 200 c.c., the solution of the " ammonium " form had a resistance of 8·8 ohms, whilst the " sulphonium " form had a resistance of 28·0 ohms. The equivalent conductivities are therefore 205·2 and 64·5 respectively.

Thiocarbamide and Nitrates.

Methyl Nitrate.—Thiocarbamide and methyl nitrate in methyl alcohol were heated on a water-bath for two or three hours. The solution gave rhombs which melted at 109—110°, and this melting point was not changed when the substance was recrystallised from nitric acid. The substance was soluble in water, and the aqueous solution responded to the usual tests for ψ-thiourea with an alkaline solution of lead acetate and with an ammoniacal solution of silver nitrate. It dissolved readily in methyl or ethyl alcohol :

0·250 gave 39·0 c.c. NO at 17° and 755 mm. N (nitratic) = 9·16.
$C_2H_7O_3N_3S$ requires N (nitratic) = 9·15 per cent.

An attempt to prepare the substance from thiocarbamide nitrate and methyl alcohol failed. With excess of methyl alcohol, no sign of combination was observed after an hour on a water-bath. On concentrating the solution to smaller bulk, a vigorous reduction of nitric acid took place; no thiocarbamide methyl nitrate could be detected.

A product similar to the direct additive product was obtained on mixing aqueous solutions of thiocarbamide methyl sulphate and barium nitrate. From the filtrate a substance was obtained melting at 108—109° and having the same crystal shape and chemical properties as the direct additive product. The two substances gave identical picrates (m. p. 221°).

Fthyl Nitrate.—Thiocarbamide and ethyl nitrate were heated together with alcohol on a water-bath at intervals for nearly a month. Considerable interaction had taken place, as the resulting solution gave only a slight blackening when heated with alkaline lead acetate solution. A picrate was obtained (m. p. 186°) similar to all the picrates obtained from ethyl-ψ-thiourea compounds.

Attempts to prepare the substance by the interaction of ethyl alcohol and thiocarbamide nitrate failed, just as in the case of methyl nitrate.

The action of silver nitrate on thiocarbamide ethiodide resulted in the formation of double silver salts.

Benzyl Nitrate.—This compound was prepared by mixing hot

concentrated solutions of either thiocarbamide benzyl chloride or benzyl sulphate and potassium nitrate. White, flattened needles separated from the cooled liquid, which when recrystallised from water melted at 118—119°.

The substance prepared by Arndt's method of dissolving benzyl-ψ-thiourea in nitric acid agreed in all respects with the material as prepared above. The melting point of a mixture of the two remained unchanged, showing their identity.

Analysis was carried out by adding an ammoniacal solution of silver nitrate to a weighed quantity of material in aqueous solution. The compound was completely decomposed according to the equation:

$$(NH_2)_2C\colon S(CH_2Ph)\cdot NO_3 + 3AgNO_3 + 4NH_4\cdot OH =$$
$$CN_2Ag_2 + CH_2Ph\cdot SAg + 4NH_4\cdot NO_3 + 4H_2O.$$
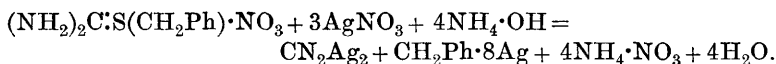
The filtered precipitate of silver cyanamide and silver benzyl mercaptide was treated with nitric acid, and the amount of silver in solution determined by Volhard's method. One hundred parts of the substance gave 139·6 parts of silver, whereas 100 parts of $CSN_2H_4,CH_2Ph\cdot NO_3$ require 141·5 parts of silver.

The nitrate readily separates on cooling a mixture of nitric acid with a hot concentrated solution of thiocarbamide benzyl chloride (compare Arndt, *loc. cit.*).

Attempts to prepare thiocarbamide benzyl nitrate from a mixture of thiocarbamide nitrate and benzyl alcohol failed in the same way as with methyl alcohol and with ethyl alcohol.

Identical products (m. p. 117—118°) were obtained by the addition of barium nitrate to solutions of either "sulphonium" or "ammonium" thiocarbamide benzyl sulphate.

Thiocarbamide and Benzyl Chloride.

Werner's work on thiocarbamide benzyl chloride (*loc. cit.*) was revised in the light of the previous experiments. He stated that on three occasions he obtained specimens which melted at 142—143°. On other occasions his product melted at 174°. He suggested the existence of polymeric modifications. It is now found that when a non-hydrolysing solvent, such as acetone, is used, no substance of lower melting point is formed. Repeated recrystallisation of the product from hydrochloric acid, in which it is much less readily soluble than in water, yielded thin, glistening plates which melted at 148°. This appears to be the "ammonium" form of the compound. The melting point of this form, following the general rule, is lower than that of the corresponding "sulphonium" form.

After the "ammonium" form has been heated in alcoholic solution for about an hour with animal charcoal and sodium phosphate, the material becomes less readily soluble in alcohol, and the crystals show scarcely any softening at the lower temperature, and if they are further heated in a steam-oven for two or three hours the substance melts at 174° without previous softening. A mixture of the two forms is, however, very readily obtained, recrystallisation from water being sufficient to transform part from "sulphonium" form to "ammonium" form. A mixture of the two forms was produced when either the "sulphonium" or "ammonium" form of thiocarbamide benzyl sulphate was transformed to chloride by barium chloride.

The hydrochloride of benzyl-ψ-thiourea may be prepared easily by dissolving the ψ-thiourea in an excess of hot dilute hydrochloric acid. The crystals which separate on cooling melt at 148° and are identical with the "ammonium" form of thiocarbamide benzyl chloride (compare Arndt, *loc. cit.*).

An exactly similar product, melting at 148°, was prepared by heating thiocarbamide hydrochloride with benzyl alcohol.

Thiocarbamide and Thiocyanates.

These compounds are the more interesting, as all attempts to combine thiocarbamide with thiocyanic acid have failed up to the present (Krall, T., 1913, **103**, 1383).

The compounds now obtained are ionic, giving the usual reactions for thiocyanates, unlike the parent materials.

Methyl Thiocyanate.—Thiocarbamide methyl thiocyanate and alcohol were heated together on a water-bath for two or three days. A considerable quantity of solid separated which melted and decomposed at 78—80°, and was very readily soluble in water or alcohol. The usual ψ-thiocarbamide reactions were shown, as well as those for thiocyanate. It yielded a picrate melting at 220°:

0·242 required 16·1 c.c. $N/10$-$CuSO_4$.   SCN $= 38·6$.

$C_3H_7N_3S_2$ requires SCN $= 38·9$ per cent.

This compound gave no sulphide when heated with an alkaline solution of lead acetate or with an ammoniacal solution of silver nitrate, nor was sulphide produced by this treatment after solutions of the substance had been repeatedly evaporated on a water-bath and the substance itself maintained in a state of fusion for several hours.

An exactly similar product melting at 78—79° was prepared by the interaction of solutions of thiocarbamide methyl sulphate and of barium thiocyanate.

Ethyl Thiocyanate.—Complete combination of the thiocarbamide could not be effected. Interaction took place, as the solution gave a picrate and lead mercaptide. Ammoniacal silver gave silver sulphide, indicating unchanged thiocarbamide. The product was a faintly brown paste.

Benzyl Thiocyanate.—Thiocarbamide was heated on a water-bath with benzyl thiocyanate and alcohol. After five or six hours reaction was complete. The product separated in bundles of long, slender needles which melted at 82—84°, and this melting point was unchanged by recrystallisation from thiocyanic acid, but its crystal shape became transformed to thin, hexagonal plates.

Found: SCN = 25·58.

$C_9H_{11}N_3S_2$ requires SCN = 25·78 per cent.

A product crystallising in long needles, but melting at 85—86°, was prepared by dissolving benzyl-ψ-thiourea in thiocyanic acid. On recrystallisation from thiocyanic acid, hexagonal plates melting at 82—84° were again obtained. None of these products gave hydrogen sulphide to alkaline lead acetate after heating to the fusion point. When heated more strongly, the substance dissociated, giving benzyl thiocyanate, and the fusion now readily gave metallic sulphides.

Allyl Thiocyanate.—To an alcoholic solution of allyl thiocyanate was added finely divided thiocarbamide, and this mixture allowed to remain, with occasional shaking, for nearly a month until the liquid gave none of the reactions for thiocarbamide. The product was a clear, yellow oil. One hundred parts of the substance gave 184·3 parts of silver, whereas 100 parts of $CSN_2H_4,C_3H_5\cdot SCN$ require 185·1 parts of silver.

Thiocarbamide and Benzyl Nitrite.

From an aqueous solution of thiocarbamide benzyl chloride and sodium nitrite this compound separated in fine needles. Its melting point (126°) was determined by plunging the melting-point tube into an already heated bath. Identical products were obtained with either "ammonium" or "sulphonium" thiocarbamide benzyl chloride as starting point. Nitrous acid was liberated by dilute acids, and the substance responded to the usual tests for ψ-thiocarbamide. One hundred parts of the substance gave 143 parts of silver, whereas 100 parts of $CSN_2H_4,C_6H_5\cdot CH_2\cdot NO_2$ require 145·2 parts of silver.

Arndt prepared a similar substance from benzyl-ψ-thiourea in an acid solution. He gave the same melting point for his product, but did not check its composition.
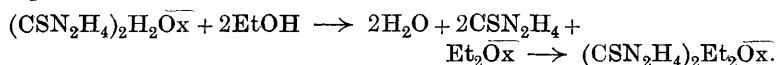
Thiocarbamide and Oxalates.

Ethyl Oxalate.—Nencki (*Ber.*, 1874, **7**, 780) and Claus (*Ber.*, 1875, **8**, 43) prepared an additive compound of thiocarbamide with ethyl oxalate, which melts at 158° and does not respond to any of the tests for ψ-thiourea or for oxalate.

An isomeride, $(CSN_2H_4)_2(CO_2Et)_2$, has now been obtained by the interaction of silver oxalate and thiocarbamide ethiodide. To the ethiodide, dissolved in alcohol, was added finely powdered silver oxalate. A considerable rise of temperature occurred and silver iodide was formed. After heating for about ten minutes on a water-bath, the hot mixture was filtered. A white, crystalline deposit of small rhombs melting at 187—189° was formed which contained no silver or halogen. It was readily soluble in water, and the solution at once responded to the tests for oxalate and for ψ-thiourea:

0·331 gave $\mathrm{Ca\overline{Ox}}$ equivalent to 22·4 c.c. $N/10\text{-}KMnO_4$, corresponding with "oxalate" = 29·7.

$C_8H_{18}O_4N_4S_2$ requires "oxalate" = 29·8 per cent.

Attempts to prepare this substance by heating thiocarbamide oxalate with ethyl alcohol resulted in the formation of Nencki's compound, melting at 155° The course of the reaction may be represented thus:

$$(CSN_2H_4)_2H_2\overline{Ox} + 2EtOH \longrightarrow 2H_2O + 2CSN_2H_4 +$$
$$Et_2\overline{Ox} \longrightarrow (CSN_2H_4)_2Et_2\overline{Ox}.$$

Benzyl Oxalate.—This compound was obtained in thin, long, oblong plates melting at 191—192° on recrystallising from hot water the precipitate formed on mixing aqueous solutions of thiocarbamide benzyl chloride and ammonium oxalate. Its chemical behaviour is similar to that of the preceding compound:

0·313 gave $\mathrm{Ca\overline{Ox}}$ equivalent to 14·8 c.c. $N/10\text{-}KMnO_4$, corresponding with "oxalate" = 20·81.

$C_{18}H_{22}O_4N_4S_2$ requires "oxalate" = 20·85 per cent.

The same compound also resulted from the interaction of (*a*) thiocarbamide benzyl chloride and silver oxalate (m. p. 192°), and (*b*) equivalent quantities of benzyl-ψ-thiourea and oxalic acid in alcoholic solution (m. p. 188°).

Thiocarbamide and Salicylates.

Methyl Salicylate.—Methyl salicylate and thiocarbamide failed to unite at the boiling point of methyl salicylate. The ionic compound was precipitated on mixing hot concentrated solutions of

thiocarbamide methyl sulphate and sodium salicylate. The sub-
stance crystallises in long needles which decompose at 155°. Its
chemical behaviour is similar to that of other salts of ψ-thioureas.
One hundred parts of the substance gave 142·8 parts of silver,
whereas 100 parts of $CSN_2H_4,HO\cdot C_6H_4\cdot CO_2Me$ require 142·2 parts
of silver.

Benzyl Salicylate.—The compound was prepared from thiocarb-
amide benzyl chloride and sodium salicylate. It crystallises in
fine needles which melt at 144—145°. One hundred parts of the
substance gave 107·5 parts of silver, whereas 100 parts of
$CSN_2H_4,HO\cdot C_6H_4\cdot CO_2\cdot CH_2Ph$ require 104·9 parts of silver.

Thiocarbamide and Acetates.

Ethyl Acetate.—This ester does not combine directly with thio-
carbamide, but when thiocarbamide ethiodide in alcoholic solu-
tion was heated with its own weight of silver acetate for three to
four hours, the solution deposited, on cooling, white, short prisms
of the required compound which decomposed at 151—152°. One
hundred parts of the substance gave 178·3 parts of silver, whereas
100 parts of $CSN_2H_4,CH_3\cdot CO_2Et,H_2O$ require 178·0 parts of
silver.

The substance therefore contains water of crystallisation.
Arndt (*loc. cit.*) prepared the acetate of benzyl-ψ-thiourea, and
showed that it also contained water of crystallisation. None of
the other salts examined possessed this property.

Benzyl Acetate.—The compound of this ester with thiocarb-
amide separated in long, flattened needles on cooling hot mixed
solutions of excess of sodium acetate with thiocarbamide, the
benzyl chloride, or either of the two forms of the benzyl sulphate.
It melts to a brown liquid at 135—136°, and its melting point and
crystal shape are unchanged by recrystallisation from acetic acid.

The compound prepared by dissolving benzyl-ψ-thiourea in
acetic acid has the same melting point and the same properties
as the one prepared by double decomposition (compare Arndt,
loc. cit.). One hundred parts of the substance gave 132·7 parts
of silver, whereas 100 parts of $CSN_2H_4,CH_3\cdot CO_2\cdot CH_2Ph,H_2O$
require 132·7 parts of silver.

Thiocarbamide and Phosphates.

Ethyl Phosphate.—The thiocarbamide compound of this ester
was obtained by heating an alcoholic solution of thiocarbamide
ethiodide with silver phosphate. The product is sparingly soluble
in alcohol and readily so in water. It crystallises from alcohol in

shining leaves which decompose at 195—196°. Its composition was checked by the silver method. Owing to the exceeding solubility of silver phosphate in ammonia, this was recovered by careful neutralisation of the ammoniacal liquors after the first precipitation. One hundred parts of the substance gave 303·3 parts of silver, whereas 100 parts of $(CSN_2H_4)_3(C_2H_5)_3PO_4$ require 305·3 parts of silver.

Benzyl Phosphate.—The product was obtained by mixing equal weights of thiocarbamide benzyl chloride and sodium ammonium phosphate in hot aqueous solution. An oil formed which presently hardened to crystals. The substance is sparingly soluble in alcohol, and when crystallised from hot water it forms small, fine needles decomposing at 191°. One hundred parts of the substance gave 216 parts of silver, whereas 100 parts of $(CSN_2H_4)_3(CH_2Ph)_3PO_4$ require 217·4 parts of silver.

An exactly similar product decomposing at 191° was obtained on mixing alcoholic solutions of benzyl-ψ-thiourea and phosphoric acid.