1.71), have been added, the metal can be quantitatively separated by a current having $N.D._{100} = 0.003$ ampere, and voltage 3. The deposition is complete in twelve to fourteen hours.

SEPARATION OF LEAD FROM MANGANESE.

Phosphate of manganese is readily soluble in an excess of phosphoric acid. With such a solution several trials showed that even strong currents produced no effect other than to develop a pink coloration, suggesting the color of weak permanganate.[1] The current was allowed to act at ordinary temperatures for seventeen hours.

When lead and manganese were in the same solution and electrolyzed with

$N.D._{100} = 0.011$ ampere,
Voltage = 3,
Dilution = 130 cc.,
Phosphoric acid = 14 cc.

manganese dioxide was thrown out on the anode, while the lead deposit gave tests for both lead and manganese.

Further work is now being done to determine whether lead can be separated from manganese in a phosphoric acid solution.

WITTENBERG COLLEGE, SPRINGFIELD, O.,
December 26, 1901.

[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(THIRD PAPER.)

BY HENRY L. WHEELER AND HENRY F. MERRIAM.

Received February 14, 1902.

IN our first paper[2] we described the results of an examination of rhodanides formed from certain alkylmonohalides and potassium thiocyanate, and showed that it is a simple matter to distinguish normal from isothiocyanates by their behavior with thiol acids.

In the case of monothiocyanates, two reactions were observed. Either a direct addition was obtained with the formation of benzoyldithiourethanes, or along with other products, an ester of thiobenzoic acid resulted. The latter reaction was observed only in the case of certain secondary and tertiary thiocyanates:

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[1] Smith: *Am. Chem. J.*, **12**, No. 5.

[2] This Journal, **23**, 283 (1901).

$$C_6H_5CO.SH + NCS.CH_2R = C_6H_5CONHCS.SCH_2R$$

and

$$C_6H_5CO.SH + NCS.CRR'R'' = C_6H_5CO.SCRR'R'' + HNCS.$$

On the other hand, isothiocyanates reacted smoothly to form benzamides and carbon disulphide:

$$C_6H_5CO.SH + SCN{-}R = C_6H_5CONHR + CS_2.$$

The work has now been extended to dirhodanides, and incidentally it has been found that not all dihalides yield dirhodanides.

The dirhodanides which have been obtained from dihalides and potassium thiocyanate have, without exception, proved to be derivatives of normal thiocyanic acid.

We have found that the action of thiobenzoic acid, in the case of 1,1-dithiocyanates, as represented by methylene thiocyanate, and of 1,2-dithiocyan derivatives, ethylene and phenylethylene (styrolrhodanide), is by no means as smooth or simple as that in the cases previously described. In fact, even when the action was moderated by heating in the presence of benzene, thick oils or varnishes were invariably formed in addition to material that could be crystallized.

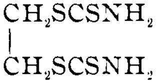
From methylene thiocyanate and thiobenzoic acid, three crystalline products were directly obtained. These, we have concluded, are methylene dithiourethane (I), benzoyldithiocarbamicmethylenethiolbenzoate (II), and the methylene derivative of benzoyldithiocarbamic acid (III):

$$\underset{\text{I.}}{CH_2(SCSNH_2)_2,} \qquad \underset{\text{II.}}{C_6H_5CO.SCH_2S.CSNHCOC_6H_5}$$

$$\underset{\text{III.}}{CH_2(SCSNHCOC_6H_5)_2.}$$

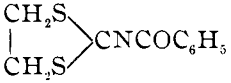
During the reaction, hydrogen cyanide and carbon disulphide were formed, the latter being due to a secondary reaction of thiocyanic acid, HNCS.

In the case of ethylene thiocyanate, we isolated two products. These were ethylene dithiocarbamate (IV), and the benzoyl-derivative of imidomethyleneethylene disulphide (V), while phenylethylene gave the corresponding imidomethylenephenylethylene disulphide (VI):



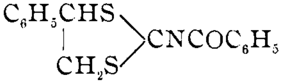
$$\begin{array}{l} CH_2SCSNH_2 \\ | \\ CH_2SCSNH_2 \end{array}$$

IV.



$$\left.\begin{array}{l} CH_2S \\ | \\ CH_2S \end{array}\right\rangle CNCOC_6H_5$$

V.

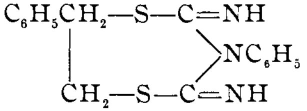


$$\left.\begin{array}{r} C_6H_5CHS \\ | \\ CH_2S \end{array}\right\rangle CNCOC_6H_5$$

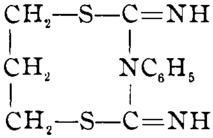
VI.

As an example of a 1,3-dithiocyanate, trimethylene rhodanide was examined. This reacted in the normal manner for a primary thiocyanate, and a bisdithiourethane was smoothly formed.

A property which appears to be unique for normal thiocyanates was observed in the case of trimethylene and phenylethylene thiocyanates. These compounds combine directly with one molecular proportion of aniline, probably to form seven- and eight-membered rings, the behavior being somewhat similar to that when pseudothiohydantoïns are formed by the action of bases on ethylphenylthiocyanacetate, etc. The compounds may be viewed as cyclopseudophenyldithiobiurets. If tautomeric forms are excluded, two isomers are possible in the case of trimethylene thiocyanate, while from phenylethylene there are three. In the latter case, the end nitrogen atoms have different positions in respect to the phenyl group (VII). Since the trimethylene compound was not obtained from phenyldithiobiuret, $C_6H_5NHCSNHCSNH_2$, trimethylene bromide, and alkali or ammonia, it appears that the following formulas best represent the structure of these compounds:



VII.



VIII.

There seems to be no mention in the literature of dithiocyanates derived from 2,3 dihalides, and it is a noteworthy fact that such dihalides of this type, as we have examined, react with alcoholic solutions of potassium thiocyanate in a peculiar manner.

In each case, with the exception of isoeugenolmethyletherdibromide, the yellow, amorphous material or mixture called pseudocyanogen sulphide[1] was formed in more or less amount. In these cases, the halides act like free bromine on potassium thiocyanate.

In addition to pseudocyanogen sulphide, 2,3-dibrombutane, $CH_3CHBr—CHBr—CH_3$. gave a yellow oil. This was found to decompose on distilling under reduced pressure. The oil was, therefore, simply washed and then dried in a vacuum. A nitrogen determination gave 12.2 per cent., while the calculated for butylene dithiocyanate is 16.2 per cent. nitrogen. These figures

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[1] Goldberg: *J. prakt. Chem.*, **64**, 166 (1901).

are given here merely to show that, in all probability, a dithiocyanate is formed in this case. Pinacone dibromide $(CH_3)_2CBr$ $CBr(CH_3)_2$ and allylbenzene dibromide, $C_6H_5CHBrCHBrCH_3$, behaved in a similar manner.

2,4-Dinitrostilbene dibromide $C_6H_3(NO_2)_2CHBrCHBrC_6H_5$, dibrommethylhydrocinnamate, $C_6H_5CHBr—CHBrCO_2CH_3$, and the dibromide from the nitrile of phenylcinnamic acid, $C_6H_5CHBr—CBr(CN)C_6H_5$, when warmed with alcoholic potassium thiocyanate gave abundant precipitates of pseudocyanogen sulphide. In these cases, the bromine was simply removed and the compounds were converted into the corresponding unsaturated products from which the bromides were prepared.

The property of forming pseudocyanogen sulphide is not confined to 2,3-dihalides, since it has been found that certain tertiary halides behave in like manner.

We have found that 1,2-dibromisobutane, $(CH_3)_2CBrCH_2Br$, gives pseudocyanogen sulphide. Monobrombenzylcyanide and bromcyanethyl acetate react in the same manner. Eugenol tetrabromide, $C_6H(OH.OCH_3Br_2)CH_2CHBrCH_2Br$, gave no pseudocyanogen sulphide, nor did isoeugenol methyl ether dibromide, $C_6H_3(OCH_3)_2CHBr—CHBrCH_3$, a 2,3-dibromide. The exceptional behavior of the latter compound shows that the formation of pseudocyanogen sulphide is not general in the case of 2,3-dibromides. That this dibromide has the structure assigned to it, and that isoeugenol methyl ether does not add bromine in the 1,4 position, *i. e.*, part in the nucleus and part in the side-chain, has been proved by us by oxidation with potassium permanganate, whereupon veratric acid and dimethoxyphenylglyoxylic acid[1] were obtained.

EXPERIMENTAL PART.

Methylene, Thiocyanate and Thiobenzoic Acid.—Nineteen grams of the thiocyanate and 35 grams of the acid were dissolved in about two volumes of benzene and the mixture was heated on the steam-bath. After five or six hours it was found that yellow crystals had separated. Ten cc. of the benzene was then distilled off and found to contain hydrogen cyanide and carbon disulphide. The insoluble material, after washing with benzene, was crystallized from glacial acetic acid, whereupon, on slowly cooling, it separated in the form of small, slender, pointed, pale

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[1] Ciamician and Silber: *Ber. d. chem. Ges.*, **23**, 1164 (1890).

yellow prisms. It melted, not sharply and with effervescence, at 166°. The yield was about 4 grams, and on analysis the following results were obtained:

	Calculated for $C_3H_6N_2S_4$.	Found. I.	II.
Nitrogen	14.1	14.2	13.9
Sulphur	64.6	65.5	...

The nitrogen determinations agree with the calculated for *methylene dithiocarbamate*, $H_2NCS.SCH_2SCSNH_2$, and this structure is confirmed by the fact that the compound dissolves in alkali and undergoes decomposition into methylene mercaptan and thiocyanic acid.

The benzene filtrate from the above was evaporated in a vacuum, and the thick oil thus obtained was stirred with ether containing a little alcohol. The solid material, thus produced, was crystallized from alcohol and benzene, whereupon yellow elongated plates melting at 138°–139° were obtained. The yield was about 4 to 5 grams, and analysis gave the following results:

	Calculated for $C_{16}H_{13}O_2NS_3$.	Found. I.	II.
Nitrogen	4.03	4.33	4.56
Sulphur	27.66	28.46	27.68

Since the material is soluble in alkali with decomposition and has a yellow color, the assumption that it contains a dithiourethane grouping seems justified. In view of the above analyses, this would then permit of the following structural formula:

$$C_6H_5CONHCS.SCH_2SCOC_6H_5.$$

The substance is, therefore, a *methylene ester of thiobenzoic and benzoyldithiocarbamic acids.*

The ether solution from the above was shaken with alkali and precipitated with carbon dioxide. The resulting oily solid was crystallized from benzene and ligroïn, whereupon bright yellow crystals melting at 130°–131° were obtained. The yield, owing to decomposition by alkali, was less than a gram and a nitrogen determination gave:

	Calculated for $C_{17}H_{14}O_2N_2S_4$.	Found.
Nitrogen	6.89	7.14

This corresponds to the calculated for, the methylene ester of benzoyldithiocarbamic acid, $(C_6H_5CONHCS.S)_2CH_2$.

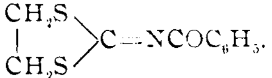
Methylene Thiolbenzoate, $(C_6H_5COS)_2CH_2$.—The possibility suggested itself that the solubility of the above compounds in alkali might be due to the presence of two negative groups attached to methylene and not to a dithiourethane group. In order to decide this point, we have prepared the methylene ester of thiolbenzoic acid by treating potassium thiolbenzoate with methylene iodide. The mixture in alcoholic solution reacted at once, and the product formed long, snow-white needles melting at 120°. It is insoluble in, and remains unaffected by dilute alkali. A sulphur determination gave:

	$C_{15}H_{12}O_2S_2$.	Found.
Sulphur	22.22	22.31

Ethylene Thiocyanate and Thiobenzoic Acid.—Thirty grams of ethylene thiocyanate were heated on the steam-bath, for six to eight hours with 56 grams of thiobenzoic acid, diluted with 125 cc. of benzene, whereupon it was found that a crystalline precipitate had separated. About 10 cc. of the benzene were then distilled off, and this gave the reactions for carbon disulphide and hydrogen cyanide. The insoluble material was crystallized from glacial acetic acid and, on slowly cooling, it came down in aggregations of flattened prisms, of a very pale cream color. Thirteen grams of this material were obtained melting, not sharply, at 188°- 89°. The analytical results were as follows:

	Calculated for $C_4H_8N_2S_4$.	Found.
Carbon	22.6	22.2
Hydrogen	3.8	3.6
Nitrogen	13.2	13.7

Since the material, on treating with alkali, is smoothly decomposed into ethylene mercaptan and thiocyanic acid it follows that the substance is *ethylene dithiocarbamate*, $H_2NCS.SCH_2CH_2S.CS-NH_2$. The second product was obtained by partly evaporating the benzene from the above filtrate, whereupon beautiful, colorless prismatic tables separated. These were crystallized from alcohol and benzene, and melted then at 80°-81°. The yield was 20 grams and a nitrogen determination agreed with the calculated for *benzoylimidomethyleneethylene disulphide*,



$$\begin{array}{l} CH_2S \\ \,| \\ CH_2S \end{array}\!\!>C=NCOC_6H_5.$$

	Calculated for $C_{10}H_8ONS_2$.	Found.
Nitrogen	6.27	6.24

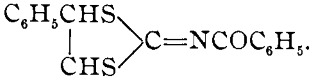
The structure of this compound was proved by preparing it from the so-called rhodanethylsulfin hydrochloride[1] and benzoyl chloride by means of the Schotten-Baumann reaction. The two products were identical in every respect. This excludes the possibility that the compound prepared by Miolati, melting at 141°–143°, is, as he supposed, benzoylimidomethyleneethylene disulphide.

When the material was treated with aqueous alkali it remained insoluble and apparently unaffected. With strong alcoholic potash it readily dissolved and was decomposed into ethylene mercaptan, (ethylene tetrasulphide), thiocyanic acid, benzoic acid, and probably some ethylbenzoate.

Chlorethylene Thiocyanate and Thiobenzoic Acid.—When these substances were heated together on the steam-bath, in benzene solution, a white solid separated. This was crystallized from alcohol and ether. Colorless, thin, square plates were thus obtained which blackened about 200°, and melted with decomposition about 212°. This material is soluble in water and the solution gives a crystalline compound with stannous chloride. Its properties and the following nitrogen determination show that the substance is *imidomethyleneethylene disulphide hydrochloride*.

	Calculated for $C_3H_6NClS_2$.	Found.
Nitrogen	9.00	9.02

Styrol thiocyanate and thiobenzoic acid, in molecular quantities, were heated in benzene for a number of hours. The presence of carbon disulphide was then detected and, on evaporating some of the benzene, solid material was obtained. This crystallized from alcohol in thin plates and melted at 135°. The following analysis shows that this compound is *benzoylimidomethylenephenylethylene disulphide*,



$$\left.\begin{array}{l} C_6H_5CHS \\ \quad | \\ \;CHS \end{array}\right\rangle C{=}NCOC_6H_5.$$

	Calculated for $C_{16}H_{13}ONS_2$.	Found.
Carbon	64.21	64.62
Hydrogen	4.34	4.85
Sulphur	21.40	22.27
Nitrogen	4.68	4.65

When this was warmed with alcoholic potash it decomposed,

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[1] Miolati : *Ann. Chem.* (Liebig), **262**, 61.

giving benzoic and thiocyanic acids. A colorless transparent varnish was also obtained but not further examined.

Trimethylene Thiocyanate and Thiobenzoic Acid.—Thirty grams of thiobenzoic acid and 17 grams of trimethylene thiocyanate were diluted with 50 cc. of benzene and heated on the steam-bath for ten hours. Ten cc. of the benzene were then distilled off, and the fact that carbon disulphide and hydrogen cyanide were present was established. On allowing the reaction product to cool, a yellow crystalline mass was obtained. This was crystallized from benzene and ligroïn, whereupon it came down in long slender yellow prisms melting at 154°–155°. The yield was about 30 grams. It was soluble in aqueous alkali and was precipitated with more or less decomposition by carbon dioxide. A nitrogen determination gave:

	Calculated for $C_{19}H_{18}O_2N_2S_4$.	Found.
Nitrogen	6.45	6.39

This is, therefore, *trimethylenebenzoyldithiocarbamate*, $C_6H_5CONHCS.SCH_2CH_2CH_2S.CSNHCOC_6H_5$.

Trimethylene Thiocyanate and Aniline.—Five grams of trimethylene thiocyanate were heated with three grams of aniline, on the steam-bath, for twenty-four hours. The product was diluted slightly with alcohol, and then ether was added until no further precipitate was formed. On crystallizing from alcohol and ether, colorless transparent tables or prisms were obtained. These sintered at about 168° and melted at 173°. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}N_3S_2$.	Found.
Nitrogen	16.73	16.72

This result agrees with the calculated for, a *pseudomethylenephenyldithiobiuret.* Attempts to prepare this from phenyldithiobiuret, $C_6H_5NHCSNHCSNH_2$, and alkali or sodium ethylate and trimethylene bromide gave only a yellow, extremely sticky varnish from which nothing was obtained in crystalline form. When aqueous ammonia was employed instead of alkali, a method used with success by Tursini[1] for the preparation of an ethyl derivative, the result was similar, except that in one case a very small amount of well-developed crystals were obtained, melting sharply at 109°.

Styrol Thiocyanate and Aniline, when heated on the water-bath

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[1] *Ber. d. chem. Ges.*, 17, 585 (1884).

in molecular proportions, gave a gummy mass. This was dissolved in a little alcohol, and ether added until no more solid was precipitated. On crystallizing from a mixture of alcohol and ether, colorless plates, melting at 205°, were obtained. The analysis showed that this material is a *pseudophenylethylenephenyldithiobiuret*:

	Calculated for $C_{16}H_{15}N_3S_2$.	Found.
Nitrogen	13.41	13.32
Sulphur	20.45	21.07

Metaxylylene Thiocyanate, $C_6H_4(CH_2SCN)_2$, from metaxylylene bromide and potassium thiocyanate, forms colorless prisms, when crystallized from alcohol, melting at 160°–161°. A nitrogen determination gave:

	Calculated for $C_{10}H_8N_2S_2$.	Found.
Nitrogen	12.72	12.74

The crude product of the action of thiobenzoic acid on this substance was a varnish from which nothing solid was obtained. Thiobenzoic acid both with 1,2-propylene dithiocyanate, and 1,2,3-tripropylene thiocyanate also gave thick oils which were not further examined.

Benzal chloride and potassium thiocyanate, in alcoholic solution, gave a mixture of benzaldehyde and ethyl thiocyanate.

Methyldibromhydrocinnamate and Potassium Thiocyanate.—In the introduction it was mentioned that certain 2,3-dibromides react with potassium thiocyanate with the removal of bromine and formation of unsaturated compounds along with pseudocyanogensulphide. This peculiar reaction is well illustrated by the behavior of the dibromide obtained by adding bromine to methylcinnamate. Fifty grams of the dibromide were heated for eight hours with 40 grams of potassium thiocyanate, and 60 cc. of alcohol. In fact on simply mixing in the cold a yellow precipitate formed at once. This was extracted with water, alcohol, and carbon disulphide and then a nitrogen determination gave 24.65 per cent., while the analyses of various pseudocyanogen sulphide preparations, made by Goldberg, gave 22 to 27 per cent. nitrogen. On the other hand isopersulphocyanic acid contains 18.6 per cent. nitrogen.

The alcoholic solution was evaporated and the residue washed and taken up in petroleum ether, which left a small amount of substance undissolved. On evaporating, crystals separated melting at 33°, the melting-point of methyl cinnamate. This product was then distilled, and the boiling-point also agreed with that of methyl cinnamate. The yield after all this treatment was found to be 15 grams or 60 per cent. of the calculated.

The *dibromide from 2,4-dinitrostilbene* (15 grams), when boiled with alcoholic potassium thiocyanate, gave 6 grams of pure 2,4-dinitrostilbene or 64 per cent. of the calculated.

The *dibromide from the nitrile of phenyl cinnamic acid* (60 grams) gave 24 grams of the unsaturated product or 70 per cent. of the calculated. These yields do not represent the total amount of unsaturated material formed, since no special effort was made to obtain the entire amounts.

NEW HAVEN, CONN.,
February 10, 1902.

LIQUID MIXTURES OF MINIMUM BOILING-POINT.

BY CLIFFORD D. HOLLEY.

Received January 21, 1902.

IN 1899, Dr. Garnett Ryland[1] reported the results of an investigation of 80 pairs of the more common liquids. He found that 45 furnished mixtures which distilled in the same proportions with a constant boiling-point below the boiling-points of the constituent liquids; one which presented no relative depression or elevation of the boiling-point; and 3 which were of an uncertain character. During the same year, E. F. Thayer[2] and J. K. Haywood[3] investigated several of the same mixtures, but instead of following the method of Ryland, and determining the minimum-point by repeated distillations, they determined the boiling-points of several mixtures of the liquid constituents, and plotted the resulting boiling-point curve. From a comparison of the two methods it is seen that the proportion in which two liquids give a minimum point on the boiling-point curve is the same in which they distil with a constant boiling-point which lies below that of either liquid constituent, and the boiling-points are the same in both cases. But little having been done along this line during the past two years, it seemed desirable to add to our knowledge of such phenomena, and continue the investigations of such systems as would be likely to furnish mixtures of minimum boiling-point.

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[1] *Am. Chem. J.*, **22**, No. 5.

[2] *Jour. Phys. Chem.*, **2**, 382; **3**, 32.

[3] *Ibid.*, **2**, 317.