

XI. *o*-Sulphobenzoic acid and acetonitril yield a compound isomeric with saccharin which may be the unsymmetrical *o*-sulphobenzimid.

XII. By varying the conditions three of the four possible imids of mellitic acid were produced by heating this acid with acetonitril. The *p*-euchronic acid is a new compound; *o*-euchronic acid and paramid were known but have resulted also by our nitril reaction. It has been shown that aluminum amalgam can be used to give the euchron test.

To sum up then briefly, I believe I have made three new imids; *viz.*, malonimid, *p*-euchronic acid, and an imid of sulphobenzoic acid. The known imids of succinic, plthalic, homoplthalic, diphenic, and mellitic acids have been made by a new method. The conclusions of Colby and Dodge, stated in the introduction, have been confirmed and the first method used by Miller and Seldner for producing fatty imids has been found applicable for producing aromatic imids. The widest general conclusion to be drawn from the work of these earlier investigators of the action of nitrils upon acids and from my own work is that when acids and nitrils are heated together they tend to form disubstituted ammonia compounds, secondary amids from monobasic acids and nitrils, imids from dibasic acids and nitrils.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 2.]

THE ACTION OF METALLIC THIOCYANATES UPON ALIPHATIC CHLORHYDRINS.¹

BY WILBER DWIGHT ENGLE.

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THE alcohols form the most important class of organic compounds which have no representatives containing the thiocyan group. It would seem that such compounds would be produced by the double decomposition between alcohols having one or more atoms of hydrogen displaced by halogen and a metallic thiocyanate, and it was with this expectation that the following experiments were undertaken. In all cases tried, a reaction occurred as was shown by the separation of the halogen

¹ Read at the meeting of the New York Section, May 6, 1898.

salt. The thiocyanates formed, however, seem to be very unstable, easily changing to resinous substances, and much difficulty was experienced in separating and purifying them. In some cases it was found impossible.

The particular thiocyan alcohols, whose preparation was undertaken, are those derived from propane; namely, α -thio-

cyanhydrin, $\begin{array}{c} \text{CH}_2\text{SCN} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array}$, α, β -dithiocyanhydrin, $\begin{array}{c} \text{CH}_2\text{SCN} \\ | \\ \text{CHSCN} \\ | \\ \text{CH}_2\text{OH} \end{array}$, and α, γ -

dithiocyanhydrin, $\begin{array}{c} \text{CH}_2\text{SCN} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{SCN} \end{array}$. As being of a somewhat similar

nature, the epithiocyanhydrin, $\begin{array}{c} \text{CH}_2\text{SCN} \\ | \\ \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{O} \end{array}$, the α -acetodithiocyan-

hydrin, $\begin{array}{c} \text{CH}_2\text{SCN} \\ | \\ \text{CHSCN} \\ | \\ \text{CH}_2\text{OOC}_2\text{H}_5 \end{array}$, and β -acetodithiocyanhydrin, $\begin{array}{c} \text{CH}_2\text{SCN} \\ | \\ \text{CHOOC}_2\text{H}_5 \\ | \\ \text{CH}_2\text{SCN} \end{array}$, were prepared.

α -THIOCYANHYDRIN.

For the attempted preparation of α -thiocyanhydrin the corresponding α -chloropropylene glycol or monochlorhydrin, $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array}$, was used.

A mixture of fourteen grams of monochlorhydrin and thirteen grams of potassium thiocyanate, with ninety-five per cent. alcohol for solution, were heated on the water-bath with a return condenser. A crystalline precipitate of potassium chloride gradually formed. After four days of heating, four grams of potassium chloride in place of ten grams, theoretical quantity,

had separated. The filtrate from the potassium chloride was again heated. Only a little more of the chloride separated but there formed a considerable amount of a white resinous substance, some of which was removed from the flask and examined. Washed with hot water and alcohol it is a white or light yellow, brittle, odorless substance. It is insoluble in ordinary organic solvents, including water, alcohol, ether, benzene, chloroform, carbon disulphide, benzine, kerosene, gasolene, and toluene. It is unaffected by hydrochloric, acetic, and sulphuric acids or by ammonium hydroxide or strong aqueous potassium hydroxide. Bromine decomposes it with the production of a tar-like substance. Strong nitric acid oxidizes it, producing sulphuric and oxalic acids. This is an interesting reaction since it shows that the sulphur is much less closely bound to the radical than in the case of thiocyanates, mercaptans, and sulphides which, by oxidation with nitric acid, yield sulphonic acid, sulphoxids, and similar compounds.

That this resinous substance is not a thiocyanate is shown by the following facts: It does not give a sulphide with potassium hydroxide. It does not give a mercaptan with zinc and sulphuric acid. It does not give a sulphide and potassium thiocyanate with potassium sulphide. It does not give a sulphonic acid by the oxidation with nitric acid. Its solubilities are not those of known thiocyanates.

An analysis of the substance carefully washed with water and alcohol and dried to a constant weight, gave the following percentages, from which it is impossible to calculate any simple formula:

	I.	II.	III.	IV	V.	Average.
Carbon	40.127	40.163	40.145
Hydrogen	5.185	5.15	5.168
Nitrogen	7.531	7.590	7.560
Sulphur	27.281	27.281
Oxygen.....	19.846

These percentages indicate that a secondary reaction has produced a complex condensation product. The absence of any solvent prevented any attempt to crystallize this compound. A flask, containing a mixture of potassium thiocyanate and monochlorhydrin, after heating was set aside. After several weeks it

was examined and well-formed crystals were found. The properties of these crystals were identical with those of the substance just described.

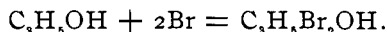
Besides the insoluble white substance there was also found, in the alcoholic filtrate from the potassium thiocyanate and monochlorhydrin, a very small amount of oil having the garlic odor characteristic of the organic thiocyanates. This oily liquid is extremely unstable. Any attempt to purify it changes it to the insoluble white substance. Apparently the monothiocyanate is first formed by the reaction, and by some secondary condensation the insoluble compound results.

The reaction between potassium thiocyanate and monochlorhydrin was also tried at higher temperatures. Sealed tubes containing these two compounds in the ratio of their molecular weights, with alcohol as a solvent, were heated to different temperatures. Below 100° the action was very slow. From 110° to 115° the reaction was complete in six hours. At 120° and above there was much decomposition. In all cases the products are the same: the insoluble white compound and a trace of what was considered the monothiocyanhydrin. It was impossible to secure this in amount sufficient for further study.

α, β -DITHIOCYANHYDRIN.

The α, β -dibromhydrin, $\begin{array}{c} \text{CH}_2\text{Br} \\ | \\ \text{CHBr} \\ | \\ \text{CH}_2\text{OH} \end{array}$, to be used in the prepara-

tion of α, β -dithiocyanhydrin, was obtained by the direct addition of bromine to allyl alcohol,

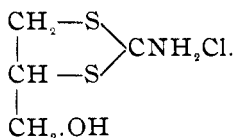


The product was purified by distillation *in vacuo*.

An alcoholic solution of forty grams of this dibromhydrin and thirty-seven grams of potassium thiocyanate were heated on the water-bath for six days. Somewhat more than half the theoretical quantity of potassium bromide separated. As there were signs of decomposition the heating was stopped. By evaporation of the alcohol, washing with water, and collecting with ether, about ten cc. of a dark-colored liquid was obtained.

Heated with potassium sulphide solution it gave potassium thiocyanate easily identified by the ferric chloride test. On heating or attempting to distil with steam it was resinified.

The reaction was next tried in sealed tubes. The tubes were charged with potassium thiocyanate and dibromhydrin, in the ratio of two molecules of the former to one of the latter. Alcohol was added as a solvent. Between 110° and 115° the reaction was complete in about eight hours. At higher temperatures there was much decomposition. In all cases there was a tendency to produce an amorphous substance similar to that from the monochlorhydrin. The contents of the tube were treated with warm alcohol. The alcoholic solution filtered from the potassium bromide was slowly evaporated to a small bulk and carefully washed with water to remove any unchanged potassium thiocyanate. There was left an oily liquid which could be further purified by solution in ether. This treatment does not remove all the unchanged dibromhydrin. The compound decomposes on heating, hence cannot be distilled. The difficulty of securing a pure sample prevented analysis. That the liquid is dithiocyanhydrin is shown by the fact that it gives potassium thiocyanate on heating with potassium sulphide, and the yield of potassium bromide is nearly equal to the theoretical. Additional proof is found in the preparation from it of imino-methanepropylalcohol disulphide hydrochloride of the formula



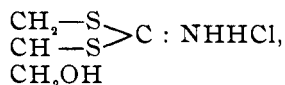
A similar reaction is found in the case of methylene dithiocyanate and propylene dithiocyanate. Both compounds have adjacent thiocyan groups as in the case of the compound under discussion and both give imino compounds similar to that above.¹

About ten cc. of dithiocyanhydrin was poured into fifty cc. of water and a few grams of granulated tin added. The mixture was carefully heated on the water-bath and hydrochloric acid added. In the course of an hour's boiling the oily dithiocyan-

¹ Hageberg: *Ber. d. chem. Ges.*, 23, 1083.

hydrin disappeared. Upon evaporation to a small bulk crystals appeared. When the liquid was left to spontaneous evaporation large octahedrons were obtained of iminomethanepropylalcohol disulphide tin hydrochloride.

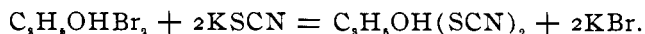
The compound is not stable in solution as the tin (stannous) is oxidized at the expense of the rest of the compound producing stannic chloride and a resinous substance. It was found advisable to precipitate the tin immediately after the dithiocyanhydrin had gone into solution, with hydrosulphuric acid, leaving the hydrochloric salt of iminomethanepropylalcohol disulphide in solution. The solution, filtered from the tin sulphide, was evaporated to dryness on the water-bath. The residue was dissolved in alcohol, filtered, evaporated to a small bulk, and allowed to crystallize. Transparent, colorless, well-formed, tetragonal crystals separated. A determination of the chlorine gave 20.21 per cent., while the formula



requires 20.08 per cent.

This iminomethanepropylalcohol disulphide hydrochloride is very easily soluble in water, somewhat soluble in alcohol, and insoluble in ether and chloroform.

The preparation of this compound taken with the reactions with potassium sulphide and the amount of potassium bromide separated, identify the dithiocyanhydrin. The reaction for its preparation is



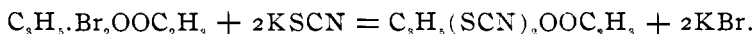
In its physical properties it closely resembles the propylene-dithiocyanate. Both are liquids of garlic-like odor, insoluble in water, but soluble in alcohol and ether. Both are decomposed by heat and resinified by acids and alkalis. By nitric acid both are oxidized, producing sulphuric acid and, in the case of dithiocyanhydrin, oxalic acid is also formed. The action of the nitric acid seems to be to first produce a substance similar to the amorphous compound from the monochlorhydrin which is then oxidized as above.

α -ACETODITHIOCYANHYDRIN.

Acetodibromhydrin, or dibrompropyl acetate, is prepared by the action of acetic anhydride on the α, β -dibrompropyl alcohol.¹ It was washed with water and a dilute carbonate solution, dried and rectified under diminished pressure.

A sealed tube containing seventeen grams of acetodibromhydrin, thirteen grams of potassium thiocyanate, and ten cc. of alcohol, was kept at 120° for four hours. On opening, nearly the theoretical quantity of potassium bromide was found. The alcoholic filtrate from the potassium bromide was poured into water and about fifteen cc. of a heavy liquid, insoluble in the water, separated. This was washed several times with water to free it from traces of potassium bromide and thiocyanate. It was then dissolved in ether to free it from decomposition-products. On evaporation there was left a clear, red-colored liquid, giving with potassium sulphide, potassium thiocyanate. This compound, like the corresponding alcohol, cannot be distilled and is easily decomposed by most reagents. With tin and hydrochloric acid it gave reactions similar to those with the alcohol.

The compound was not analyzed but the reactions show it to be acetodithiocyanhydrin. The reaction is :

 α, γ -DITHIOCYANHYDRIN.

The dichlorisopropyl alcohol or dichlorhydrin was prepared by treating anhydrous glycerine with chloride of sulphur at 100°. The product was fractionally distilled and the fraction collected between 176° and 178° was used in these experiments.

A mixture of twelve and five-tenths grams of the dichlorhydrin and nineteen grams of potassium thiocyanate in alcoholic solution was heated on the water-bath for four days. About six grams of potassium chloride had separated, less than half the theoretical amount. The contents of the flask had the odor of the thiocyanates. In addition to the potassium chloride there had also separated a spongy mass, of a yellow color, and in appearance not unlike the insoluble compound obtained from the monochlorhydrin. On examination it showed the same properties. It was insoluble in the organic solvents. It was unaffected by acids or alkalis.

¹ Aschan : *Ber. d. chem. Ges.*, 23, 1827.

lies. Reducing agents do not change it; strong nitric acid oxidizes it to sulphuric and oxalic acids. It is apparently a condensation-product similar to that obtained in case of monochlorhydrin.

In the alcoholic filtrate from the above compound was found a very small amount of a liquid, insoluble in water, having the characteristic odor of the thiocyanates. It may have been either the dithiocyanhydrin sought or the chlorthiocyanhydrin. Its insolubility in water would distinguish it from the dichlorhydrin. It was unstable and attempts to purify it sufficiently to test resulted in its decomposition.

This reaction was also tried in sealed tubes. A tube, heated to 130° for six hours, contained much unchanged potassium thiocyanate. Considerable of the spongy substance was found and a trace of the oily compound mentioned above. A tube heated to 175° for two hours gave the best results. The action was nearly complete. Less of the amorphous substance was formed. At higher temperatures there was much decomposition and pressure produced. In all cases the same results were obtained. I was unable to separate and purify a compound containing the thiocyan group.

β -ACETO- α , γ -DITHIOCYANHYDRIN.

The corresponding acetic ester, the dichlorisopropylacetate, was also tried. The ester was prepared according to the method of Berthelot and Luca.¹ Anhydrous glycerine was treated with acetyl chloride and the product purified by fractional distillation.

A sealed tube containing dichlorpropyl acetate and potassium thiocyanate in the ratio of one molecule of the former to two of the latter, with alcohol for solution, was heated to 130° for six hours. The action was incomplete and the tube was heated to 180° . There was some decomposition. A large amount of amorphous substance resembling those already described was present. A small amount of oil was also found as in the case of the corresponding alcohol. Here, again, apparently the thiocyanate is formed but suffers secondary decomposition resulting in the insoluble amorphous substance.

¹ *Ann. chim. phys.* [3], 52, 459.

EPITHIOCYANHYDRIN.

Epithiocyanhydrin proved much easier in preparation and more interesting in reactions. For its preparation both epichlor-

hydrin, $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CH} \\ | \\ \text{CH}_2 \end{array} > \text{O}$, and epibromhydrin were used. Epichlorhy-

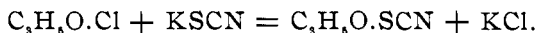
drin was obtained by the action of a strong aqueous solution of potassium hydroxide on dichlorisopropyl alcohol. The epibromhydrin was obtained in a similar manner from α, β -dibrompropyl alcohol. Both compounds were purified by distillation.

There is no reaction between epibrom- or epichlorhydrin and potassium thiocyanate at ordinary temperatures. Mixtures of these substances have stood for several days without reaction. At 40° to 50° , however, the action goes on nicely. The theoretical amount of potassium halogen salt is separated in a few hours. At higher temperatures the action is violent; at 100° it is very rapid and there is much decomposition. The purification of the epithiocyanate is somewhat difficult as heat decomposes it. The alcoholic solution, filtered from the separated potassium chloride or bromide is evaporated to a small bulk, keeping the temperature below 50° . Water is then added to wash out the excess of potassium thiocyanate. A thick insoluble liquid separates; this is the epithiocyanhydrin holding in solution much decomposition matter. It can be freed from this, after washing with water, by solution in ether. The evaporation of the ether leaves the epithiocyanhydrin as a clear liquid of a dark red color, and having a disagreeable garlic odor. It is insoluble in water but soluble in alcohol, ether, and chloroform. It cannot be distilled. On the skin it produces a burning or smarting sensation. With potassium sulphide it gives potassium thiocyanate. With nitric acid it behaves like the compounds already described: the acid first resinifies and then oxidizes to sulphuric and oxalic acids.

A determination of the nitrogen confirms the qualitative results:

	Per cent.
Nitrogen found	11.914
Necessary for formula, $\begin{matrix} \text{CH}_2\text{SCN} \\ \text{CH} \\ \text{CH}_2 > \text{O} \end{matrix}$	12.17

The reaction is :



ACTION OF HYDROSULPHURIC ACID ON EPITHIOCYANHYDRIN.

Dry hydrosulphuric acid has an interesting reaction on the thiocyanates of the marsh-gas series. It forms the esters of dithiocarbamic acid which are readily crystallizable. About ten cc. of epithiocyanhydrin was treated with hydrogen sulphide under a pressure of one atmosphere and eight inches of mercury. The experiment was tried both at ordinary temperatures and at 100°. In both cases the result was the same. No carbamic ester was formed, but thick sirupy liquid of a very disagreeable odor, insoluble in water and sparingly soluble in alcohol, carbon disulphide, and chloroform. Its alcoholic solution was precipitated by soluble lead, mercury, silver, and copper salts, but was unaffected by mercuric or lead oxids. These reactions indicate the formation of a sulphide.

EPIHYDRINDIMETHYLSULPHIN IODIDE.

A reaction similar to that used by Cahours in the preparation of trimethylsulphin iodide was tried. About five cc. of epithiocyanhydrin with fifteen cc. of methyl iodide (an excess) were sealed in a tube and kept at 100° for six hours. On examination crystals were found in the tube. A similar mixture was allowed to stand for several days at the ordinary temperature, and crystals also separated in this case. The crystals were clear, colorless, monoclinic plates. They were purified by recrystallizing from water and washing with alcohol. They gave good qualitative tests for both sulphur and iodine. The iodine was determined both by titration, with a standard silver nitrate solution, and by weighing the precipitated silver iodide :

	Per cent.
Iodine found	51.392
Necessary for the formula, $\begin{matrix} \text{CH}_2(\text{CH}_3)_2\text{SI} \\ \text{CH} \\ \text{CH}_2 > \text{O} \end{matrix}$	51.430

The crystals decompose without melting between 195° to 200°.

The small amount of material prevented farther experiments.

The compounds most closely related to epithiocyanhydrin are the thiocyanacetone and thiocyanpropyl aldehyde. It resembles both in physical properties and in its unstable character.

The thiocyanacetone was reported by Tscherniac in 1883. It is an oil of very disagreeable odor and easily decomposed by heat.

The β -thiocyanpropyl aldehyde was prepared by Chautard.² It is a liquid of fetid odor, is decomposed by heat, and is easily resinified by acids and alkalies.

CONCLUSION.

The results of the experiments may be summarized as follows :

The monochlorhydrin, the α,γ -dichlorhydrin, and the acetodichlorhydrin, form corresponding thiocyanates which are very unstable and immediately change to complex secondary compounds.

The α,β -dibromhydrin and its acetic ester form dithiocyanates which are somewhat more stable and can be separated and purified. Treated with tin and hydrochloric acid they give double chlorides of tin and iminomethanepropylalcohol disulphide.

The epichlorhydrin forms the epithiocyanhydrin readily. It is a liquid of garlic odor, insoluble in water, but soluble in alcohol and ether. It cannot be distilled. With dry hydrosulphuric acid it forms epihydrin sulphide rather than a dithiocarbamic ester. With methyl iodide it forms epihydrindimethylsulphine iodide.

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LUBRICANTS FOR GLASS STOP-COCKS.

BY FRANCIS C. PHILLIPS.

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THE success of modern chemical research work depends frequently upon the maintenance in position for considerable periods of complex forms of apparatus in which glass stop-

¹ Tscherniac: *Ber. d. chem. Ges.*, 16, 349.

² Chautard: *Ann. chim. phys.* [6], 16, 197.