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ON SOME ADDITION-REACTIONS OF THIO ACIDS.

BY HENRY L. WHEELER.

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The appearance of an article by A. Eibner[1] on a halogen-substituted aminomercaptan, in which some addition-reactions of thioacetic acid to compounds containing the unsaturated grouping C=N are described, has induced the writer to publish an account of some experiments which have been done here along similar lines. In the article referred to, it is shown that thioacetic acid acts on trichlorethylidendiphenamine,

$$CCl_3CH(NHC_6H_5)_2,$$

with the formation of acetanilide, hydrogen sulphide and a compound which is said to have the properties of acetylphenyl-α-aminotrichlorethyl mercaptan. It is also stated that benzylidenaniline unites with thioacetic acid to form the addition-product, $C_6H_5CH(SH)NC_6H_5.COCH_3$.

It was shown by Wheeler and Barnes[2] that the phenylhydrazone of diethylthiocarbonic ester, $C_6H_5NH—N=C(SC_2H_5)OC_2H_5$, reacts with thiobenzoic acid, yielding ethylthiolbenzoate, $C_6H_5CO.SC_2H_5$, and phenylthiolcarbazinic ethyl ester,

$$C_6H_5NH—NHCO.SC_2H_5.$$

This reaction evidently involves a sort of addition different from

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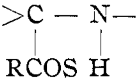
[1] *Ber. d. chem. Ges.*, **34**, 656 (1901).

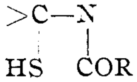
[2] *Am. Chem. J.*, **24**, 62 (1900).

that described by Eibner. These two modes of addition can be represented as follows :



$$\begin{array}{ll} >C - & N- \\ | & | \\ RCOS & H \end{array}$$

I.



$$\begin{array}{ll} >C- & N \\ | & | \\ HS & COR \end{array}$$

II.

The ease with which Eibner's addition-products give acetanilide indicates that the addition takes place according to (II). The possibility, however, that they may have the structure $RCH(SCOCH_3)NHC_6H_5$, and that the addition takes place according to (I) is not excluded by the evidence thus far produced.

Chanlaroff[1] found that thioacetic acid combines with the $-C\equiv N$ group in thiocyanates; and in papers from this laboratory it has been proved that the addition takes place according to (II),

$$CH_3COSH + RSCN = CH_3CONHSCSR.$$

It has been shown by Wheeler and Merriam[2] that isothiocyanates, $RN{=}CS$, in general, react readily and quantitatively with thioacetic and thiobenzoic acid, even in boiling benzene, yielding substituted amides and carbon disulphide.

The final result of the action in this case is in all probability preceded by the formation of an unstable addition-product, according to (II), which decomposes as follows :

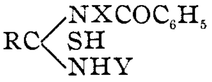
$$C_6H_5N{=}CS + HS.COC_6H_5 = C_6H_5CO(C_6H_5N\boxed{CSS}H.$$

This is confirmed by the fact that thiobenzoic acid and phenyl isocyanate give the addition-product, $C_6H_5CO(C_6H_5)NCOSH$, which can easily be isolated. It may be crystallized from alcohol, and is stable at temperatures below 97°.

Thiobenzoic acid unites with amidines, and, as might be expected, quite stable addition-products or salts result. Whether the addition takes place according to the first method, giving esters of thiolbenzoic acid (III), or according to the second, with the formation of diamidomercaptan derivatives (IV), can not be definitely decided at present.

$$RC\begin{cases} NHX \\ SCOC_6H_5 \\ NHY \end{cases}$$

III.



$$RC\begin{cases} NXCOC_6H_5 \\ SH \\ NHY \end{cases}$$

IV.

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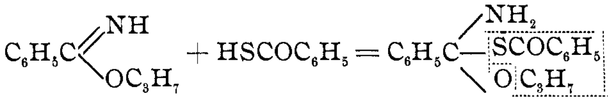
[1] *Ber. d. chem. Ges.*, **15**, 1987 (1882).

[2] This Journal, **23**, 283.

The evidence thus far obtained appears to favor the view that the addition takes place as represented by (III). Such a compound would not separate hydrogen sulphide without decomposition, while if the products have the structure (IV), or are simple pentavalent nitrogen derivatives, they might easily be desulphurized.

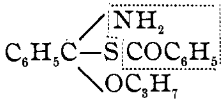
The addition-product in the case of diphenylformamidine decomposes on fusion, with evolution of little more than traces of hydrogen sulphide, into thioformanilide and benzanilide. Alkalies remove thiobenzoic acid and not hydrogen sulphide.

The above view receives further support from the behavior of imidoesters. Thiobenzoic acid readily reacts with imidoesters, and the products are a thiol ester and an amide. The reaction evidently takes place by addition to the double union according to I, as in the case of the above-mentioned phenylhydrazone. It may be represented as follows:



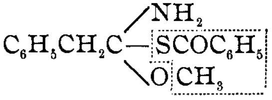
$$C_6H_5C\begin{array}{l}\diagup\!\!\diagup NH\\ \diagdown OC_3H_7\end{array} + HSCOC_6H_5 = C_6H_5C\begin{array}{l}\diagup NH_2\\ - SCOC_6H_5\\ \diagdown OC_3H_7\end{array}$$

That the decomposition proceeds in the above manner, and not as represented by (V), is shown by the behavior of phenylacetimidomethyl ester towards thiobenzoic acid (VI):



$$C_6H_5C\begin{array}{l}\diagup NH_2\\ - S\,COC_6H_5\\ \diagdown OC_3H_7\end{array}$$

V.



$$C_6H_5CH_2C\begin{array}{l}\diagup NH_2\\ - SCOC_6H_5\\ \diagdown OCH_3\end{array}$$

VI.

The amide obtained in the latter case is phenyl acetamide, instead of benzamide, and consequently the esters formed in these reactions are thiol and not thion derivatives.

An analogous reaction takes place in the case of acylpseudothioureas. Benzoylpseudobenzylphenylthiourea gave benzoylphenylthiourea, when heated on the water-bath with thiobenzoic acid:

$$C_6H_5CON{=}C(SCH_2C_6H_5)NHC_6H_5 \rightarrow C_6H_5CONHCSNHC_6H_5.$$

Thiobenzoic acid readily reacts with acetonephenyl hydrazone, on the steam-bath in an entirely different manner from that of benzoyl chloride[1], and the mixture shows very little loss in weight. *s*–Monobenzoylphenylhydrazine separates in quantity, while only a small amount of dibenzoylphenylhydrazine is

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[1] Freer: *Am. Chem. J.*, **21**, 18 (1899).

obtained. In addition to this, considerable neutral oil results which cannot be purified by distillation under diminished pressure. The thio acid acts in this case, therefore, according to (II).

The action of thiobenzoic acid on ureas has been examined in the case of diphenylthiourea. It has been shown by Deninger[1] that, in the presence of pyridine, benzoyl chloride and this urea give a dibenzoyl derivative, while, according to Dains,[2] to produce a reaction without pyridine it is necessary to heat the materials to a high temperature. At 150° phenyl mustard oil and benzanilide are quantitatively obtained.

I have found that thiobenzoic acid acts on this urea in boiling benzene, and that the action is similar to that of benzoyl chloride, although the products obtained are benzanilide, carbon disulphide, hydrogen sulphide, and regenerated diphenylthiourea.

The action can be explained by the assumption that the thiourea contains a $C=N$ group, and that either addition takes place according to II, or, that the acid decomposes the urea into aniline and phenyl mustard oil as the first stage of the reaction.

It has been found, in regard to the use of thiobenzoic acid as a means of introducing the benzoyl group into aryl amines, that it reacts as easily as thioacetic acid[3]. For example, when mixed with aniline, hydrogen sulphide is evolved in the cold, and benzanilide is quantitatively formed.

On the other hand it combines with ammonia and alphyl amines to form more or less stable salts. The product of the union of thiobenzoic acid and diisobutyl amine, $C_6H_5COSH.HN(C_4H_9)_2$, can be repeatedly crystallized from alcohol without evolution of hydrogen sulphide. A similar behavior of the phenylsulphocarbazinic acid salts of aryl and alphyl amines, $C_6H_5NH—NHCS.SH.H_2NR$, has been observed by Busch and Rider.[4] The former give thiosemicarbazides while the alphyl salts do not. Thiobenzoic acid also reacts on the steam-bath with alcohols and phenols, forming benzoic esters.

EXPERIMENTAL PART.

Benzoylthiolcarbanilic Acid, $C_6H_5CO(C_6H_5)NCO.SH$.—When a

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[1] *Ber. d. chem. Ges.*, **28**, 1322 (1895).

[2] This Journal, **22**, 192 (1900).

[3] Pawlewsky : *Ber. d. chem. Ges.*, **31**, 661 (1898).

[4] *Ber. d. chem. Ges.*, **30**, 843 (1897).

benzene solution of phenyl isocyanate (3 grams) and thiobenzoic acid (3.5 grams) were mixed, heat was evolved and the yellow color of the thio acid disappeared. On cooling, a mass of fine colorless needles separated. These, crystallized from alcohol, melted at 97°–99° with effervescence and a nitrogen determination gave:

	Calculated for $C_{14}H_{11}O_2NS$.	Found.
Nitrogen	5.44	5.35

When this compound was heated, it gave off a combustible gas (COS) and on crystallizing the residue from alcohol, benzanilide melting at 161° was obtained.

Alcoholic ammonia converts this addition-product into ammonium thiolbenzoate and phenylurea.

When thioacetic acid was added to para-tolyl isocyanate under similar conditions para-acettoluide was directly obtained.

Diphenylformamidine and Thiobenzoic Acid (by Bayard Barnes).—When 3 grams of the amidine were dissolved in benzene and 2.1 grams of thiobenzoic acid were added, a mass of colorless needles separated, weighing 4 grams. These melted at 130°–131° and could be crystallized from benzene or a mixture of benzene and ligroin, with only slight decomposition. A nitrogen determination gave:

	Calculated for $C_{20}H_{18}ON_2S$.	Found.
Nitrogen	8.38	8.56

Two grams of this addition-product were melted in an oil-bath at 145°–150°. On cooling and treating the mass with dilute sodium hydroxide a residue remained which crystallized from alcohol in plates melting at 160°–161° (benzanilide). On adding hydrochloric acid to the alkaline extract a precipitate was obtained which crystallized from alcohol in plates and melted at 137°–138° (thioformanilide). When the addition-product was treated with alkali, diphenylformamidine was obtained.

Benzenylmonophenylamidine and Thiobenzoic Acid (by Bayard Barnes).—This product crystallized from benzene in yellowish-white needles and melted at 141°–142°. A nitrogen determination gave:

	Calculated for $C_{20}H_{18}ON_2S$.	Found.
Nitrogen	8.38	8.50

Benzenylphenylparatolylamidine and Thiobenzoic Acid (by

Bayard Barnes).—The amidine was prepared from benzanilide-imide chloride and paratoluidine. On mixing this in benzene with thiobenzoic acid a pale yellow precipitate separated, melting at 131°–132°. A nitrogen determination gave:

	Calculated for $C_{27}H_{24}ON_2S$.	Found.
Nitrogen	6.60	6.68

This compound did not decompose as smoothly, on heating, as that in the case of diphenylformamidine. The yellow product soluble in alkali as well as that which was insoluble was a mixture. In all probability both thiobenzanilide and thiobenztoluide were formed.

Benzimidonormalpropylester and Thiobenzoic Acid (by William Valentine).—Thirty grams of the imido ester were treated with 25.5 grams of thiobenzoic acid at 0°. A solid separated and on allowing the mixture to warm a little the solid melted and a reaction took place with the formation of a precipitate. This weighed 18.5 grams and it crystallized from alcohol in tables which melted at 128°. A nitrogen determination gave 11.5 per cent. of nitrogen, while the calculated for *benzamide* is 11.5 per cent.

The oil removed from the above weighed 36 grams. It was taken up in ether, shaken with dilute alkali, washed, dried, and distilled at 16 mm. pressure. The portion boiling at 130°–150° was distilled at ordinary pressure whereupon the larger portion boiled at 251°–255°, a little distilling above 255°. A sulphur determination in the former agreed with the calculated for *n-propylthiolbenzoate*, $C_6H_5CO.SC_3H_7$.

	Calculated for $C_{10}H_{12}OS$.	Found.
Sulphur	17.8	17.6

Phenylacetimidomethyl ester and Thiobenzoic Acid (by William Valentine).—Twenty-five grams of the ester and 24 grams of thiobenzoic acid reacted immediately. The solid material that separated weighed 15 grams, it was crystallized from alcohol whereupon it melted at 154°–155° and a nitrogen determination agreed with the calculated for *phenylacetamide*, $C_6H_5CH_2CONH_2$:

	Calculated for C_8H_9ON.	Found.
Nitrogen	10.37	10.37

The oil from the above contained benzyl cyanide and was not obtained in a pure condition.

Acetonephenylhydrazone and Thiobenzoic Acid (by William Valentine).—Thirty grams of the hydrazone and 28 grams of thiobenzoic acid were warmed for a number of hours on the steam-bath, whereupon some solid material (22 grams) separated and the loss in weight was about 1 gram. The solid material crystallized from alcohol in small prisms and melted at 168°–169° and a nitrogen determination agreed with the calculated for *benzoylphenylhydrazine.*

	Calculated for $C_{13}H_{12}ON_2$.	Found.
Nitrogen	13.1	13.0

On adding ether to the oil filtered from the above about 2 grams of solid material separated which, on crystallizing from alcohol, melted at 176°–177° and contained no sulphur. A nitrogen determination agreed with the calculated for *dibenzoylphenylhydrazine.*

	Calculated for $C_{20}H_{16}O_2N_2$.	Found.
Nitrogen	8.8	8.8

The ether solution of the oil was shaken with soda and then with dilute hydrochloric acid, whereupon about 10 grams of unaltered hydrazone were obtained. The remaining oil decomposed on attempting to purify it by distilling at reduced pressure.

Methyl Alcohol and Thiobenzoic Acid.—Ten grams of thiobenzoic acid and 25 cc. of methyl alcohol were boiled for twenty hours. The alcoholic solution was then treated with water and a little sodium bicarbonate, whereupon 7 grams of methylbenzoate boiling at 198°–200° were obtained. Calculated yield, 9.9 grams. The action of thiobenzoic acid and phenol under the same conditions was much slower.

Diisobutylammoniumthiolbenzoate, $C_6H_5COSH.HN(C_4H_9)_2$.—When the calculated quantity of thiobenzoic acid was added to diisobutyl amine, cooled in a freezing-mixture, the material solidified to a crystalline mass, while only a very little hydrogen sulphide was evolved. On crystallizing the material twice from alcohol it formed beautiful colorless flattened prisms which melted in a closed tube at 124°. A nitrogen determination gave:

	Calculated for $C_{15}H_{25}ONS$.	Found.
Nitrogen	5.24	5.43

This salt dissolved in water, and silver nitrate gave a pure white precipitate which blackened on boiling.

NEW HAVEN, CONN., May 31, 1901.