pare chloroform, but the yields so far obtained have not been as satisfactory as in the case of iodoform.

CORNELL UNIVERSITY,
November, 1903.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

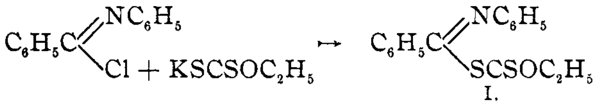
ON SOME THIODIACYLANILIDES.

BY GEORGE S. JAMIESON.

Received December 15, 1903.

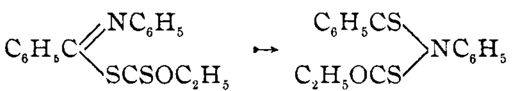
THE object of the work described in this paper was to investigate the compounds formed by the reaction of imide chlorides upon some salts of thioacids and thioanilides.

Tschugaeff[1] has described a series of colored compounds, which he obtained by the action of anilidimide chlorides upon potassium xanthates. He considered these compounds to be imidothioanhydrides, or as he called them, imidoxanthides (Formula I). He represents the reaction, in the case of benzanilidimide chloride as follows:



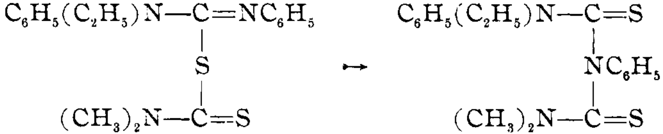
I.

From work done in this laboratory on analogous oxygen compounds[2] it would be expected that a compound having the structure represented by Formula I would undergo a molecular rearrangement, on heating, into the isomeric diacylanilide form as follows:



I. II.

Billeter[3] has shown that a rearrangement takes place in the case of certain imidothiocarbamic anhydrides. He states that dimethylethyl-diphenylpseudodithiobiuret III, at 100° is transformed smoothly into dimethylethyldiphenyldithiobiuret IV.



$$\begin{array}{c} C_6H_5(C_2H_5)N{-}C{=}NC_6H_5 \\ \vert \\ S \\ \vert \\ (CH_3)_2N{-}C{=}S \end{array} \longmapsto \begin{array}{c} C_6H_5(C_2H_5)N{-}C{=}S \\ \vert \\ NC_6H_5 \\ \vert \\ (CH_3)_2N{-}C{=}S \end{array}$$

III. IV.

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[1] *Ber. d. chem. Ges.*, **35**, 2470 (1902).

[2] Wheeler and Johnson: *Am. Chem. J.*, **30**, 24 (1903).

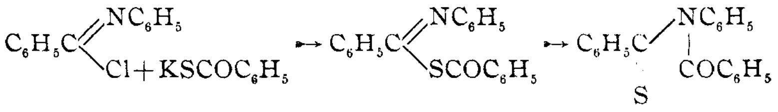
[3] *Ber. d. chem. Ges.*, **26**, 1688 (1893).

Gabriel and Colman[1] were able to isolate the benzoyl derivative of methylaminothiopyrimidine in which the benzoyl group was attached to the sulphur. This compound undergoes a molecular rearrangement, giving a nitrogen benzoyl derivative, when heated.

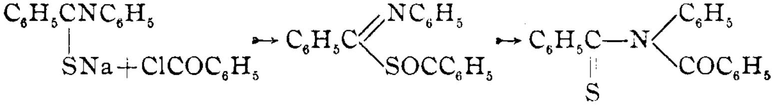
The compound from benzanilidimide chloride and potassium xanthate, however, shows no tendency to undergo a molecular rearrangement. It can be heated above its melting-point without change. When it was heated with concentrated ammonia, a small amount of phenylthionurethane ($C_2H_5OCSNHC_6H_5$) was obtained. The decomposition was not smooth and the chief product was thiobenzanilide. It is concluded, however, from these results that Tschugaeff's compounds are dithiodiacylanilides and not imidoxanthides.

Tschugaeff states that his imidoxanthides have a red color. He discusses the possibility of the complex (C—S—S—C=N) playing the part of a chromophore. It may be stated, however, that the thioamides are more or less colored substances and it appears that thiodiacylanilides have a still more intense color. Benzoylthiotoluylamide ($CH_3C_6H_4CSNHCOC_6H_5$), recently prepared by Wheeler and Johnson[1] from toluene, benzoylrhodanide and aluminum chloride, has a red color, similar to Tschugaeff's compound.

When benzanilidimide chloride and potassium thiobenzoate were mixed in benzene, a reaction took place at the ordinary temperature. A bright red compound was obtained which was found to be stable on heating. It is, therefore, concluded that the reaction took place as follows:



The same diacylanilide was obtained from the action of benzoyl chloride upon the sodium salt of thiobenzanilide. The reaction being:



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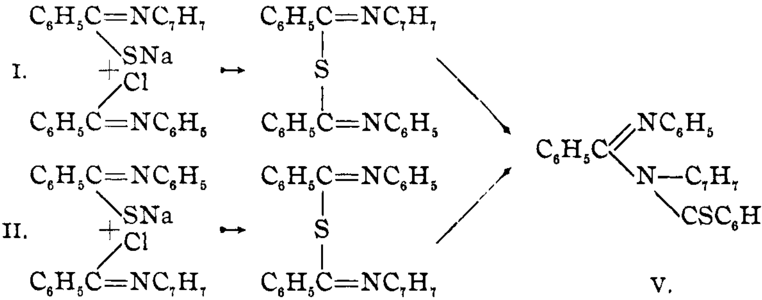
[1] *Ber. d. chem. Ges.*, **32**, 2927.

[2] *Am. Chem. J.*, **26**, 360 (1901).

In a similar manner to the preceding, benzanilidimide chloride and potassium parabromthiobenzoate gave the orange-colored parabrombenzoylthiobenzanilide ($C_6H_5CSN(C_6H_5)COC_6H_4Br$), which was not changed by being melted.

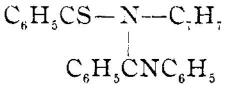
Parabrombenzanilidimide chloride and potassium thiobenzoate reacted to give the isomeric compound, benzoylthioparabrombenzanilide ($BrC_6H_4CSN(C_6H_5)COC_6H_5$). This substance could also be heated above its melting-point without undergoing a metastatic change.

Benzanilidimide chloride and sodium thiobenzparatoluide gave a bright yellow compound. The same compound resulted from the reaction of benzparatoluidimide chloride and the sodium salt of thiobenzanilide.



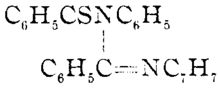
The amidine formula, V, is assigned to this yellow compound, because the material is stable on heating and not readily attacked by alkali. The thiobenzoyl group is attached as represented, since when the compound was boiled with hydrochloric acid, thiobenztoluide was one of the chief products obtained. The di-imidoacid-anhydride, which is first formed, in both cases undergoes a molecular rearrangement into the stable isomeric thiobenzoylphenyltolylbenzenylamidine.

The fact that we obtained the same compound by these two reactions shows that the sodium is attached to sulphur and not to the nitrogen of the thioanilide and that the reaction proceeds as represented above. If the reaction of the imidechloride on these salts involved an addition or a direct replacement of sodium attached to nitrogen, two different isomers—thiobenzoylamidines—would result. From benzanilidimide chloride and sodium thiobenztoluide, the amidine, represented by Formula V, would be obtained, while from benzparatoluidimide chloride and the sodium salt of the thiobenzanilide, that shown by formula VI, would be formed:



$$\begin{array}{c} C_6H_5CS-N-C_7H_7 \\ | \\ C_6H_5CNC_6H_5 \end{array}$$

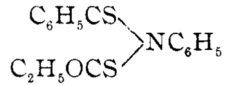
V.



$$\begin{array}{c} C_6H_5CSNC_6H_5 \\ | \\ C_6H_5C{=}NC_7H_7 \end{array}$$

VI.

EXPERIMENTAL PART.

The imidoxanthide  $\begin{array}{l} C_6H_5CS \\ C_2H_5OCS \end{array}\!\!>NC_6H_5$ of Tschugaeff was prepared according to his directions with the exception, that we allowed our reaction to proceed at ordinary temperature, while he heated the solution four or five hours on the water-bath.

Five grams of potassium xanthate and 6.3 grams of benzanilidimide chloride in a solution of ether and benzene were allowed to react for two days. Then the insoluble potassium chloride was filtered from the solution. By evaporating slowly, large garnet red tables were obtained. They melted at 97°, which is the temperature given by Tschugaeff.

The material was not changed by being melted. When heated with dilute aqueous sodium hydroxide, thiobenzanilide was formed as the chief product of decomposition, although a small amount of benzanilide was obtained. When heated with concentrated ammonia until it was decomposed, a small amount of oil resulted which, on standing two days, deposited crystals. These were filtered, washed free from oil and dried. They melted at about 68° and when mixed with thionurethane, which melted at 68°-69°, no lowering of the melting-point was observed. Another experiment with ammonia gave a considerable amount of thiobenzanilide. Concentrated hydrochloric acid decomposed the compound and benzanilide was the only product obtained.

Benzanilidimide Chloride and Potassium Thiobenzoate were allowed to react at ordinary temperature in a benzene solution. The reaction began in a few minutes after adding the constituents. The solution became red. In order to ensure complete reaction, the solution was shaken frequently for two days. Then the insoluble chloride was filtered and the benzene evaporated. The material crystallized from alcohol in bunches of bright red prisms. They melted at 108°-109°. This compound was decomposed by boiling with hydrochloric acid and thiobenzanilide was the chief product obtained.

A nitrogen determination gave:

	Calculated for $C_{20}H_{15}ONS$.	Found.
Nitrogen	4.41	4.25

This same compound was prepared from the sodium salt of thiobenzanilide and benzoyl chloride.

Benzanilidimide Chloride and Potassium Parabromthiobenzoate.—2.4 grams of the former and 2 grams of the latter were mixed in a benzene solution. The solution became red in a few minutes and considerable heat was evolved. It was allowed to stand several hours and then it was heated half an hour to complete the reaction. The insoluble chloride was filtered and the benzene evaporated. The compound crystallized from alcohol in slender orange-colored prisms. They melted at 120°-121° without decomposition or alteration.

A nitrogen determination gave:

	Calculated for $C_{20}H_{14}ONSBr$.	Found.
Nitrogen	3.53	3.83

By concentrating the alcoholic mother-liquors and cooling, material separated which was found to be parabrombenzanilide. This decomposition was probably brought about by a little free hydrochloric acid in the solution, formed by the decomposition of the imide chloride in contact with moisture.

Parabrombenzanilidimide Chloride and Potassium Thiobenzoate were allowed to stand several days in a benzene solution in order to obtain a complete reaction. The solution became bright red and potassium chloride separated. This was filtered and the benzene was evaporated. The residue was crystallized from alcohol, in which it is only moderately soluble. The slender red prisms melted at 133°-134° to a red liquid. The compound was not altered by heating to 140° for five minutes.

A nitrogen determination gave:

	Calculated for $C_{20}H_{14}ONSBr$.	Found.
Nitrogen	3.53	3.45

Parabromthiobenzanilide was obtained by evaporating the alcoholic mother-liquors of the above compound. This thioanilide is readily soluble in hot alcohol. It melts at 161°-162°. It is soluble in aqueous alkali and is precipitated by mineral acids.

A nitrogen determination gave:

	Calculated for $C_{13}H_{10}NSBr$.	Found.
Nitrogen..................	4.80	4.55

Benzanilidimide Chloride and Sodiumthiobenz-p-toluide.—1.9 grams of the former and 1.23 grams of the latter were brought together in a benzene solution. After standing three days at ordinary temperature, the insoluble chloride was filtered and the benzene was evaporated by a draught of air. An oily residue remained, which solidified when stirred with ether and alcohol. The bright yellow powder was very soluble in benzene and amyl acetate. It was very difficultly soluble in alcohol. The material was crystallized from a mixture of petroleum ether and benzene, and melted from 198°-201° without decomposition.

A nitrogen determination gave:

	Calculated for $C_{27}H_{23}N_2S$.	Found.
Nitrogen..................	6.92	7.24

This compound was boiled with hydrochloric acid until it was decomposed. A mixture of anilides was obtained. Thiobenztoluide was separated from the mixture by sodium hydroxide. The insoluble anilides were filtered and the thiobenztoluide was precipitated from the alkaline solution by hydrochloric acid. The thiodiacylanilide is only slowly attacked by sodium hydroxide. This same compound was obtained by the reaction of benzparatoluidimide chloride upon the sodium salt of thiobenzanilide in a benzene solution.

A nitrogen determination gave:

	Calculated for $C_{27}H_{23}N_2S$.	Found.
Nitrogen..................	6.92	7.22

Benzanilidimide Chloride and Sodiumthiobenzanilide were brought together in a benzene solution. After standing two days at ordinary temperature, the insoluble chloride was filtered and the benzene solution was concentrated. A bright yellow powder was obtained. It crystallized from this solvent in prisms. It was soluble in hot amyl alcohol, but did not separate well upon cooling. It crystallized, however, from alcohol, in which it was quite difficultly soluble, in minute plates, and it melted at 202°-204° without decomposition.

A nitrogen determination gave:

	Calculated for $C_{26}H_{20}N_2S$.	Found.
Nitrogen	7.16	6.90

I wish to express my thanks to Prof. H. L. Wheeler for suggestions in carrying out this work.

THE DIRECT ESTIMATION OF FREE CARBONIC ACID IN NATURAL WATERS.

BY A. McGILL.

Received December 7, 1903.

FOLLOWING the valuable papers on this subject that have recently appeared in this Journal,[1] the accompanying description of an apparatus which I have used for some time past, will probably be found interesting.

Much experience has convinced me that accurate knowledge of the amount of free carbonic acid (as distinguished from bound and half-bound) held in solution in deep well and spring waters, requires that the determination should be made at the source. No doubt it is possible by quite filling the container, by opening it only after thorough cooling, and by taking other precautions, to arrive at a very close approximation to the facts; but the observation of all the conditions of accuracy entails usually more labor than would the many times repeated determination at the source of supply. This latter affords the basis for a trustworthy average result, and with the apparatus about to be described, can be carried out quite satisfactorily.

The principles involved are simply the separation of the gas from the water holding it in solution, and the absorption of the liberated gas by appropriate solvents, properly standardized, and having automatic power of indicating the point of saturation.

The disengagement of the gas offers no difficulty. It is effected as in Drown's method,[2] by aspirating (or forcing) air through the water.[3] Instead, however, of merely driving off the free acid,

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[1] J. W. Ellms and J. C. Beneker: This Journal, **23**, 405 (1901); F. B. Forbes and G. H. Pratt: *Ibid.*, **25**, 742 (1903).

[2] This Journal, **25**, 747 (1903).

[3] When air is bubbled through water containing alkaline or earthy bicarbonates in such dilute solutions as these occur in natural waters, there results no appreciable decomposition of such bicarbonates provided that the rate is not more rapid than 3 to 5 bubbles per second, or continued for more than an hour at the ordinary temperature. If, how-