These analytical results made it quite clear that we did not have the free diquinazolyl in hand. The air-dried substance was, therefore, dried to constant weight at 145°. In this drying at 145° it lost 12.1 per cent. of acetic acid, which would make the nitrogen percentage in the acetic acid-free substance, 20.3. The crystals analyzed apparently contained one molecule of the diquinazolyl to one of acetic acid.

Calculated for $C_{18}H_{12}O_6N_6.CH_3COOH$: N, 17.95.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
July, 1906.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(SIXTH PAPER.)

BY TREAT B. JOHNSON.

Received July 19, 1906.

THE object of the work[1] described in this paper was to prepare some new thiol acids, I, and examine their behavior towards thiocyanates, II, and isothiocyanates, III.

$$\underset{\text{I.}}{R.COSH,} \qquad \underset{\text{II.}}{R.SCN,} \qquad \underset{\text{III.}}{R.NCS.}$$

It has been shown in several papers from this laboratory[2] that thiocyanates and isothiocyanates can be sharply distinguished by their behavior towards thiol acids, I. Thiocyanates, II, react with thiol acids in two ways. The most commonly observed reaction is a direct addition to the acid to give a dithiourethane, IV. Certain ones, on the other hand, react in a complicated manner to give thiol esters, V, and thiocyanic acid, VI.

$$R.COSH + R'.SCN = \underset{\text{IV.}}{R.CONHCSSR'.}$$

$$R.COSH + R'.SCN = \underset{\text{VI.}}{HSCN} + \underset{\text{V.}}{R.COSR'.}$$

Alkyl isothiocyanates, VII, and acyl isothiocyanates, VIII, react

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[1] All the experimental work described in this paper was accomplished by advanced Senior students (1906), who had completed the required laboratory course in practical organic chemistry.—T. B. JOHNSON.

[2] Wheeler and Merriam: This Journal, 23, 283; 24, 439; Wheeler and Johnson: Ibid. 24, 680; 26, 185; Wheeler and Jamieson: Ibid. 24, 744.

in an entirely different manner with thiol acids to form substituted acid amides, IX, and carbon bisulphide as follows:

$$\underset{\text{VII.}}{R'.NCS} + R.COSH = \underset{\text{IX.}}{R.CONHR'} + CS_2.$$

$$\underset{\text{VIII.}}{R'CO.NCS} + R.COSH = \underset{\text{IX.}}{RCONHCOR'} + CS_2.$$

The above reactions have hitherto been applied with only two thiol acids, *viz.*, thiolbenzoic, X, and thioacetic acids, XI. It seemed of interest to the writer to decide whether other thiol

$$\underset{\text{X.}}{C_6H_5COSH} \quad \text{and} \quad \underset{\text{XI.}}{CH_3COSH}$$

acids might be used to distinguish between thiocyanates and isothiocyanates. Furthermore, we wished to determine whether the tendency for a thiocyanate to give a dithiourethane, IV, or a thiol ester, V, might be influenced by the negative character of the thiol acid.

We describe in this paper four new thiol acids, *viz.*, phenylthioacetic, $C_6H_5CH_2COSH$, meta- and parabromthiobenzoic, $Br.C_6H_4COSH$, and metanitrothiobenzoic, $NO_2C_6H_4COSH$, acids. They were prepared by dissolving the corresponding acid chlorides in an aqueous or alcoholic solution of potassium hydrosulphide and then treating the resulting potassium salts with hydrochloric or sulphuric acids.

$$R.COCl + 2KSH = R.COSK + KCl + H_2S$$
$$R.COSK + HCl = R.COSH + KCl.$$

Meta- and parabromthiobenzoic acids and metanitrothiobenzoic acid are of especial interest as the first members of this class of thiol acids that have been obtained as solids at ordinary temperature. They were very stable and could be kept for several weeks without change in a dry atmosphere. Phenylthioacetic acid was obtained as an oil.

Carius[1] has described a solid thiosalicylic acid, $OH.C_6H_4COSH$. He prepared it by acting on salicylic acid with phosphorus pentachloride and then treating the acid chloride with barium hydrosulphide. It does not seem probable that Carius was dealing with this thiol acid, since Anschütz and his co-workers[2] have shown that phosphorus halides do not react with salicylic acid to give the acid chloride, $HO.C_6H_4COCl$. The first oxy-acid chloride

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[1] Ann. 129, 11.

[2] Ibid. 228, 308; 239, 316, 333; 239, 304.

isolated was 3,5-dichlorsalicyl chloride, $Cl_2(HO).C_6H_2COCl$.[1] Anschütz and his students have recently described a large number of aromatic oxy-acid chlorides.[2]

We examined the behavior of the above thiol acids towards methyl, ethyl and benzyl thiocyanate. They reacted with these thiocyanates to give the corresponding dithiourethanes. The reactions were very smooth and we did not detect any evidence of the formation of thiol esters. So far as we were able to judge, the four acids did not show any appreciable difference in their tendency to combine with thiocyanates.

Our thiol acids reacted normally with an isothiocyanate. Phenylthioacetic, parabromthiobenzoic and metanitrothiobenzoic acids reacted quantitatively with phenyl isothiocyanate to give the corresponding acid anilides.

Phenylacetanilide, $C_6H_5CH_2CONHC_6H_5$.[3]

Parabrombenzoylanilide, $\overset{4}{Br}.C_6H_4\overset{1}{C}ONHC_6H_5$.[4]

Metanitrobenzoylanilide, $\overset{3}{N}O_2.C_6H_4\overset{1}{C}ONHC_6H_5$.[5]

COMPARATIVE BOILING- AND MELTING-POINTS OF THE THIOL ACIDS USED IN OUR THIOCYANATE RESEARCHES, AND THE BOILING- AND MELTING-POINTS OF THEIR CORRESPONDING ACID CHLORIDES.

Acid Chloride	B. P.	M. P.
Acetyl chloride, CH_3COCl	55°	..
Phenylacetyl chloride, $C_6H_5CH_2COCl$	102° at 17 mm.	..
Benzoyl chloride, C_6H_5COCl	198°	..
Metabrombenzoyl chloride, $\overset{3}{B}r.C_6H_4\overset{1}{C}OCl$	243°	..
Parabrombenzoyl chloride, $\overset{4}{B}r.C_6H_4\overset{1}{C}OCl$	..	41°
Metanitrobenzoyl chloride, $\overset{3}{N}O_2.C_6H_4\overset{1}{C}OCl$	..	35°
Thiol Acid.		
Thioacetic acid, CH_3COSH	93°	..
Phenylthioacetic acid, $C_6H_5CH_2COSH$	..	..
Thiobenzoic acid, C_6H_5COSH	..	24°
Metabromthiobenzoic acid, $\overset{3}{B}r.C_6H_4\overset{1}{C}OSH$	..	58°
Parabromthiobenzoic acid, $\overset{4}{B}r.C_6H_4\overset{1}{C}OSH$	..	78–79°
Metanitrothiobenzoic acid, $\overset{3}{N}O_2.C_6H_4\overset{1}{C}OSH$	..	89–90°

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[1] Anschütz: Ann. 346, 300; Ber. 30, 221.

[2] Ann. 346, 286–360.

[3] Hofmann: Ber. 13, 1225.

[4] Raveill: Ann. 222, 178.

[5] Schotten: Ber. 21, 2245.

EXPERIMENTAL PART.

BY ERNEST BATEMAN, ERIK SCHJÖTH PALMER AND CHARLES ANDREW BRAUTLECHT.

Phenylthioacetic Acid, $C_6H_5CH_2COSH$.—This acid was obtained in the form of its potassium salt when phenylacetyl chloride was warmed on the steam-bath with an aqueous solution of potassium hydrosulphide. After the acid chloride had completely dissolved the solution was acidified with sulphuric acid. The thiol acid separated as a limpid oil. It did not solidify after standing for several weeks. When exposed to the atmosphere it was slowly oxidized to the disulphide.

Diphenylacetyl Disulphide $(C_6H_5CH_2COS)_2$.—This compound was prepared by suspending finely pulverized iodine in an aqueous solution of the sodium salt of phenylthioacetic acid. The sulphide separated as a crystalline deposit. It was purified for analysis by recrystallization from 95 per cent. alcohol. It deposited in transparent plates that melted at 62°. It was insoluble in sodium hydroxide solution. Carbon and hydrogen determinations gave; C, 63.73; H, 5.0; calculated for $C_{16}H_{14}O_2S_2$, C, 63.57; H, 4.63.

Action of Phenylthioacetic Acid on Phenyl Isothiocyanate.—Molecular proportions of phenylthioacetic acid and phenyl isothiocyanate were heated together at 100°. Carbon bisulphide was evolved and we obtained a crystalline substance. It deposited from 95 per cent. alcohol in prisms that melted at 117–118°. It was identified as phenylacetanilide.[1] It did not contain sulphur and when mixed with phenylacetanilide the melting-point was not lowered.

Phenylacetyldithiomethylcarbamate, $C_6H_5CH_2CO.NH.CSSCH_3$.—Molecular proportions of phenylthioacetic acid and methyl thiocyanate were heated together in a boiling water-bath for about one hour. We obtained a thick oil that solidified on cooling. The compound crystallized from alcohol in slender prisms that melted at 133° to an oil. They were dissolved by sodium hydroxide and were reprecipitated from the alkaline solution by acids. The analysis (Kjeldahl) gave: N, 6.24; calculated for $C_{10}H_{11}ONS_2$, 6.22.

Phenylacetyldithioethylcarbamate, $C_6H_5CH_2CO.NH.CSSC_2H_5$.—This compound was obtained when a mixture of molecular proportions of phenylthioacetic acid and ethyl thiocyanate was heated

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[1] Hoffman : Loc. cit.

at 100° for three hours. It deposited from alcohol in lemon-yellow prisms that melted at 125° to an oil. The analysis (Kjeldahl) gave, N, 5.74; calculated for $C_{11}H_{13}ONS_2$, 5.85.

Phenylacetyldithiobenzylcarbamate, $C_6H_5CH_2CO.NH.CSSCH_2C_6H_5$.—From phenylthioacetic acid and benzyl thiocyanate. It was purified for analysis by recrystallization from alcohol. It deposited in lemon-yellow prisms that melted at 123°. The analysis gave: N, 4.68; calculated for $C_{16}H_{15}ONS_2$, 4.65.

Metabromthiobenzoic Acid, $\overset{3}{Br}.C_6H_4.\overset{1}{C}OSH$.—Metabrombenzoyl chloride[1] did not react readily with potassium hydrosulphide in aqueous solution. In order to obtain a complete reaction it was necessary to heat them at 100° for several hours. When the alkaline solution was acidified with hydrochloric acid the thiol acid separated as an oil. This oil was extracted with ether and the solution dried over calcium chloride. When the ether was removed by distillation we obtained the thiol acid as an oil which finally solidified. It was crystallized from petroleum ether and deposited as a light yellow, crystalline powder that melted at 58°. The acid was very soluble in alcohol, ether and benzene. The analysis gave: Br, 36.35. Calculated for C_7H_5OBrS, 36.85.

Metabrombenzoyldithiomethylcarbamate, $\overset{3}{Br}.C_6H_4.\overset{1}{C}ONHCSSCH_3$.—This compound was prepared by heating a mixture of metabromthiobenzoic acid and methyl thiocyanate in a boiling water-bath for a few minutes. It deposited from 95 per cent. alcohol in distorted needles that melted at 124°. The analysis gave: N, 5.1; calculated for $C_9H_8ONBrS_2$, 4.83.

Metabrombenzoyldithioethylcarbamate, $\overset{3}{Br}C_6H_4.\overset{1}{C}O.NHCSSC_2H_5$.—From metabromthiobenzoic acid and ethyl thiocyanate. It deposited from alcohol in needle-like prisms that melted at 131°. The analysis gave: N, 4.3; calculated for $C_{10}H_{10}ONBrS_2$, 4.60.

Metabrombenzoyldithiobenzylcarbamate, $\overset{3}{Br}.C_6H_4\overset{1}{C}ONHCSSCH_2C_6H_5$.—From benzyl thiocyanate and metabromthiobenzoic acid. It deposited from 95 per cent. alcohol in prismatic crystals. They melted at 113°. The analysis gave· N, 4.0; calculated for $C_{15}H_{12}ONBrS_2$, 3.82.

Parabromthiobenzoic Acid,[2] $\overset{4}{Br}.C_6H_4.\overset{1}{C}OSH$.—When parabrom-

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[1] Sudborough : J. Chem. Soc. 67, 590.

[2] This acid was first prepared by Dr. G. S. Jamieson in 1903.

benzoyl chloride was added to an alcoholic solution of potassium hydrosulphide an immediate reaction took place with separation of potassium chloride. The solution was warmed a few minutes to complete the reaction, then concentrated to a small volume and the insoluble potassium chloride removed by filtration. When the filtrate was cooled we obtained a deposit of yellow prisms. They were very soluble in water and were identified as the potassium salt of parabromthiobenzoic acid. A bromine determination gave: Br, 30.85; calculated for C_7H_4OBrSK, 31.35.

When this potassium salt was dissolved in cold water and the solution acidified with hydrochloric acid the thiol acid deposited in the form of colorless, flat prisms. It dissolved in hot alcohol and deposited on cooling in prisms that melted at 78–79° to a clear oil. A bromine determination gave; Br, 36.50; calculated for C_7H_5OBrS, 36.85.

Action of Parabromthiobenzoic Acid on Phenyl Isothiocyanate.—When the thiol acid was heated with the isothiocyanate an immediate reaction took place with evolution of carbon bisulphide. We obtained a compound that deposited from alcohol in plates. They melted at 201–202° to a clear oil and did not respond to a test for sulphur. A nitrogen determination (Kjeldahl) agreed with the calculated value in *parabrombenzoylanilide*,[1] $\overset{4}{Br}C_6H_4\overset{1}{C}ONHC_6H_5$. Found, 5.3; calculated for $C_{13}H_{10}ONBr$, 5.07.

This same anilide[2] melting at 201–202° was also prepared by warming the thiol acid with a molecular proportion of aniline.

Parabrombenzoyldithiomethylcarbamate, $\overset{4}{Br}.C_6H_4\overset{1}{C}O.NHCSSCH_3$.—From parabromthiobenzoic acid and methyl thiocyanate. It deposited from 95 per cent. alcohol in distorted needles that melted at 152° to a clear oil. The analysis gave: N, 4.80; calculated for $C_9H_8ONBrS_2$, 4.82.

Parabrombenzoyldithioethylcarbamate, $\overset{4}{Br}.C_6H_4.\overset{1}{C}O.NH.CSSC_2H_5$.—From ethyl thiocyanate and parabromthiobenzoic acid. It deposited from alcohol in pale yellow needles that melted at 116° to a yellow oil. The analysis gave; N, 4.63; calculated for $C_{10}H_{10}ONBrS_2$, 4.60.

Metanitrothiobenzoic Acid, $\overset{3}{N}O_2.C_6H_4\overset{1}{C}OSH$.—This acid was ob-

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[1] Loc. cit.

[2] Raveill states that this anilide melts at 197°. Ann. 222, 178.

tained in the form of its potassium salt by adding metanitrobenzoyl chloride to an aqueous or alcoholic solution of potassium hydrosulphide. When an aqueous solution of the salt was acidified with sulphuric or hydrochloric acid the thiol acid separated as an oil which soon solidified. This acid is unstable if moist, and all operations must be performed at low temperatures in order to avoid decomposition. The acid was insoluble in water, but very soluble in acetone, warm alcohol and benzene. It deposited from dilute alcohol in light yellow, prismatic crystals that showed signs of melting at 85° and then melted sharply at 89–90° to a clear oil. The analysis gave: N, 7.69 and 7.7; calculated for $C_7H_5O_3NS$, 7.65.

The sodium salt was very soluble in water. It deposited from 95 per cent. alcohol in irregular prisms. The analysis gave: N, 6.85; calculated for $C_7H_4O_3NSNa$, 6.82.

Action of Metanitrothiobenzoic Acid on Phenyl Isothiocyanate.— A mixture of molecular proportions of the isothiocyanate and thiol acid was heated in a boiling water-bath for about two hours. Carbon bisulphide was copiously evolved. We obtained a crystalline substance that was difficultly soluble in water. It deposited from alcohol in plates that melted at 154° and did not respond to a test for sulphur. A nitrogen determination agreed with the calculated value in *metanitrobenzoylanilide*,[1] $\overset{3}{NO_2}.C_6H_4\overset{1}{C}ONHC_6H_5$. The analysis gave: N, 12.0; calculated for $C_{13}H_{10}O_3N_2$, 11.6.

Metanitrobenzoyldithiomethylcarbamate, $\overset{3}{NO_2} . C_6H_4 . \overset{1}{C}O . NH CSSCH_3$.—This compound was prepared by heating together molecular proportions of methyl thiocyanate and metanitrothiobenzoic acid. The reaction was very smooth and complete in a few minutes. The urethane was very soluble in benzene and sparingly soluble in alcohol. It deposited from benzene in yellow needles that melted at 162°. The analysis gave: N, 10.64; calculated for $C_9H_8O_3N_2S_2$, 10.93.

Metanitrobenzoyldithioethylcarbamate, $\overset{3}{NO_2}.C_6H_4.\overset{1}{C}O.NH.CSSC_2H_5$. —From ethyl thiocyanate and metanitrothiobenzoic acid. This compound was sparingly soluble in cold alcohol and deposited from hot alcohol in yellow prisms that melted at 158° to a

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[1] Schotten: Ber. 21, 2245.

clear oil. The analysis gave: N, 10.5; calculated for $C_{10}H_{10}O_8N_2S_2$, 10.37.

NEW HAVEN CONN.,
July 16, 1906.

THE CHLOR-HYDROCHLORIDES OF PINENE AND FIRPENE.

BY G. B. FRANKFORTER AND FRANCIS C. FRARY.

Received August 2, 1906.

The Purification of Pinene and Firpene.—The pinene used in the preparation of the following compounds was obtained from the common white turpentine by distilling with steam, drying and redistilling until the boiling-point was constant at 156–157°. An analysis showed that the substance consisted entirely of hydrogen and carbon, and the physical properties corresponded with those of pure pinene.

The firpene used was obtained from the western fir by distilling the crude pitch with steam. The water-white terpene was dried and redistilled several times. Combustion gave numbers which corresponded with the formula $C_{10}H_{16}$. Molecular weight determinations also gave numbers which corresponded well with the above formula. Its odor, its specific gravity, its refractive index and its optical activity differed from the pure pinene. The chemical properties, likewise, differed from pinene.

The following is a comparison of the physical properties of the two substances:

	Pinene.	Firpene.
Boiling-point	156°–157°	153°–153.5°
Sp. gr. at 20°	0.8647	0.8598
Index of refraction at 20°	1.46336	1.47299
Optical activity $(\alpha)_D$	+14.34	—47.2

Preparation of Pinene Hydrochloride.—The pinene hydrochloride prepared by the common method contains a considerable quantity of soluble oily and resinous matter from which it is separated with great difficulty. In fact, we were unable to find a satisfactory method for the separation of the hydrochloride from these oily and resinous substances. A new method therefore seemed important. After many trials, the following process was finally chosen as being entirely satisfactory. Pure pinene was mixed with about an equal volume of dry chloroform in a large round-bottomed flask, mixed thoroughly and cooled below 0°. Pure