[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PRODUCTION OF IMIDO THIOL ESTERS BY THE CONDENSATION OF THIOCYANATES WITH RESORCINOL OR PHLOROGLUCINOL

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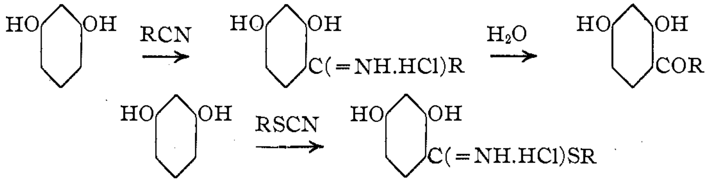
The similarity in the reactivity of the cyano grouping in organic thiocyanates and cyanides is striking. The following table represents some of the commoner reactions of each which have already been described in the literature.

Reagent	Product with RCN	Product with RSCN
H_2	RCH_2NH_2	$RSH + CH_3NH_2$[2]
H_2O (HCl)	$RCONH_2$	$RSCONH_2$, $[RSC(=NH)(OH)]$[3]
R'OH (HCl)	$RC(=NH.HCl)OR'$	$RSC(=NH.HCl)OR'$[4]
H_2S	$RCSNH_2$	$RSCSNH_2$, $[RSC(=NH)(SH)]$[5]

In this communication is described the condensation of alkyl and aryl thiocyanates with resorcinol and phloroglucinol in the presence of hydrogen chloride and zinc chloride. This reaction corresponds to that studied by Hoesch in which alkyl and aryl cyanides are condensed with resorcinol and phloroglucinol under similar conditions. Whereas the cyanides yield imido hydrochlorides which hydrolyze to ketones, the thiocyanates readily yield imido thiol ester hydrochlorides, the expected products providing the cyano grouping in the thiocyanates react in the same way as the cyano in the cyanides. Methyl, ethyl, *n*-butyl and phenyl thiocyanates were condensed with resorcinol, thus showing the reaction to be a general one. Only methyl thiocyanate was condensed with phloroglucinol, but



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[1] This communication is an abstract of a thesis submitted by R. J. Kaufmann in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Hofmann, *Ber.*, **1**, 177 (1868). Gerlich, *Ann.*, **178**, 82 (1875). Sestini and Funaro, *Gazz. chim. ital.*, **12**, 184 (1882). Fichter and Beck, *Ber.*, **44**, 3636 (1911).

[3] (a) Salomon, *J. prakt. chem.*, [2] **7**, 256 (1873). (b) Conrad and Salomon, *ibid.*, [2] **10**, 32 (1874). (c) Blankenhorn, *ibid.*, [2] **16**, 372 (1877). (d) Pinner, *Ber.*, **14**, 1082 (1881). (e) Knorr, *ibid.*, **49**, 1735 (1916).

[4] Ref. 3b.

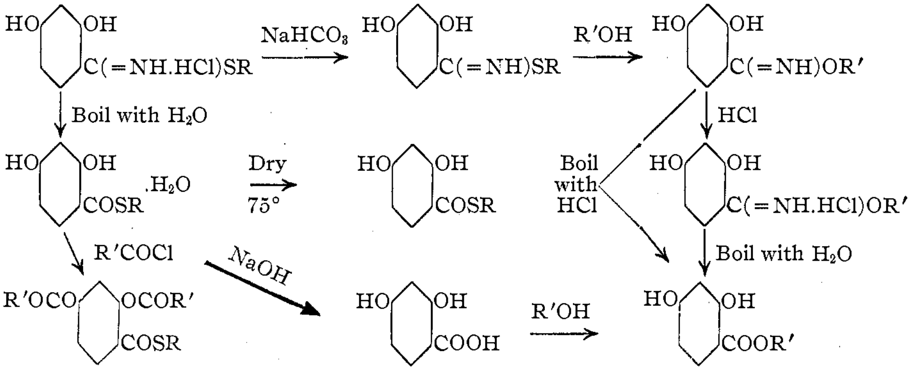
[5] Jeanjean, *Jahresber.*, **1866**, 501. Ref. 3b, p. 29. Gerlich, *Ann.*, **178**, 82 (1875). v. Braun, *Ber.*, **35**, 3369, 3380 (1902). Bogert, THIS JOURNAL, **25**, 290 (1903). Delepine and Schving, *Bull. soc. chim.*, [3] **29**, 48 (1903); [4] **7**, 895 (1910).

unquestionably the other thiocyanates would condense in an analogous way. The products thus obtained resembled in chemical reactivity known imido thiol ester hydrochlorides. Their exact constitution was proved by conversion into substances of known structure.

By the action of sodium bicarbonate these imido thiol ester hydrochlorides were decomposed into the free imido thiol esters. The latter substances, in contrast to many of this class of compounds previously described, were perfectly stable.[6]

The imido thiol ester hydrochlorides were readily decomposed into thiol esters by refluxing in very dilute aqueous hydrochloric acid solution. Since the thiol esters thus obtained were converted by alkali into the corresponding carboxylic acids which were made directly from resorcinol or phloroglucinol, the constitution of the original substances was definitely established.

The free imido thiol esters reacted readily with alcohols to give the corresponding imido esters and mercaptans. This is a reaction that is being investigated further. The imido esters obtained by this latter reaction were converted by hydrochloric acid to the corresponding salt and by boiling with dil. hydrochloric acid into the corresponding esters which, in the examples at hand, were known compounds and could readily be made by the esterification of the corresponding acids. The following chart gives in concise form the various reactions just discussed.



The formation of the imido thiol ester hydrochlorides was very simple but there was some difficulty in their isolation on account of the zinc chloride used as a condensing agent. Washing with acetone removed a large amount of impurity from the crude condensation products but solution of the crude product in cold hydrochloric acid and reprecipitation of the base was necessary in order to eliminate completely the impurity of zinc. At least part of the zinc in the crude products was present not

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[6] Autenrieth and Brüning, *Ber.*, **36**, 3464 (1903). Bernthsen, *Ann.*, **197**, 341 ff, (1879).

merely as zinc chloride, but actually as a zinc salt of the phenol and in the condensation of the phenyl thiocyanate with resorcinol, it was actually possible to isolate and purify such a zinc compound. The initial condensations were also carried out without any zinc chloride, but under these conditions the reactions went much more slowly and did not yield so great an amount of the products. The materials obtained in this way, however, were always much purer.

Experimental Part

General Procedure for the Condensation of Alkyl and Aryl Thiocyanates with Resorcinol and Phloroglucinol.—A 1.5-liter wide-mouth bottle was equipped with a 3-hole rubber stopper through which were passed a mechanical stirrer with a mercury seal, an inlet tube with a wide mouth reaching to the bottom of the bottle, and an outlet tube which extended just through the stopper. To this outlet tube was attached a small upright water condenser, the upper end of which was closed with a tube leading through a sulfuric acid wash bottle. The moisture was thus prevented from returning to the reaction bottle and at the same time the speed with which the hydrogen chloride was flowing could be determined. In the bottle were placed 1 molecular equivalent each of phenol and thiocyanate, 0.2 to 1 molecular equivalent of pulverized anhydrous zinc chloride, and 250 to 1000 cc. of anhydrous ether. The stirrer was started and the mixture agitated for about 1 hour, until solution was complete. Dry hydrogen chloride was then bubbled into the solution for 30 to 40 hours, while rapid agitation was constantly maintained. Noticeable warming took place at the beginning and continued for 2 to 3 hours.

After 15 to 25 hours the separation of orange to deep red crystals began and continued for some time until complete. In some cases the reaction mixture at the end was semisolid, particularly when the smaller amounts of ether mentioned were used. The mixture was allowed to settle and the clear mother liquors decanted. The residue which was frequently sticky and dark colored, was extracted with cold acetone until a test portion imparted practically no further color to fresh solvent. The products thus obtained were light colored, granular solids.

It was advisable to return the mother liquors to the reaction bottle and again to pass in dry hydrogen chloride for some hours with vigorous stirring. In many cases an additional quantity of condensation product was thus obtained.

The further purification varied somewhat with the individual substances.

Methyl-thiol-β-resorcylate-imide Hydrochloride, $(HO)_2C_6H_3C(=NH.HCl)SCH_3$.—From 110 g. of resorcinol, 73 g. of methyl thiocyanate, 136 g. of zinc chloride and 275 cc. of anhydrous ether was obtained 130 to 160 g. of crude dry condensation product. In order to purify it from the zinc which it contained, it was crystallized twice from hot 15%

hydrochloric acid, washed with cold acetone and then dried at 100–110°. The product thus obtained was practically pure white and melted at 244–245° (corr.) decomp.

Analyses. Subs., 0.1340, 0.1944: AgCl, 0.0886, 0.1289. Subs., 0.1963, 0.2242: $BaSO_4$, 0.2085, 0.2399. Subs., 0.2190, 0.2042: 5.290, 5.041 cc. of 0.1930 *N* HCl. Calc. for $C_8H_{10}O_2ClNS$: Cl, 16.15; S, 14.60; N, 6.38. Found: Cl, 16.36, 16.40; S, 14.59, 14.69; N, 6.53, 6.67.

Methyl-thiol-β-resorcylate-imide Sulfate, $(HO)_2C_6H_3C(=NH.\frac{1}{2}H_2SO_4)SCH_3$.—A solution of 5 g. of the crude hydrochloride in 10 cc. of water was filtered and the filtrate treated with 10 cc. of 50% (by volume) sulfuric acid. After 24 hours, crystals of the sulfate separated. These were recrystallized once from 25% (by weight) sulfuric acid, then from alcohol and finally washed with dry ether. The product formed white crystals; m. p., 230–231.5° (corr.).

Analyses. Subs., 0.2305, 0.2339; 4.951, 5.071 cc. of 0.1917 *N* HCl. Calc. for $C_{16}H_{20}O_8N_2S_3$: N, 6.03. Found: 5.77, 5.82.

Ethyl-thiol-β-resorcylate-imide Hydrochloride, $(HO)_2C_6H_3C(=NH.HCl)SC_2H_5$.—From 110 g. of resorcinol, 87 g. of ethyl thiocyanate, 136 g. of zinc chloride and 275 cc. of ether was obtained 140–160 g. of crude solid. This product tended to remain pink even after action of the acetone. The color could be removed, however, by dissolving the product in ice water and adding concd. hydrochloric acid. The cream-colored product was then recrystallized from 15% hydrochloric acid and, after it had dried, melted at 229.5–231.5° (corr.) decomp.

Analyses. Subs., 0.3452, 0.3499; 7.534, 7.627 cc. of 0.1930 *N* HCl. Calc. for $C_9H_{12}O_2NClS$: N, 6.00. Found: 5.90, 5.89.

Ethyl-thiol-β-resorcylate-imide Sulfate, $(HO)_2C_6H_3C(=NH.\frac{1}{2}H_2SO_4)SC_2H_5$.—The method of preparation was similar to that of the corresponding methyl compound. The substance was purified by crystallization from 95% alcohol or glacial acetic acid. It formed a white powder; m. p., 214–217° (corr.).

Analyses. Subs., 0.2112, 0.4461; 4.285, 8.870 cc. of 0.1930 *N* HCl. Calc. for $C_{18}H_{24}O_8N_2S_3$: N, 5.69. Found: 5.49, 5.38.

***n*-Butyl-thiol-β-resorcylate-imide Hydrochloride,** $(HO)_2C_6H_3C(=NH.HCl)SC_4H_9$ (*n*).—The butyl derivative was readily obtained from resorcinol, *n*-butyl thiocyanate,[7] zinc chloride and anhydrous ether. It was purified by crystallization from a mixture of equal volumes of 95% alcohol and 15% hydrochloric acid. When pure the substance was white and melted at 226–228° (corr.) decomp.

Analyses. Subs., 0.1591, 0.1146: AgCl, 0.0865, 0.0608. Subs., 0.2083, 0.1265: $BaSO_4$, 0.1856, 0.1115. Subs., 0.3332, 0.4236; 6.701, 8.218 cc. of 0.1930 *N* HCl. Calc. for $C_{11}H_{16}O_2NSCl$: Cl, 13.55; S, 12.26; N, 5.35. Found: Cl, 13.45, 13.13; S, 12.24, 12.11; N, 5.44, 5.25.

Phenyl-thiol-β-resorcylate-imide Hydrochloride, $(HO)_2C_6H_3C(=NH.HCl)SC_6H_5$.—From 22 g. of resorcinol, 27 g. of phenyl thiocyanate, 5 g. of zinc chloride and 250 cc. of anhydrous ether was obtained 12 g. of crude product. When this substance was crystallized from approximately 2% aqueous hydrochloric acid, a white product was formed. This was crystallized further by dissolving in the smallest amount of alcohol

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[7] *n*-Butyl thiocyanate has not been described in the literature. It was made by the general procedure described in *Ann.*, **178**, 85 (1882) from *n*-butyl bromide and ammonium thiocyanate; yield, 85–90%. The product had the following constants: b. p.,$_{743\ mm.}$ 184.5–185.5°; d_4^{25}, 0.9563; $n^{21.5}_D$, 1.4636.

Analysis. Subs., 0.3369, 0.3084: 14.940, 13.959 cc. of 0.1917 *N* HCl. Calc. for C_5H_9NS: N, 12.17. Found: 11.91, 12.16.

possible and gradually precipitating with dry ether in the cold. The substance was then pure and white, and melted at 220–222° (corr.) decomp.

Analysis. Subs., 0.1511, 0.1533: $BaSO_4$, 0.1228, 0.1252. Subs., 0.0950, 0.3681: 1.771, 6.850 cc. of 0.1892 *N* HCl. Calc. for $C_{13}H_{12}O_2NClS$: S, 11.38; N, 4.98. Found: S, 11.16, 11.22; N, 4.95, 4.93.

The crude material was apparently a fairly pure zinc salt of the condensation product. The zinc salt was prepared for analysis by dissolving the acetone-washed substance, in 10 times its weight of cold 95% alcohol, filtering the solution and adding an equal volume of concd. hydrochloric acid. The substance then separated in the form of small, light-yellow crystals which were finally washed with acetone. Repetition of this treatment did not raise the melting point, which was 225–227° (corr.) decomp.

Analysis. Subs., 0.1711, 0.1663; $BaSO_4$, 0.1105, 0.1099. Subs., 0.2517, 0.2756; 3.769, 4.202 cc. of 0.1892 *N* HCl. Calc. for $C_{13}H_{10}O_2NClSZn$: S, 9.29; N, 4.06. Found: S, 8.87, 9.08; N, 3.97, 4.04.

Methyl-thiol-2,4,6-trihydroxy-benzoate-imide Hydrochloride, $(HO)_3C_6H_2C(=NH.HCl)SCH_3$.—From 35 g. of phloroglucinol, 21 g. of methyl thiocyanate, 7 g. of zinc chloride and 250 cc. of anhydrous ether, was obtained after about 20 hours 22 g. of crude product. When the filtrate was treated for another 10–15 hours with dry hydrogen chloride, an additional 14.3 g. of crude product was formed. It was purified by dissolving it in a hot mixture of 2 parts by volume of alcohol and 3 parts of 15% hydrochloric acid, boiling the mixture with charcoal, filtering and cooling the filtrate. The product was white when pure and melted at 255–256° (corr.).

Analyses. Subs., 0.2299, 0.3698; 4.842, 8.000 cc. of 0.1892 *N* HCl. Calc. for $C_8H_{10}O_3NClS$; N, 5.95. Found: N, 5.58, 5.73.

General Procedure for Conversion of the Imido Thiol Ester Hydrochlorides to Imido Thiol Esters.—The pure imido thiol ester hydrochlorides were dissolved in 3 to 5 times their weight of water, the solutions cooled and sufficient saturated sodium bicarbonate solution was added to make the mixtures alkaline. The bases which precipitated were filtered, and washed with water.

When the crude imido thiol ester hydrochlorides which contained zinc were converted into the free bases, it was necessary to add only enough sodium bicarbonate in the precipitation to leave the mixture just acid to litmus. The major portion of the zinc thus remained in solution. The bases were filtered, dissolved again in the minimum amount of dil. hydrochloric acid, and again precipitated as just described. In this way bases entirely free from zinc salts were obtained.

Methyl-thiol-β-resorcylate-imide, $(HO)_2C_6H_3C(=NH)SCH_3$.—For complete purification, this substance was crystallized from hot methyl alcohol. This must be done rapidly since methyl alcohol gradually reacts with the compound. When pure, the substance was obtained in the form of small yellow needles; m. p., 197–199° (corr.) decomp.

Analyses. Subs., 0.1397, 0.1115: $BaSO_4$, 0.1744, 0.1409. Subs., 0.1585, 0.2298: 4.394, 6.710 cc. of 0.1930 *N* HCl. Calc. for $C_8H_9O_2NS$: S, 17.50; N, 7.65. Found: S, 17.14, 17.35; N, 7.50, 7.90.

Ethyl-thiol-β-resorcylate-imide, $(HO)_2C_6H_3C(=NH)SC_2H_5$.—This product was crystallized from ethyl alcohol from which it formed yellow crystals; m. p., 196–197°

(corr.) decomp. It was not allowed to stand with the ethyl alcohol since these substances gradually reacted.

Analyses. Subs., 0.2482, 0.2814: 6.383, 7.378 cc. of 0.1930 *N* HCl. Calc. for $C_9H_{11}O_2NS$: N, 7.11. Found: 6.95, 7.09.

***n*-Butyl-thiol-β-resorcylate-imide,** $(HO)_2C_6H_3C(=NH)SC_4H_9(n)$.—This substance was finally purified by crystallization from methyl alcohol. It was not allowed to stand with the methyl alcohol since the 2 substances gradually reacted. Bright yellow needles were formed; m. p., 173–174° (corr.) decomp.

Analyses. Subs., 0.1626, 0.1613: $BaSO_4$, 0.1661, 0.1630. Subs., 0.3710, 0.4816; 8.575, 10.860 cc. of 0.1930 *N* HCl. Calc. for $C_{11}H_{15}O_2NS$: S, 14.24; N, 6.22. Found: S, 14.03, 13.88; N, 6.25, 6.10.

Phenyl-thiol-β-resorcylate-imide, $(HO)_2C_6H_3C(=NH)SC_6H_5$.—The base was crystallized by solution in alcohol and precipitation with water or by partial evaporation of an alcohol-ether solution. The compound formed yellow crystals which, after they were dried at 80°, melted at 156–158° (corr.) decomp.

Analyses. Subs., 0.1882, 0.1568: 3.880, 3.340 cc. of 0.1892 *N* HCl. Calc. for $C_{13}H_{11}O_2NS$: N, 5.72. Found: 5.47, 5.65.

Methyl-thiol-2,4,6-trihydroxy-benzoate-imide, $(HO)_3C_6H_2C(=NH)SCH_3$.—This substance proved to be very much less soluble in the common organic solvents than any of the other imido thiol esters studied. No satisfactory solvent was found. The base was made from very pure hydrochloride and prepared for analysis by washing with boiling water, boiling alcohol, and absolute ether, giving then a cream colored product; m. p., 223–226° (corr.).

Analyses. Subs., 0.1386, 0.2258: $BaSO_4$, 0.1586, 0.2632. Subs., 0.2150, 0.3040: 5.331, 7.601 cc. of 0.1917 *N* HCl. Calc. for $C_8H_9O_3NS$: S, 16.10; N, 7.04. Found: S, 15.71, 16.01; N, 6.66, 6.72.

General Procedure for the Formation of Thiol Esters from the Imido Thiol Ester Hydrochlorides.—Pure imido thiol ester hydrochloride was dissolved in very dilute hydrochloric acid and refluxed for 2 to 5 hours in the case of the resorcinol derivatives, or 8 to 10 hours in the case of phloroglucinol derivatives which were more difficult to hydrolyze. Solid products, which separated as the solutions cooled, were filtered directly; liquids were extracted with ether.

Methyl-thiol-β-resorcylate-monohydrate, $(HO)_2C_6H_3COSCH_3.H_2O$.—From 35 g. of once recrystallized methyl-thiol-β-resorcylate-imide hydrochloride in 1500 cc. of water and 5 cc. of concd. hydrochloric acid was obtained after 5 hours 25 g. of product which solidified as the reaction mixture cooled. This was purified by solution in a little boiling alcohol to which bone charcoal was added, filtration and reprecipitation with water. Finally, it was recrystallized from 50% alcohol, as colorless needles; m. p., 70–71° (corr.).

Analyses. Subs., 0.1424, 0.1510: $BaSO_4$, 0.1625, 0.1699. Subs., 0.9051: H_2O, 0.0823. Calc. for $C_8H_8O_3S.H_2O$: S, 15.87; H_2O, 8.92. Found: S, 15.67, 15.45; H_2O, 9.09.

The monohydrate was readily converted to the anhydrous ester by drying it in a vacuum desiccator or by warming it first at 55° and later at 70° for 4–6 hours. The anhydrous ester was recrystallized from benzene or chloroform, and when pure melted at 97–98° (corr.).

Analyses. Subs., 0.1447, 0.1409: $BaSO_4$, 0.1833, 0.1762. Calc. for $C_8H_8O_3S$: S, 17.41. Found: 17.40, 17.17.

Bis(*p*-nitrobenzoyl)-methyl-thiol-β-resorcylate, $((p)\mathrm{NO_2C_6H_4CO_2})_2\mathrm{C_6H_3COCSH_3}$.—Three g. of methyl-thiol-β-resorcylate in 40 cc. of 10% sodium hydroxide solution was shaken with 11.1 g. of pulverized *p*-nitrobenzoyl chloride and the shaking continued until heat was no longer evolved and the acid chloride had disappeared. The precipitate was filtered, washed with water, extracted with boiling alcohol and finally recrystallized from ethyl acetate as colorless crystals; m. p., 214–216° (corr.).

Analyses. Subs., 0.1203, 0.1176: $\mathrm{BaSO_4}$, 0.0597, 0.0570. Subs., 0.1351, 0.3062: 2.881, 6.399 cc. of 0.1930 *N* HCl. Calc. for $\mathrm{C_{22}H_{14}O_9N_2S}$: S, 6.65; N, 5.81. Found: S, 6.81, 6.66; N, 5.77, 5.65.

Ethyl-thiol-β-resorcylate, $\mathrm{(HO)_2C_6H_3COSC_2H_5}$.—Five g. of pure imide hydrochloride in 200 cc. of water and 5 cc. of 15% hydrochloric acid, refluxed for 2 hours, gave a reddish oil. This was extracted with ether and the solution washed with dil. hydrochloric acid, then dil. sodium bicarbonate and finally with water. The ether solution was placed in a vacuum desiccator over sulfuric acid. The ether was evaporated and an oil was left which gradually solidified. It was a substance difficult to purify. The crude product was dissolved in a little ether, and a little petroleum ether added to precipitate the colored material, the solution filtered, evaporated in a vacuum desiccator over sulfuric acid, and the residual oil inoculated with a crystal of thiol ester. After two such treatments, white crystals were obtained melting at 60–61°.

Analyses. Subs., 0.1614, 0.1241: $\mathrm{BaSO_4}$, 0.1846, 0.1410. Calc. for $\mathrm{C_9H_{10}O_3S}$: S, 16.18. Found: 15.71, 15.60.

Bis(*p*-nitrobenzoyl)-ethyl-thiol-β-resorcylate, $((p)\mathrm{NO_2C_6H_4CO_2})_2\mathrm{C_6H_3COSC_2H_5}$.—This substance was made by the method described for the methyl derivative. The product was crystallized from ethyl acetate as white crystals; m. p., 190–191° (corr.).

Analyses. Subs., 0.1962, 0.2413: 4.210, 5.190 cc. of 0.1917 *N* HCl. Calc. for $\mathrm{C_{23}H_{16}O_9N_2S}$: N, 5.65. Found: 5.76, 5.78.

***n*-Butyl-thiol-β-resorcylate,** $\mathrm{(HO)_2C_6H_3COSC_4H_9}(n)$.—After refluxing 13 g. of pure *n*-butyl-thiol-β-resorcylate-imide hydrochloride in 200 cc. of water for 2–3 hours, thiol ester was obtained in the form of a light brown oil. To obtain this as a solid was impossible and consequently purification was difficult. For identification it was converted into the bis-*p*-nitrobenzoate.

Bis(*p*-nitrobenzoyl)*n*-butyl-thiol-β-resorcylate, $((p)\mathrm{NO_2C_6H_4CO_2})_2\mathrm{C_6H_3COSC_4H_9}$-$(n)$.—Upon treatment of this oil with *p*-nitrobenzoyl chloride as described for the methyl ester, a solid product was obtained. This was extracted twice with boiling alcohol, then recrystallized from ethyl acetate. When pure it was a colorless compound; m. p., 115–116° (corr.).

Analyses. Subs., 0.1555, 0.1200: $\mathrm{BaSO_4}$, 0.0657, 0.0561. Subs., 0.2968, 0.2819; 6.073, 5.518 cc. of 0.1930 *N* HCl. Calc. for $\mathrm{C_{25}H_{20}O_9N_2S}$: S, 6.12, N, 5.35. Found: S, 5.80, 6.42; N, 5.53, 5.29.

Methyl-thiol-2,4,6-trihydroxy-benzoate, $\mathrm{(HO)_3C_6H_2COSCH_3}$.—A solution of 3.5 g. of pure methyl-thiol-2,4,6-trihydroxy-benzoate-imide hydrochloride in 250 cc. of water and 15 cc. of 15% hydrochloric acid was refluxed for 8 to 10 hours, cooled and extracted with ether. A pink solid was obtained which was purified by recrystallization from 10% alcohol. After drying at 100–110° the product was white and melted at 190° (corr.).

Analyses. Subs., 0.1474, 0.1142: $\mathrm{BaSO_4}$, 0.1735, 0.1341. Calc. for $\mathrm{C_8H_8O_4S}$: S, 16.02. Found: 16.16, 16.13.

Methyl-β-resorcylate-imide, $\mathrm{(HO)_2C_6H_3C({=}NH)OCH_3}$.—A mixture of 200 cc. of absolute methyl alcohol and 7 g. of methyl-thiol-β-resorcylate-imide was refluxed for 2 hours. The alcohol was then distilled, leaving a reddish-brown solid. This was recrystallized from methyl alcohol, giving white needles; m. p., 210° (corr.).

Analyses. Subs., 0.1648, 0.1809: 5.026, 5.643 cc. of 0.1930 *N* HCl. Calc. for $C_8H_9O_3N$: N, 8.39. Found: 8.25, 8.44.

This base was converted into the corresponding hydrochloride by saturation of a small amount of a hot 15% hydrochloric acid solution with the free imido ester and filtration. The crystals, formed as the solution cooled, were purified by recrystallization from 15% hydrochloric acid, and the purified product melted at 166–168° and was presumably a hydrate, since upon drying in a vacuum desiccator the melting point changed to 224–226° (corr.) where it remained constant.

Analyses. Subs., 0.2585, 0.2182: 6.399, 5.415 cc. of 0.1930 *N* HCl. Calc. for $C_8H_{10}O_3NCl$: N, 6.88. Found: 6.70, 6.71.

n-Butyl-thiol-β-resorcylate-imide also was readily converted into the methyl-β-resorcylate-imide in the same way. After a mixture of 5 g. of pure *n*-butyl-thiol-β-resorcylate-imide and 50 cc. of absolute methyl alcohol was refluxed for about 1 hour a homogeneous solution formed and in another hour colorless crystals began to appear. The refluxing was continued for 2–3 hours longer and then the mixture was allowed to stand overnight. The product was filtered and more crystals were obtained by dilution of the filtrate. The material was purified from methyl alcohol after which it melted at 210° (corr.). This material was also converted into the hydrochloride which corresponded exactly to the one described just above.

Ethyl-β-resorcylate-imide, $(HO)_2C_6H_3C(=NH)OC_2H_5$.—A mixture of 5 g. of pure ethyl-thiol-β-resorcylate-imide and 100 cc. of absolute ethyl alcohol was refluxed for 5 hours and then cooled when crystals separated. These were removed and from the filtrate more were recovered by evaporation of the alcohol. The product was purified by crystallization from ethyl alcohol; m. p., 214° (corr.).

Analyses. Subs., 0.2301, 0.1681: 6.461, 4.896 cc. of 0.1930 *N* HCl. Calc. for $C_9H_{11}O_3N$: N, 7.74. Found: 7.59, 7.88.

Methyl-β-resorcylate from Methyl-β-resorcylate-imide, $(HO)_2C_6H_3CO_2CH_3$.—A suspension of 0.5 g. of methyl-β-resorcylate-imide in 20 cc. of water, treated with just enough dil. hydrochloric acid to cause complete solution, was refluxed for 2 hours and then cooled, whereupon white crystals separated. These were filtered, washed with a little cold water and crystallized from benzene or a little 50% alcohol. After crystallization they melted at 116–117° (corr.) and proved to be identical with methyl-β-resorcylate made by esterification of β-resorcylic acid.[8] The methyl ester was also obtained by merely boiling methyl-β-resorcylate-imide hydrochloride with water.

Ethyl-β-resorcylate from Ethyl-β-resorcylate-imide $(HO)_2C_6H_3CO_2C_2H_5$.—A solution of 0.75 g. of ethyl-β-resorcylate-imide in 30 cc. of water and 1 cc. of 15% hydrochloric acid was refluxed for about 1 hour. Hydrolysis took place and ethyl-β-resorcylate separated as an oil. This was cooled with ice until it solidified, and the solid was filtered and recrystallized from water. After drying for 36 hours in a desiccator it melted at 69–70° (corr.). The same product was obtained also from β-resorcylic acid by refluxing it for 10 hours with absolute alcohol saturated with dry hydrogen chloride. The alcohol was then distilled, the residue washed with dil. sodium bicarbonate solution, and the red oil which resulted was distilled under diminished pressure (b. p., 13–15 mm., 170–176°). The distillate solidified and was purified further by crystallization from water. After drying, it melted at 69–70° and proved to be identical with the product described above.

Analysis. Subs., 0.2605: 331 cc. of CO_2 (25°, 742.5 mm.). Calc. for $C_9H_{10}O_4$: C, 59.31. Found: 59.00.

β-Resorcylic Acid from Methyl-thiol-β-resorcylate.—A solution of 10 g. of methyl-thiol-β-resorcylate in 100 cc. of 10% potassium hydroxide solution was heated on a water-

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[8] Baeyer, *Ann.*, **372**, 85 (1910).

bath at about 70° for 30 hours, cooled and acidified just to the point at which congo red paper changed color, when a precipitate of β-resorcylic acid formed. The solution and precipitate were extracted a few times with ether, and the β-resorcylic acid again obtained in an aqueous solution by shaking the ether extract with a solution of sodium bicarbonate. The aqueous solution was neutralized as before, the free acid extracted with ether, and the ether solution dried and then evaporated. About 4 g. of solid was thus obtained which was crystallized once from water and bone charcoal and once from water. White crystals resulted which after drying melted at 215–217° with evolution of carbon dioxide. A mixed melting point with resorcylic acid[9] made in the usual way gave no depression.

Summary

1. Alkyl and aryl thiocyanates, as represented by methyl, ethyl, *n*-butyl and phenyl thiocyanates, were condensed with resorcinol and phloroglucinol in the presence of anhydrous ether, dry hydrogen chloride and anhydrous zinc chloride. The products which were obtained were imido thiol ester hydrochlorides.

2. These substances, upon treatment with sodium bicarbonate, were converted into the imido thiol esters.

3. The imido thiol ester hydrochlorides, refluxed in aqueous solution, were hydrolyzed to thiol esters. These substances, upon saponification, yielded compounds containing a carboxyl group.

4. The imido thiol esters, upon treatment with alcohols as represented by the formula R'OH, were converted upon long standing or refluxing into the corresponding imido esters. These oxygen imido esters, upon treatment with acids, yielded the corresponding salts, or when boiled with acids were decomposed into the corresponding carboxylic esters.

5. From these results it is obvious that the cyanogen group in thiocyanates acts similarly to the cyanogen group in alkyl cyanides when treated with certain types of phenols, hydrogen chloride and anhydrous zinc chloride.

URBANA, ILLINOIS

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[9] Kostanecki, *Ber.*, **18**, 1985 (1885). Nierenstein, *J. Chem. Soc.*, **107**, 1494 (1915).