Summary

1. Potassium azido-dithiocarbonate, found by analysis to have the formula $KSCSN_3$, may be prepared by the action of carbon disulfide upon potassium trinitride in aqueous solution.

2. The colorless, unstable, deliquescent crystals of this azido salt decompose quantitatively when gently heated, yielding potassium thiocyanate, sulfur and nitrogen, or explode when rapidly heated, with formation of potassium sulfide, carbon dioxide, sulfur dioxide and trioxide in addition to these products.

3. Solutions of the azido salt when treated with various oxidizing agents, or when subjected to electrolysis yield azido-carbondisulfide, $(SCSN_3)_2$.

ITHACA, NEW YORK

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

CONDENSATION OF CERTAIN NITRILES AND VARIOUS POLYHYDROXYPHENOLS TO FORM PHENOLIC ACIDS

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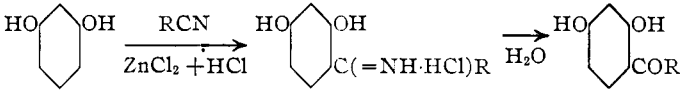
From the time Hoesch[2] first discovered that nitriles reacted with certain phenols in the presence of anhydrous zinc chloride and dry hydrogen chloride to give ketones according to the following equations



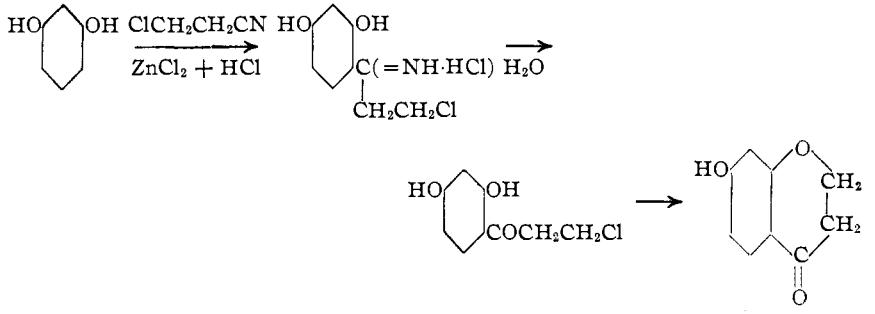
this reaction has been applied extensively in organic chemistry. It has proved of particular value in the synthesis of various natural products, in the preparation of certain synthetic drugs, in the formation of coumaranones, and various other types of ketones and aldehydes.[3]

Another application of this reaction, namely, the condensation of β-chloro-propionitrile with resorcinol to prepare 7-hydroxychromanone-4 was tried as follows:

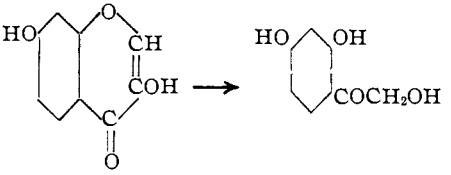
[1] This communication is an abstract of a thesis submitted by W. D. Langley in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Hoesch, *Ber.*, **48**, 1122 (1915).

[3] (a) Hoesch, *ibid.*, **50**, 462 (1917). (b) Sonn, *ibid.*, **50**, 1262 (1917); (c) **51**, 821. 1829 (1918); (d) **52**, 923 (1919). (e) Stephen, *J. Chem. Soc.*, **117**, 309, (f) 1529 (1920). (g) Karrer, *Helvetica Chim. Acta*, **2**, 89, 462, 486 (1919); **3**, 261, 392, 541 (1920); **4**, 203, 707 (1921). (h) Fischer, *Ber.*, **50**, 611, 693 (1917). (i) Bauer, *Arch. Pharm.*, **259**, 53 (1921).

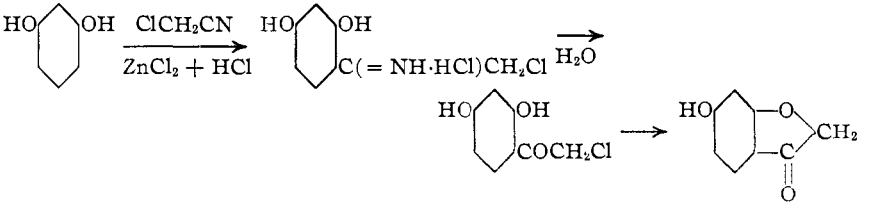


from which by treatment with butyl nitrite and acid the compound 3,7-dihydroxychromone-4 would be produced. This compound with alcoholic sodium hydroxide should give fisetol.



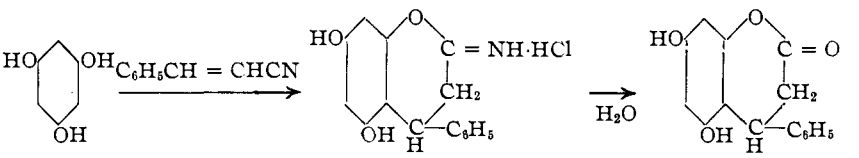
The initial reaction, however, did not take place as expected and the results of the abnormal reaction are reported in this communication.

The condensation of β-chloro-propionitrile with resorcinol takes place smoothly. The final product is not a ketone but an acid, β-(2,4-dihydroxy-phenyl)propionic acid (III). The formation of analogous compounds takes place when resorcinol monomethyl ether, orcinol or phloroglucinol is used; in the cases of orcinol or phloroglucinol unstable acids are produced which immediately decompose into water and the corresponding lactones. In no instance during these experiments, however, was the formation of any ketone observed. This is a surprising type of reaction in view of the fact that chloro-acetonitrile condenses normally with resorcinol[3b] as follows.



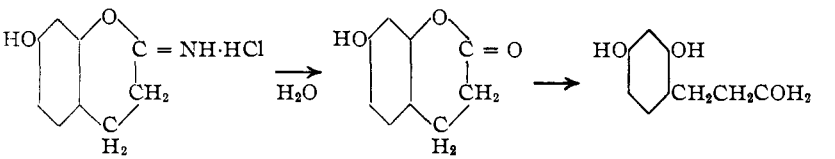
There have already been described in the literature other types of nitriles which condense abnormally with resorcinol in the presence of hydrogen chloride and zinc chloride. E. Fischer discovered that cinnamo-

nitrile and certain substituted cinnamonitriles condense with phloroglucinol,[3h] not as would be expected, but instead to give the corresponding substituted chromanones according to the following equation,



a reaction which is very similar to that observed in this research. Fischer assumed as a mechanism for this reaction that the phloroglucinol first adds to the unsaturated nitrile and that the hydrogen chloride then converts the nitrile produced into the imide lactone which in turn is readily hydrolyzed to the lactone. This mechanism seems unlikely in view of the observations made with β-chloro-propionitrile. It is well known that unsaturated nitriles add halogen acid[4] with great ease so that the primary reaction with cinnamonitrile is undoubtedly the addition of hydrogen chloride. There will thus be produced a β-chloro-propionitrile derivative and the subsequent mechanism will undoubtedly be similar to that observed with β-chloro-propionitrile itself.

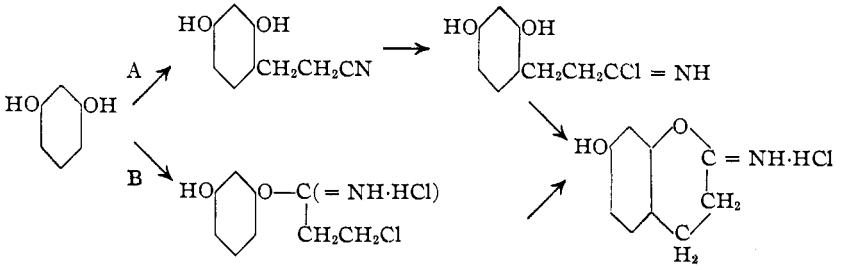
When the β-chloro-propionitrile is condensed with resorcinol in anhydrous ether in the presence of hydrogen chloride, a white solid slowly separates. This is difficult to purify, contains both chlorine and nitrogen, and probably has Structure I.



When I is treated with cold water, it dissolves completely, and within about a minute an oil separates which on cooling solidifies. This is the lactone, II, and is formed in practically quantitative yields. The structure of this lactone is certain, as shown by a direct synthesis from umbelliferone, the corresponding unsaturated lactone. Upon heating either the lactone or the imide hydrochloride with water, the corresponding β-(2,4-dihydroxyphenyl)propionic acid (III) is obtained.

There are two possible mechanisms by which these substances might be formed.

[4] Moureu, *Bull. soc. chim.*, **27**, 901 (1920).



IV II

At first Mechanism B might seem the more likely since Stephen[3f] has presented evidence that the mechanism of the reaction of nitriles with resorcinol to give ketones is first a condensation of the cyano group with the phenolic hydroxyl group yielding a structure similar to that in (IV), then rearrangement of the group into the ring, and finally hydrolysis. If such a primary mechanism is assumed in the case at hand, it is necessary merely to suppose that in Compound IV the reaction of the chlorine attached to the carbon atom with the hydrogen in the *ortho* position in the benzene ring to eliminate the halogen acid and to form a ring structure, has a greater tendency to take place than the rearrangement of the $-C(=NH\cdot HCl)CH_2CH_2Cl$ group from the oxygen to the *ortho* carbon atom, and then the formation of a ring. This mechanism B, is shown to be incorrect, however, since it is possible in the case of the condensation of β-chloro-propionitrile with resorcinol monomethyl ether to isolate a nitrile V. The formation of such an intermediate excludes the possibility of the primary formation of Compound IV, and is strong evidence for Mechanism A.

The condensation of β-chloro-propionitrile with resorcinol does not take place in the presence of anhydrous zinc chloride alone. From this it might be concluded that the hydrogen chloride which must be present for the condensation to take place first reacts with the β-chloro-propionitrile to give a chloro-imide and that this resulting compound condenses with the resorcinol. The fact that the condensation takes place slowly in the presence of hydrogen chloride alone is further evidence for this mechanism. However, conclusive proof that the correct mechanism is presented by Mechanism A is afforded in the condensation with resorcinol monomethyl ether, by the isolation of the nitrile, V.

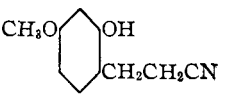
The condensation of resorcinol, orcinol and phloroglucinol with acrylic nitrile also runs smoothly and yields the same phenolic lactones or acids as are produced by using β-chloro-propionitrile.

It seemed possible, since the chlorine in the β position to a cyano group reacts so readily with resorcinol, that the chlorine in β-chloro-propionic ester, or even that the halogen in such compounds as allyl bromide, or trimethylene bromide might also condense under the same conditions.

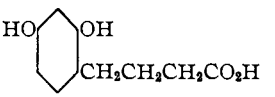
However, it is impossible to cause any condensation with these substances, thus indicating that the cyano group undoubtedly plays an important part in the reaction.

An attempt was also made to condense β-chloro-propionitrile with phenol in presence of zinc chloride and hydrogen chloride, but no reaction occurred.

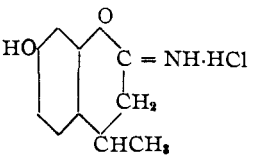
More surprising is the fact that γ-chloro-butyronitrile also reacts abnormally with resorcinol to give 2 unstable intermediate compounds which hydrolyze to γ-(2,4-dihydroxyphenyl)butyric acid, VI.



V



VI



VII

The compound which is obtained directly from the original reaction mixture, is probably the chloro-imide hydrochloride. Upon washing with water, it is converted into a compound containing less chlorine, perhaps a chloro-imide, which by contact with water for a longer time is hydrolyzed to the acid. The intermediate compounds were difficult to obtain pure so that their structure was not definitely established. The yields are lower, to be sure, than in the case of the β-chloro-propionitrile–resorcinol condensation; nevertheless, the reaction takes place with comparative ease and apparently gives no product in which the cyano group condenses directly with the ring to give a ketone. The reaction of γ-chloro-butyronitrile with orcinol or phloroglucinol does not go readily and no well defined products were isolated.

The constitution of Compound VI from γ-chloro-butyronitrile and resorcinol was proved by analysis, and by the fact that it does not form the corresponding lactone under the same conditions as does β-(2,4-dihydroxyphenyl)propionic acid. This fact excludes the possibility that γ-chloro-butyronitrile undergoes a transformation before reacting with the resorcinol, namely the elimination and re-addition of hydrogen chloride to give β-chloro-butyronitrile, which then would condense to give β-methyl β-(2,4-dihydroxyphenyl)propionic acid lactone imide hydrochloride, VII.

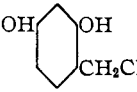
An attempt was made to condense ethylene cyanohydrin with resorcinol, but only a small amount of β-(2,4-dihydroxyphenyl)propionic acid was obtained from the reaction mixture. If any ketone was formed, it could not be isolated. The reaction does not run smoothly and this is probably due to the molecule of water which must necessarily be eliminated in the reaction. It is interesting, however, that the cyanohydrin of acetaldehyde condenses normally with resorcinol.[3e]

Experimental

β-Chloro-propionitrile, $ClCH_2CH_2CN$.—This substance was prepared according to the method of Henry[5], by the action of phosphorus pentachloride on ethylene cyanohydrin. The reaction was carried out in toluene suspension in preference to no solvent. For successful results in the following experiments, the product must be pure. After being freed as thoroughly as possible from phosphorus oxychloride by fractionation in a vacuum (20–25 mm.), the β-chloro-propionitrile fraction boiling at 65–72° at 20 mm. was poured carefully into cold water and shaken, the temperature being kept low. The oily nitrile was separated, washed with sodium carbonate solution, then with water, dried over anhydrous sodium sulfate, and finally purified by distillation in a vacuum.

Acrylic Nitrile, $CH_2=CHCN$.—This substance was prepared by the method of Moureu.[4]

γ-Chloro-butyronitrile, $ClCH_2CH_2CH_2CN$.—This was prepared from trimethylene chlorobromide and sodium cyanide according to the method of Gabriel.[6]

β-(2,4-Dihydroxyphenyl)propionic Acid  .—In a 2-liter round-bottom flask protected with a calcium chloride tube were placed 130 g. of C. P. resorcinol, 90 g. of pure β-chloro-propionitrile and 700 cc. of dry ether. To this solution was added 40 g. of zinc chloride which had been freshly fused and then powdered, and dry hydrogen chloride was passed in as long as there was any absorption. The flask was then tightly stoppered and allowed to stand overnight. Dry hydrogen chloride was again slowly passed in for 5 hours and the flask was allowed to stand for 36 hours longer. The mass of crystals which separated was sticky and hard to handle due to the presence of zinc chloride but was filtered from the red solution and washed with dry ether. The original filtrate was again stoppered and allowed to stand for 48 hours, during which 38 g. more of solid formed. After filtering and allowing the filtrate to stand for a week longer, 25 g. more of crystals was produced.

The total quantity of crystals was dissolved in 450 cc. of water and heated on a steam-bath for 4 hours. An oily layer of β-(2,4-dihydroxyphenyl)propionic acid lactone first separated which, if cooled, solidified. The layer however, was not removed, but the reaction mixture was heated further, thus causing the lactone to go gradually into solution. After this had cooled and stood for some hours, 86.5 g. of β-(2,4-dihydroxyphenyl)propionic acid crystallized and was filtered. The aqueous filtrate, upon evaporation in a vacuum to 175 cc. and cooling, yielded a second crop of crystals which weighed 22.5 g. Further concentration and cooling of the filtrate yielded only inorganic salts. The total yield of product was thus 109 g. (56%). The substance was almost always light brown and this color was difficult to remove even though several crystallizations from water and bone black were made. The substance always separated from the aqueous solution very slowly. In spite of the color, the product melted sharply at 165° with decomposition, the same point as pure white material obtained by hydrolysis of the pure lactone.

Analyses. Subs., 0.3679: CO_2, 0.7967; H_2O, 0.1799. Subs., 0.2973: 24.24 cc. of 0.0717 *N* NaOH. Calc. for $C_9H_{10}O_4$: C, 59.34; H, 5.49; neut. equiv., 182. Found: C, 59.05; H, 5.43; neut. equiv., 171.

This substance was prepared by Hlasiwetz[7] by the reduction of umbelliferone, but he stated that the acid decomposed when heated above 110°. In order to make certain

[5] Henry, *Bull. acad. roy. med. Belg.*, [3] **35,** 360 (1898).

[6] Gabriel, *Ber.*, **23,** 1771 (1890).

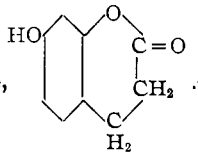
[7] Hlasiwetz, *Ann.*, **139,** 102 (1866).

that the compound which was obtained in this investigation had the structure assigned to it, umbelliferone was made by the action of malic acid upon resorcinol by means of conc. sulfuric acid. The product was carefully purified and then reduced with sodium amalgam as described by Hlasiwetz. Upon acidification with hydrochloric acid, red crystals formed, which were boiled with bone black in water solution, and filtered. Nearly colorless crystals melting at 165° were obtained which, when mixed with β-(2,4-dihydroxyphenyl)propionic acid, melted at the same temperature as when alone. For further confirmation, another sample of the acid was treated with excess of acetic anhydride and boiled for 20 minutes. The reaction mixture was poured into water to decompose the excess of anhydride, and the brown solid which separated was filtered, washed and crystallized from 20% methyl alcohol. A white powder, the acetate of dihydro-umbelliferone, [β-(2-hydroxy-4-acetoxyphenyl)propionic acid lactone], was thus produced which melted at 112° and proved to be identical with the compound prepared by the action of acetic anhydride on β-(2,4-dihydroxyphenyl)propionic acid made from resorcinol and β-chloro-propionitrile.

β-(2,4-Dihydroxyphenyl)propionic acid may also be made by the action of acrylic nitrile upon resorcinol. A solution of 12 g. of resorcinol and 6 g. of acrylic nitrile in 70 cc. of dry ether was treated with 4 g. of freshly fused and powdered zinc chloride, after which dry hydrogen chloride was passed in until the solution was saturated. At the end of 12 hours, a heavy white crystalline product had formed. The ether was decanted and a small portion of the solid treated directly with water. There was thus produced β-(2,4-dihydroxyphenyl)propionic acid lactone, which melted at 133–134°, and proved to be identical with the substance prepared from resorcinol and β-chloro-propionitrile.

The remainder of the solid was boiled with 50 cc. of water for a half hour, and then allowed to stand. Crystals separated which proved to be β-(2,4-dihydroxyphenyl)-propionic acid.

β-(2,4-Dihydroxyphenyl) propionic Acid Lactone,

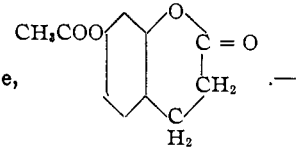


.—β-(2,4-Dihydroxyphenyl)propionic acid was heated in an oven at 130–135° for 2 hours. The melt which formed was allowed to cool and the product then crystallized from toluene. White cubical crystals resulted which, upon complete purification melted at 132–133°. This substance is identical in all respects with that obtained by the treatment of the original reaction product of resorcinol and β-chloro-propionitrile with cold water.

Analyses. Subs., 0.1560: CO_2, 0.3795; H_2O, 0.0072. Calc. for $C_9H_8O_3$: C, 65.85; H, 4.88. Found: C, 66.33; H, 4.96.

The substance was insoluble in sodium carbonate until the solution was heated, when it dissolved. Upon acidification with acid β-(2,4-dihydroxyphenyl)propionic acid gradually deposited in the form of hard crystals.

β-(2-Hydroxy-4-acetoxyphenyl)propionic Acid Lactone,



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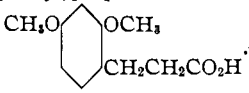
A solution of 7 g. of β-(2,4-dihydroxyphenyl)propionic acid in 10 g. of acetic anhydride was heated on a water-bath for an hour. A red solution was produced; this was cooled and then poured into 70 cc. of cold water when a yellow crystalline solid separated

which weighed 9 g. Upon crystallization from 20% methyl alcohol the substance was readily obtained pure and formed white crystals melting at 111–112°.

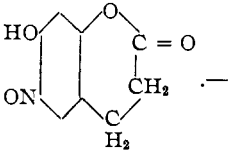
Analyses. Subs., 0.3116, 0.3278: CO_2, 0.7382, 0.7742; H_2O, 0.1357, 0.1387. Calc. for $C_{11}H_{10}O_4$: C, 64.1; H, 4.89. Found: C, 64.63, 64.40; H, 4.83, 4.67.

It was insoluble in sodium carbonate until heated. Upon hydrolysis either with sodium carbonate or water, β-(2,4-dihydroxyphenyl)propionic acid resulted.

β-(2,4-Dimethoxyphenyl)propionic Acid,  .—A solution of 35 g. of β-(2,4-dihydroxyphenyl)propionic acid in 100 cc. of 10% sodium hydroxide was treated with 36 g. of dimethyl sulfate. The mixture was thoroughly shaken for some minutes and then heated on a water-bath under a reflux condenser. After the initial reaction had taken place, 100 cc. more of 10% sodium hydroxide solution and 35 g. of dimethyl sulfate were added and the mixture was again heated until the dimethyl sulfate was completely decomposed. Upon cooling the reaction mixture and acidifying with hydrochloric acid, needle-like crystals separated. The yield was 28.5 g. (68%). It was readily purified by crystallization from water and then melted at 102.5–103.5°.

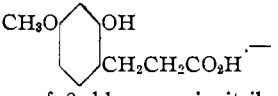
Analyses. Subs., 0.2991: CO_2, 0.6896; H_2O, 0.1739. Subs., 0.1260: 8.7 cc. of 0.0717 *N* NaOH. Calc. for $C_{11}H_{14}O_4$: C, 62.8; H, 6.6; neut. equiv., 210. Found: C, 62.87; H, 6.5; neut. equiv., 201.

This substance is without doubt the same as that prepared by W. Will[8] by the reduction of dimethoxy-umbellic acid. He reported the melting point as 105°.

β-(5-Nitroso-2,4-dihydroxyphenyl)propionic Acid Lactone,  .—A solution of 3 g. of β-(2,4-dihydroxyphenyl)propionic acid in 50 cc. of alcohol was treated with 4 g. of freshly distilled butyl nitrite. The flask was then cooled and 10 cc. of conc. hydrochloric acid added. Fumes of nitrogen dioxide were evolved, heat was generated, and a red precipitate was formed. An additional 40 cc. of conc. hydrochloric acid was then added and the flask allowed to stand for about 30 minutes. The solid was filtered, washed twice with cold water, and dried. The yield was 4 g. The crude material varied in color in different experiments from a cream color to red, and upon exposure to air it generally turned green. The crude substance was purified by dissolving 4 g. in 70 cc. of boiling water, filtering hot and allowing to cool. In spite of the fact that the aqueous solution was green, a cream-colored solid separated. Upon filtering, washing and drying over sulfuric acid in a vacuum desiccator, the product did not change color and melted sharply at 147.5–148°, with decomposition.

Analysis. Subs., 0.1873: N_2, 13.1 cc. (26° and 737 mm.). Calc. for $C_9H_7O_4N$: N, 7.25. Found: 7.61.

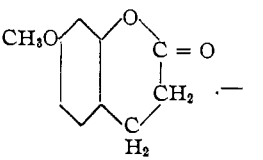
This substance could not be formed by treatment of β-(2,4-dihydroxyphenyl)-propionic acid lactone with butyl nitrite, but had to be prepared from the acid.

β-(2-Hydroxy-4-methoxyphenyl)propionic Acid,  .—A mixture of 30 g. of resorcinol monomethyl ether and 22 g. of β-chloro-propionitrile

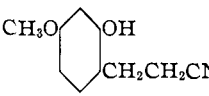
[8] Will, *Ber.*, **16**, 2116 (1883).

in 300 cc. of dry ether was treated with 20 g. of freshly fused and powdered zinc chloride. The mixture was cooled in an ice-bath and dry hydrogen chloride passed in until the ether was saturated. Upon standing overnight, a sirupy mass deposited. The ether was decanted and the residue treated with 30 cc. of water. After standing for 15 hours, a small amount of solid and some liquid separated. The oil (10 g.) was filtered from the solid (3.5 g.) by the use of suction. The solid, upon crystallization from water, was obtained pure and melted at 138–139.5°. It proved to be β-(2-hydroxy-4-methoxyphenyl)propionic acid.

Analyses. Subs., 0.3819: CO_2, 0.8604; H_2O, 0.1982. Calc. for $C_{12}H_{10}O_4$: C, 61.2; H, 6.1. Found: C, 61.4; H, 5.8.

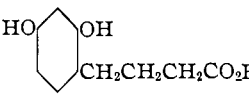
β-(2-Hydroxy-4-methoxyphenyl)propionic Acid Lactone,  .—

The oil obtained by filtration of the β-(2-hydroxy-4-methoxyphenyl)propionic acid was insoluble in cold sodium hydroxide solution, but dissolved on heating. It could not be distilled under a pressure of 6 mm. It was found, however, that by boiling the oil with sodium carbonate solution for some time, and acidifying the resulting solution, it was converted completely into β-(2-hydroxy-4-methoxyphenyl)propionic acid, which melted at 138–139°. The same oil was produced by heating β-(2-hydroxy-4-methoxyphenyl)-propionic acid in an oven at 132° and was, therefore, without doubt β-(2-hydroxy-4-methoxyphenyl)propionic acid lactone.

β-(2-Hydroxy-4-methoxyphenyl)propionitrile,  .—The ether solution which was decanted from the original reaction mixture between β-chloropropionitrile and resorcinol monomethyl ether was evaporated in a vacuum and about 12 g. of unchanged β-chloro-propionitrile recovered. A higher-boiling fraction of resorcinol monomethyl ether (21 g.) was also obtained. The residue in the flask solidified on cooling. It was purified by crystallization from dil. alcohol and then melted at 126.5–127.5°. Analysis showed it to be β-(2-hydroxy-4-methoxyphenyl)propionitrile.

Analyses. Subs., 0.3718: N_2, 27.2 cc. (28° and 749 mm.). Subs., 0.2968: CO_2, 0.7353. Calc. for $C_{10}H_{11}O_2N$: C, 67.6; H, 6.2; N, 7.9. Found: C, 67.5; H, 6.5; N, 8.0.

It was insoluble in sodium carbonate but soluble in sodium hydroxide solution and was recovered unchanged upon acidification. When it was boiled with alkali ammonia was evolved and, after acidification, β-(2-hydroxy-4-methoxyphenyl)propionic acid was obtained.

γ-(2,4-Dihydroxyphenyl)butyric Acid,  .—A mixture of 64 g. of resorcinol and 60 g. of γ-chloro-butyronitrile was dissolved in 400 cc. of dry ether; 30 g. of fused and powdered zinc chloride was added, and dry hydrogen chloride was passed in rapidly for 2 hours. The flask was then sealed, and allowed to stand. Hydrogen chloride was passed in for 1 hour on each of 2 successive days, and the flask was allowed to remain sealed for 4 more days. By that time the oil which had separated had entirely crystallized. The ether was filtered and the solid dissolved in 250 cc. of water, heated for 3 hours on a steam-bath and then cooled. The crystals which slowly formed were filtered and dried, and weighed 24.5 g. (20.8%).

For purification, 10 g. of the product was dissolved in 57 cc. of boiling water, and filtered hot. An oil separated, which when cooled and stirred, solidified. The weight recovered was 9.5 g., and the substance melted at 89–99°. Repeated crystallization did not make this melting point sharper, but after the melt had been allowed to solidify, it remelted at 118–119°. This indicated that the low-melting product contained water of crystallization, and a moisture determination confirmed this.

Analyses. Subs., 0.7322, 0.5297: H_2O, 0.0655, 0.0471. Calc. for $C_{11}H_{12}O_4.H_2O$: H_2O, 8.4. Found: H_2O, 8.94, 8.89.

The anhydrous product was readily crystallized from benzene in the form of colorless plates, and melted at 118.5–119°.

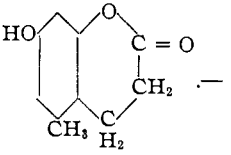
Analyses. Subs., 0.1628: CO_2, 0.3640; H_2O, 0.0865. Subs., 0.1491: 9.98 cc. of 0.0717 *N* NaOH. Calc. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.12; neut. equiv., 198. Found: C, 60.96; H, 5.95; neut. equiv., 208.

A portion of the anhydrous γ-(2,4-dihydroxyphenyl)butyric acid was heated in an oven at 133–134° for 0.5 hour. The solid melted to a red liquid which solidified on cooling and, upon recrystallization from benzene, proved to be unchanged starting material. Therefore, no lactone of this acid formed under the same conditions as were used with β-(2,4-dihydroxyphenyl)propionic acid.

In order to study the intermediate products formed in the condensation of resorcinol and γ-chloro-butyronitrile, another condensation was made under the same conditions as are given above. The initial crystalline reaction product was treated with water, warmed to 50°, cooled, and the solution partly neutralized with dil. sodium carbonate solution. The oil which formed solidified, and the resulting substance was filtered and washed with dil. hydrochloric acid. It was a white powder, melting at 214–216°, but when it was washed with water the color changed to a canary-yellow, and the melting point dropped to 190–192°. When the yellow compound was washed with methyl alcohol saturated with hydrogen chloride, it became white, and the original higher-melting product resulted.

The wash waters, on standing, gave a small amount of white solid which proved to be β-(2,4-dihydroxyphenyl)butyric acid.

β-(2,4-Dihydroxy-6-methylphenyl)propionic Acid Lactone,



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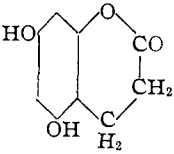
Five g. of orcinol and 5 g. of β-chloro-propionitrile were dissolved in 100 cc. of dry ether, and 5 g. of freshly fused and powdered zinc chloride added. The ether was cooled in an ice-bath, and dry hydrogen chloride passed in until the ether was saturated. A white solid formed overnight, and after 10 hours there appeared to be no more deposit forming. The ether was decanted, the solid washed with dry ether, treated with 20 cc. of water, warmed to 50° and cooled in an ice-bath. The oil which formed could not be made to crystallize, even when dry toluene was used as the solvent. The heating was, therefore, continued and ammonia was added until the solution was just neutral. After 1 hour the solution was boiled with bone black, filtered and acidified with hydrochloric acid. On cooling, an oil layer separated which slowly solidified on standing. This was filtered and dried, when it weighed 4 g. and melted at 125–133°. It was recrystallized from hot dil. methyl alcohol, 4 g. dissolving in 90 cc. of 10% alcohol; 1.7 g. of solid was obtained melting at 140–141.5°. The remainder of the product came out as an oil which solidified after 2 weeks' standing. This was again boiled with bone black and filtered, when 0.2 g. more of solid was obtained.

Analyses. Subs., 0.3923: CO_2, 0.9641; H_2O, 0.1934. Calc. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.6. Found: C, 67.01; H, 5.5.

This product was difficultly soluble in hot water, but readily soluble in hot alkali. Since the lactone was obtained on acidification of the alkaline solution, the acid is not stable under ordinary conditions. The same product was obtained in a purer form from acrylic nitrile, 3.6 g. being obtained from 5 g. of orcinol and 2.3 g. of acrylic nitrile.

β-(2,4,6-Trihydroxyphenyl)propionic Acid Lactone,  .—Five g. of pure phloroglucinol, dried at 120° to free it from water of crystallization, and 5 g. of β-chloro-propionitrile were dissolved in 100 cc. of dry ether, and 4 g. of powdered zinc chloride was added. The flask was cooled and dry hydrogen chloride was passed in until the solution was saturated. The mixture was allowed to stand for 20 hours, the ether was decanted from the solid which had separated and the residue washed with dry ether. It was then treated with 20 cc. of water, warmed to about 40° for 5 minutes, and cooled with ice. No oil layer separated. After standing for 24 hours, the water solution was extracted twice with 50 cc. portions of butyl alcohol, the butyl alcohol in turn washed with water, and the wash water extracted with fresh butyl alcohol. The butyl alcohol was distilled in a vacuum and 10–12 g. of dark brown liquid was obtained. This was taken up in 150 cc. of boiling water, heated until all of the butyl alcohol had been removed, treated with bone black, and filtered. The filtrate was light brown, and from it there separated about 5 g. of a viscous oil. This could not be obtained crystalline. It changed to a glassy mass on standing for a long time in a desiccator over sulfuric acid, and could not be crystallized from anhydrous solvents.

This oil decomposed carbonate solutions when heated, and went into solution. On acidification, the oil formed again. Attempts were made to prepare derivatives of the oil, such as those with phenyl-isocyanate, diphenyl-carbamine chloride, and the acetate and benzoate. None of these could be obtained in crystalline form. Acrylic nitrile gave the same type of oil, which possessed all the properties of that obtained above.

Summary

1. β-Chloro-propionitrile condenses with resorcinol in the presence of anhydrous zinc chloride, hydrogen chloride and dry ether to give a crystalline intermediate product which hydrolyzes to form β-(2,4-dihydroxyphenyl)propionic acid.

2. By a similar procedure β-chloro-propionitrile and resorcinol-monomethyl ether give a mixture of β-(2,4-dihydroxyphenyl)propionitrile and the corresponding acid and lactone. From orcinol and phloroglucinol intermediate products are formed which give on hydrolysis the analogous lactones.

3. γ-Chloro-butyronitrile and resorcinol condense under similar conditions to give a product which hydrolyzes to form γ-(2,4-dihydroxyphenyl)butyric acid.

4. The mechanism by which the above products are formed is discussed.

URBANA, ILLINOIS