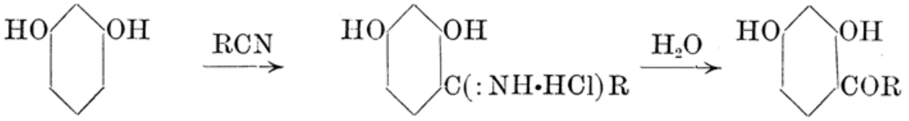
THE CONDENSATION OF RESORCINOL WITH ETHYLENE DICYANIDE.

By **Junkichi MURAI.**

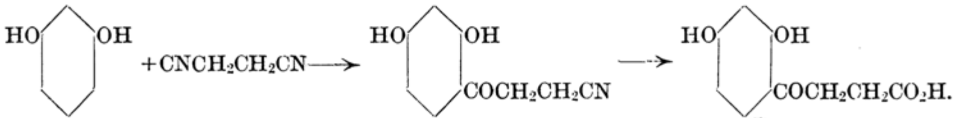
Received April 20, 1926. Published June 28, 1926.

Since Hoesch⁽¹⁾ first discovered that nitriles reacted with certain phenols, in the presence of anhydrous zinc chloride and dry hydrogen chloride, to give aromatic hydroxy-ketones according to the following scheme :



this reaction has been applied extensively in the preparation of carbonyl compounds. Sonn'⁽²⁾ applied this method to a dicyanide and found that o-cyanoacetyl phloroglucinol, $CNCH_2CO{\cdot}C_6H_2(OH)_3$, and 2:4:6:2':4':6'-hexahydroxydibenzoylmethane, $C_6H_2(OH)_3COCH_2COC_6H_2(OH)_3$, were obtained by the condensation of malonitrile with phloroglucinol.

With the view of synthesising phenolic γ-diketones, the author attempted to condense resorcinol with ethylene dicyanide by Hoesch's method. However, the action of ethylene dicyanide on resorcinol resulted in the production of a compound, which, from its composition and method of formation, was regarded as β-2:4-dihydroxybenzoylpropionic acid (I) :



(I)

The constitution of this acid was confirmed beyond doubt by the preparation of its salt, and by the formation of the dibenzoyl derivative and of the oxime of the dimethyl derivative.

Experimental.

Synthesis of β-2:4-Dihydroxybenzoylpropionic Acid, $C_6H_3(OH)_2COCH_2CH_2CO_2H$. (a) Twenty two grams of resorcinol (2 mols) and 8 grams of ethylene dicyanide (1 mol) were dissolved in absolute ether (100 c. c.) and, after the addition of 8 grams of freshly fused and powdered zinc chloride, a gentle stream of dry hydrogen chloride was passed into the liquid for four hours, the mixture being kept warm during this operation, when a red syrup

---

(1) *Ber.*, **48** (1915), 1122.

(2) *Ber.*, **50** (1917), 1292.

separated. After allowing to remain overnight and decanting the ether, the syrup was dissolved in 150 grams of ice-cold water, concentrated to about 100 c. c. on the water-bath and then cooled. The dark brown substance thus separated was crystallised once from water with the addition of animal charcoal, when it separated in grey crystals melting at 197–199.° The yield was 5.7 grams. As it is difficult to obtain these crystals so that they are free from any mineral matter by further recrystallisation, the acid was converted into its sodium salt, and, after recrystallising from water, the salt was acidified with hydrochloric acid, in order to regenerate the free acid, and again recrystallised several times from water. It was colourless crystals melting at 199–200°:

4.297 mg. subst. gave 9.020 mg. CO_2 and 1.966 mg. H_2O. (Found: C=57.25; H=5.12. $C_{10}H_{10}O_5$ requires C=57.12; H=4.80%).

(b) Since the interaction between resorcinol (2 mols) and ethylene dicyanide (1 mol) resulted in the formation of β-2:4-dihydroxybenzoylpropionic acid, the condensation was again carried out under the same conditions as in (a), except that 11 grams of resorcinol (1 mol) were used. The yield of β-2 : 4-dihydroxybenzoylpropionic acid was 5.7 grams after once crystallising from water.

The Sodium Salt. For the preparation of this salt, 3 grams of the crude β-2:4-dihydroxybenzoylpropionic acid were shaken with a concentrated solution of sodium carbonate until the evolution of carbon dioxide had ceased. The salt thus obtained was collected and recrystallised from small quantity of water, when it separated in colourless crystals (yield 3.9 grams). The air-dried salt lost 18.53% in weight when heated at 130° under reduced pressure. The anhydrous salt gave, on analysis, the following results:

5.154 mg. subst. gave 1.282 mg. Na_2SO_4 and 4.347 mg. subst. gave 1.102 mg. Na_2SO_4. (Found: Na=8.05 and 8.21. $C_{10}H_9O_5Na\cdot3H_2O$ requires H_2O=18.89; Na=8.04 %.)

The Benzoyl Derivative One gram of β-2:4-dihydroxybenzoylpropionic acid was dissolved in 5.5 c.c. of a 10% solution of sodium hydroxide and shaken with 1.1 c.c. of benzoyl chloride for two hours. After acidifying with dilute hydrochloric acid, the precipitate was collected, washed with water and dried (yield 1.3 grams). It crystallised from dilute methyl alcohol in colourless crystals, m. p. 146–147°:

4.698 mg. subst. gave 11.840 mg. CO_2 and 1.931 mg. H_2O. (Found: C=68.73; H=4.59. $C_{24}H_{18}O_7$ requires C=68.88; H=4.34%).

β-2:4-Dimethoxybenzoylpropionic Acid, $C_6H_3(OCH_3)_2COCH_2CH_2CO_2H$. β-2:4-Dihydroxybenzoylpropionic acid (5 grams) was dissolved in 25 c.c. of a 10% sodium hydroxide and shaken with 4.5 c.c. of methyl sulphate for two hours, when a small quantity of oil deposited, which was extracted with ether. The aqueous residue (A) and the ethereal extract (B) were treated in the following way.

The aqueous residue (A) was acidified with dilute hydrochloric acid and the precipitate was collected, washed with water and dried. After recrystallising several times from methyl alcohol with the addition of animal charcoal, it separated in colourless crystals and melted at 124–125.° The yield was 4.5 grams after one crystallisation.

The ethereal extract (B) was washed with water until free from alkali. After the evaporation of the ether, the residual oil was hydrolysed by warming it with a dilute solution of sodium hydroxide and the alkaline solution was acidified with hydrochloric acid. The precipitate was collected, washed with water, dried, and recrystallised from alcohol, when it melted at 124–125° and produced no depression of the melting point by admixture with β-2:4 dimethoxybenzoylpropionic acid:

4.645 mg. subst. gave 10.262 mg. CO_2 and 2.473 mg. H_2O. (Found: $C=60.25$; $H=5.96$. $C_{12}H_{14}O_5$ requires $C=60.48$; $H=5.93$ %).

The Oxime. A mixture of β-2:4-dimethoxybenzoylpropionic acid (0.2 gram), hydroxylamine hydrochloride (0.06 gram) and sodium acetate (0.12 gram) was dissolved in dilute alcohol and boiled for two hours under a reflux condenser. After the removal of the alcohol, the oxime separated, which crystallised from dilute methyl alcohol as colourless crystals melting at 155–156.° The quantity of the crude oxime amounted to 0.2 gram:

6.516 mg. subst. gave 0.307 c. c. nitrogen at 13° and 755.3 mm. (Found: $N=5.59$. $C_{12}H_{15}O_5N$ requires $N=5.53$%).

In conclusion, the author wishes to express his hearty thanks to Dr. Hiroshi Nomura, in whose laboratory this investigation was carried out.

Chemical Institute, Faculty of Science,
Tohoku Imperial University, Sendai.