THE APPLICATION OF THE HOESCH REACTION TO NITROBENZONITRILES.

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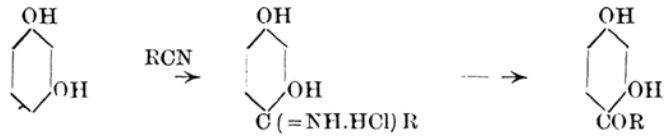
Since Hoesch[1] synthesised various aromatic hydroxy-ketones from nitriles and certain phenols in the presence of anhydrous zinc chloride and dry hydrogen chloride, as indicated in the following scheme :—



this reactions has been applied extensively in the preparation of various aromatic carbonyl compounds. So far as I am aware, this reaction has not yet been applied to the aromatic nitriles containing a nitro-group. The synthesis of such compounds seems interesting in that the resulting compounds might be used for the preparation of the derivatives of benzophenone having various substituents in the benzene nucleus, by converting these compounds into the corresponding amino-derivatives, and then diazotising the latter. When the condensation was over and the reduction of the condensation products was in progress, Korczynski and Nowakowski[2] had recently published the synthesis of *p*-nitrobenzoresorcinol and *p*-nitrobenzophloroglucinol for another purpose. Accordingly, the results already obtained are published in the present communication.

The present author attempted to condense resocinol or phloroglucinol with *o*-, *m*-, and *p*-nitrobenzonitriles by the Hoesch reaction. Whilst *o*-nitrobenzonitrile did not react with resorcinol or with phloroglucinol, *m*- and *p*-nitrobenzonitriles condensed to yield the nitro-derivatives of benzophenones. The yield of the derivative of phloroglucinol was much better than that of the corresponding derivative of resorcinol.

The reduction of the condensation products is now in progress.

(1) *Ber.*, **48** (1915), 1122.
(2) *Bull. Soc. Chim.*, 4 série, **43** (1928), 329.

Experimental.

In order to improve the yield of the condensation product of resorcinol with *m*- or *p*-nitrobenzonitrile, the quantity of the components was first varied and the following were found to be the best for the purpose.

4′-Nitro-2 : 4-dihydroxybenzophenone, $(NO_2)C_6H_4COC_6H_3(OH)_2$. Three grams of *p*-nitrobenzonitrile and 2.5 grams of resorcinol were dissolved in 150 c.c. of absolute ether, and, after adding two grams of freshly fused and powdered zinc chloride, a gentle stream of dry hydrogen chloride was passed into the solution for five hours at room temperature, when a brownish red oil separated. After allowing the solution to remain overnight and decanting the ether, the oil was washed with ether in order to remove the unchanged *p*-nitrobenzonitrile, and boiled with 50 c.c. of water for half an hour. As the crystals thus separated were contaminated with tarry matter, they were freed from the latter by collecting them while still hot. The yield of the crude product amounted to 0.9 gram. After being recrystallised from dilute alcohol, they separated in pale yellow crystals melting at 203° (Found : C = 60.29 ; H = 3.59 ; N = 5.97 ; Mol. wt., by the Rast method, 267. $C_{13}H_9O_5N$ requires C = 60.23 ; H = 3.50 ; N = 6.00%. Mol. wt., 259. 1).

Korczynski and Nowakowski[1] gave 200° as its melting point.

The Methyl Derivative, $(NO_2)C_6H_4COC_6H_3(OCH_3)_2$. 4′-Nitro-2 : 4-dihydroxybenzophenone (0.2 gram) was dissolved in 6 c.c. of a 10 per cent solution of sodium hydroxide and shaken with 1 c.c. of methyl sulphate for an hour, when a brownish compound (0.1 gram) separated. It crystallised from a mixture of ether and petroleum ether in pale yellow crystals, m.p. 123–124° (Found : C = 62.52 ; H = 4.65. $C_{15}H_{13}O_5N$ requires C = 62.71 ; H = 4.56%).

3′-Nitro-2 : 4-dihydroxybenzophenone, $(NO_2)C_6H_4COC_6H_3(OH)_2$. Three grams of *m*-nitrobenzonitrile and 2.5 grams of resorcinol were dissolved in 100 c.c. of absolute ether, and, after adding 3 grams of freshly fused and powdered zinc chloride, dry hydrogen chloride was gently passed into the solution for five hours at room temperature, as in the preparation of 4′-nitro-2 : 4-dihydroxybenzophenone, when a reddish brown oil was deposited. After allowing it to stand overnight and decanting the ether, the oil was washed with ether, and boiled with 50 c.c. of water for half an hour, when brownish yellow crystals were obtained. In order to remove tarry matter, the crystals were collected while still hot. The yield of the crude product amounted to 0.6 gram. After being recrystallised from dilute alcohol, they separated in yellow needles melting at 228° (Found : C = 60.34 ; H = 3.72 ; N = 6.02. $C_{13}H_9O_5N$ requires C = 60.23 ; H = 3.50 ; N = 6.00%).

(1) loc. cit., p. 333.

The Methyl Derivative, $(NO_2)C_6H_4COC_6H_3(OCH_3)_2$. 3′-Nitro-2 : 4-dihydroxybenzophenone (0.5 gram) was dissolved in 6 c.c. of a 10 per cent solution of sodium hydroxide and shaken with 1 c.c. of methyl sulphate for an hour, when colourless crystals were deposited. After recrystallisation from alcohol several times, they melted at 116–117° (Found : C=62.82 ; H =4.61. $C_{15}H_{13}O_5N$ requires C=62.71 ; H=4.56%).

4′-*Nitro*-2 : 4 : 6-*trihydroxybenzophenone*, $(NO_2)C_6H_4COC_6H_2(OH)_3$. One gram of freshly fused and powdered zinc chloride was added to a solution of 2 grams of *p*-nitrobenzonitrile and 1.8 grams of phloroglucinol in 100 c.c. of absolute ether, and a gentle stream of dry hydrogen chloride was passed into the solution for four hours at room temperature, when a reddish brown oil was separated. The oil was boiled for half an hour with 100 c. c. of water and the faint, yellow crystals which separated were collected and recrystallised from dilute alcohol. The gamboge yellow crystals thus obtained melted at 246–247° (Found : C=56.52 ; H=3.52 ; N=4.87. $C_{13}H_9O_6N$ requires C=56.71 ; H=3.30 ; N=5.10%).

Korczynski and Nowakowski[1] gave 244-245° as its melting point.

3′-*Nitro*-2 : 4 : 6-*trihydroxybenzophenone*, $(NO_2)C_6H_4COC_6H_2(OH)_3$. One and a half grams of freshly fused and powdered zinc chloride were added to a solution of four grams of *m*-nitrobenzonitrile and 3.6 grams of phloroglucinol in 250 c.c. of absolute ether, and a current of dry hydrogen chloride was then gently passed into the solution for six hours at room temperature. After being allowed to stand overnight, the product was freed from the unchanged nitrile, by decanting the ether and washing it several times with ether, and then decomposed by boiling with 100 c.c. of water for half an hour, or by dissolving it in 100 c.c. of 2*N*-H_2SO_4 and subsequent boiling for half an hour. The yellow crystals thus separated were recrystallised from water, when they crystallised in faint, yellow needles melting at 194° (Found : C=56.44 ; H=3.40 ; N=5.05. $C_{13}H_9O_6N$ requires C= 56.71 ; H=3.30 ; N=5.10%).

Attempts to condense *o*-nitrobenzonitrile with resorcinol or with phloroglucinol under various conditions were made, but without success, the unchanged nitrile being always recovered.

In conclusion, the author wishes to express his hearty thanks to Professor Hiroshi Nomura for his kind guidance and encouragement during this investigation.

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(1) loc. cit., p. 334.