PREPARATION OF 2-HYDROXY-4-NITRO-PROPIOPHENONE

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The FRIES rearrangement of 3-nitro-phenyl-propionate was carried out by the authors. The product of rearrangement proved to be 2-hydroxy-4-nitro-propiophenone, a compound not described so far. This ketone was characterised by its sodium salt and phenylhydrazone, respectively.

In the course of our work [1], [2] undertaken in connection with the investigation of the mechanism of the FRIES-reaction we succeeded in carrying out the rearrangement of 3-nitro-phenyl--propionate (I). The rearrangement was conducted both in a solvent and without it. The reaction afforded 2-hydroxy-4-nitro-propiophenone (II) in yields of 20,0% and 14,0%, respectively. Lower yields may be due to the effect of deactivation of the nitrogroup.

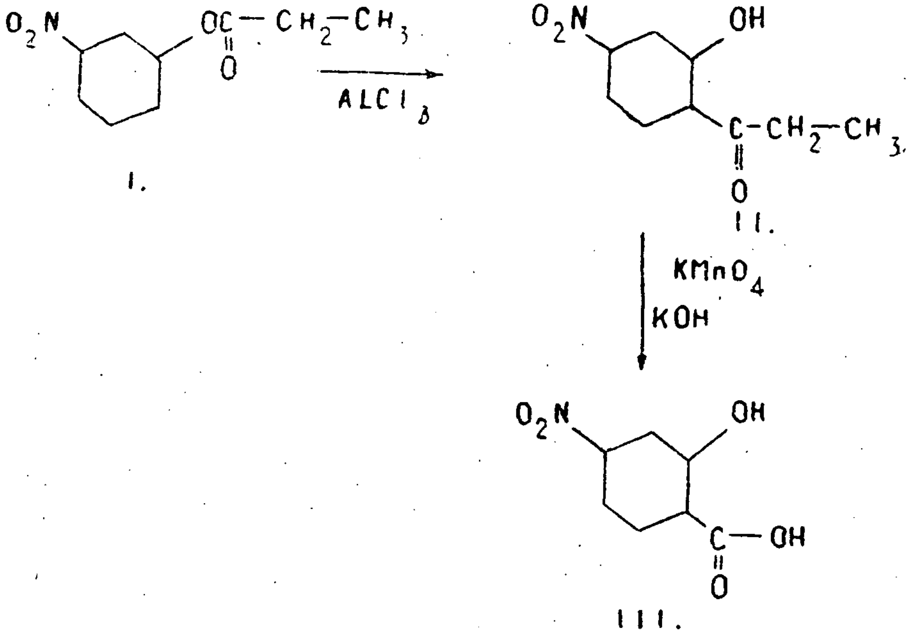

Fig. 1

The structure of 2-hyroxy-4-nitro-propiophenone (II) was proved by oxidation with potassium permanganate in alkaline medium leading to 2-hydroxy-4-nitro-benzoic acid (III). The *ortho*-positioned hydroxy-group of the ketone takes part presumably in a chelate structure, for its phenylhydrazone can only be acetylated under drastic conditions, and it hydrolyses at a far lower rate than the phenylhydrazones of the appropriate 4-hydroxy-ketones e. g. 3-nitro-4-hydroxy-acetophenone and propiophenone, respectively, in aqueous alcoholic hydrochloric acid.

We characterized 2-hydroxy-4-nitro-propiophenone, a compound not described so far by preparing its sodium salt and phenylhydrazone, respectively.

Experimental[1]

A./ *3-nitro-phenyl-propionate* was obtained from 3-nitro-phenol (20 g) crystallized from toluol by acylation with propionic anhydride (40 ml) by heating on steam bath for an hour and a half. The propionate (16 g; 98% yield) was isolated by pouring the mixture in water (100 ml). After recrystallization from petrolether m. p.: 49°.

B./ *Preparation of 2-hydroxy-4-nitro-propiophenonephenylhydrazone; Fries reaction of 3-nitro-phenyl-propionate in nitrobenzene.* 10 g 3-nitro-phenyl-propionate and 7,3 g anhydrous aluminium chloride (freshly sublimed) were dissolved in 60 ml nitrobenzene (freshly distilled), the mixture was poured into a flask provided with a reflux condenser fitted with a tube filled with calcium-chloride, then heated in an oil bath at 125°—130° for 25 hours. The cooled solution was poured onto the mixture of 50 g of ice and 10 ml of concentrated hydrochloric acid, the nitrobenzene layer was washed until neutral to Congo, dried (Na_2SO_4), the solvent removed *in vacuo.* The residual oil was dissolved in 30 ml of methanol, then mixed with a calculated amount of phenylhydrazine and allowed to stand overnight in a refrigerator. The separated brick-red needles (2,91 g; 20% yield) melted at 192°—194°. After recrystallization from butanol the phenylhydrazone of 2-hydroxy-4-nitro-propiophenone was obtained. Long carmine coloured needles, m. p.: 195°—196°. (Found: N 14,44 $C_{15}H_{15}O_3N_3 = 285,3$ requires: N 14,73%.)

C./ *Preparation of 2-hydroxy-4-nitro-propiophenone by Fries reaction without solvent*

10 g 3-nitro-phenyl-propionate and 7,3 g anhydrous aluminium chloride (freshly sublimed) were mixed. The mixture was allowed to stand for 20 hours at 125° in a thermostat in a flask provided with a calcium chloride tube. Hydrogen chloride evolved vigorously at the beginning of the reaction. When the material was cooled, 40 g of ice and 10 ml of concentrated hydrochloric acid was added to the solidified mixture. The oily-aqueous mixture of deep brown colour was extracted, in turn, by 4 × 20 ml of CCl_4, dried and the solvent removed. The oily residue containing 3-nitro-phenol and the hydroxy-ketone was completed with methanol to 20 ml, and 15 ml of sodium-ethylate (0,75 g sodium-metal was dissolved in 15 ml of 99% ethanol) added, then allowed to stand

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[1] Melting points are not corrected.

overnight in a refrigerator. The sodium salt of 3-nitro-phenol remained dissolved while the red-coloured sodium salt of 2-hydroxy-4-nitro-propiophenone separated. After filtration it was liberated into the hydroxy-compound by treating with 15 ml of N H_2SO_4 on a steam bath, allowed to stand overnight in a refrigerator. The solidified material was recrystallized from ethanol. Yellowish-brown needle crystals were obtained (1,4 g; 14% yield). After several recrystallizations from 96% ethanol m. p.: 68°—69°. (Found C 55,03; H 4,74; N 7,09, $C_9H_9O_4N$ = 195,17 requires: C 55,38; H 4,65; N 7,18%.)

D./ *Oxidation of 2-hydroxy-4-nitro-propiophenone into 2-hydroxy-4-nitrobenzoic acid*

0,3 g of 2-hydroxy-4-nitro-propiophenone was dissolved in 1,3 ml of equimolecular (10%) potassium hydroxide, then 22,2 ml of a 5% solution of potassium permanganate (25% excess) was dropped at the temperature of the water bath, the mixture allowed to stand on the water bath for an hour and a half. Then the unchanged potassium permanganate was decomposed by $NaHSO_3$, the mixture filtered through cotton, washed with 3 × 10 ml of water and the filtrate acidified with 1,5 ml of concentrated hydrochloric acid. The rose-red filtrate was extracted with 3 × 10 ml of chloroform, then the combined chloroformic solutions dried and distilled *in vacuo.*

The residue was recrystallized from 5 ml of water furnishing 2-hydroxy-4-nitro-benzoic acid (0,18 g). M. p.: 224°—225°. (Found: C 45,94; H 2,81; N 7,89, $C_7H_5O_5N$ = 183,12 requires: C 45,90; H 2,73; N 7,65%.)

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