

FRIES REARRANGEMENT OF MONONITROPHENYL BENZOATES

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Mononitrophenyl benzoates have been subjected to FRIES rearrangement in nitrobenzene using anhydrous aluminium chloride as catalyst. In the case of 2- and 4-nitrophenolic esters the products of the isomerisation were the para and ortho isomers, respectively, while 3-nitrophenyl benzoate gave no nitrohydroxy ketone.

It has been reported [1] that our attempt to subject mononitrophenyl benzoates to FRIES rearrangement had been unsuccessful. Further experiments showed, however, that under proper conditions FRIES rearrangement takes place in the presence of 1—1,25 moles of aluminium chloride using nitrobenzene as solvent. In the case of 2-nitrophenyl benzoate 3-nitro-4-hydroxybenzophenone, in that of 4-nitrophenyl benzoate 5-nitro-2-hydroxybenzophenone could be isolated in a yield of 3,5% and 4%, respectively. The 3-nitro-4-hydroxybenzophenone was identified by its known 2,4-dinitrophenylhydrazone [2]. The 5-nitro-2-hydroxybenzophenone which proved to be identical with an authentic prepartate [3], was characterized by its so far unknown phenylhydrazone and 2,4-dinitrophenylhydrazone. The expected corresponding ketone, however, could not be so far isolated on rearrangement of 3-nitrophenyl benzoate under the conditions described above. Attempts to realize this rearrangement are still in progress.

*Experimental**

Rearrangement of 2-nitrophenyl benzoate

5,5 g of anhydrous aluminium chloride (41,2 millimoles) was dissolved in 20 ml of nitrobenzene. 10 g of 2-nitrophenyl benzoate (41,2 millimoles, prepared from 2-nitrophenol and benzoyl chloride, m. p.: 54° C) was added, and kept at 165—175° C for an hour. A vivid evolution of hydrogen chloride was observed. The solution was decomposed with 10 ml of concentrated hydrochloric acid, and nitrobenzene removed by steam distillation. The residue was cooled and filtered. The solid mixture, remained on the filter, was dissolved in 20 ml of hot ethanol which was previously used to extract the

* Melting points are not corrected.

material stuck at the wall of the flask. The filtrate was extracted with 4×40 ml of tetrachloro-methane. The combined extract was heated and added to the hot ethanol solution, then it was diluted with 20 ml of water, and filtered. The resinous products separated, remained on the filter. The tetrachloro-methane solution was extracted with 5×20 ml of sodium hydroxide (6 g pro 100 ml of water). The combined extract was heated and acidified with concentrated hydrochloric acid. The upper aqueous layer was decanted from the brown oil separated. In order to dry the oil, it was dissolved in 10 ml of ethanol, and the solvent evaporated. The residue was extracted with three portions of 20 ml of hot ligroin. Having removed the ligroin the yellowish-brown residue was recrystallized from ethanol, giving 0,35 g of brownish-yellow crystals melting at $76-81^\circ \text{C}$. Recrystallization twice from methanol and twice from ligroin gave yellow 3-nitro-4-hydroxy-benzophenone m. p. $91-92^\circ \text{C}$ (R. A. ABRAMOVICH *et al* found 90°C [2]). (Found: N 5,94 %, $\text{C}_{18}\text{H}_9\text{O}_4\text{N} = 243,2$ requires: N 5,76 %). The 2,4-dinitrophenylhydrazone was prepared from a 50% aqueous ethanol solution of 3-nitro-4-hydroxy-benzophenone by adding a solution of 2,4-dinitrophenylhydrazin (1 g dissolved in 100 ml of concentrated sulphuric acid) to it. On heating orange-yellow crystals precipitated, m. p.: 261°C (R. A. ABRAMOVICH *et al* found 261°C [2]). (Found: N 16,2 %, $\text{C}_{19}\text{H}_{13}\text{O}_7\text{N}_5 = 423,3$ requires: N 16,5 %).

Rearrangement of 4-nitrophenyl benzoate

3,5 g of anhydrous aluminium chloride (26,2 millimoles) was dissolved in 20 ml of nitrobenzene. 5 g of 4-nitrophenyl benzoate (20,6 millimoles, prepared from 4-nitro-phenol and benzoyl chloride, m. p.: 142°C) was added and kept at 170°C for an hour. Hydrogen chloride evolved vigorously during the reaction. The cooled solution was poured into the mixture of 100 g of water and 10 ml of concentrated hydrochloric acid and stirred for an hour. The nitrobenzene layer was added to a mixture of 20 ml of 10 N sodium hydroxide and 20 ml of sodium fluoride solution (35 g per litre) and subjected to steam distillation until free from nitrobenzene. The residue was filtered, acidified with concentrated hydrochloric acid.

The aqueous layer was decanted from the resinous product separated, and extracted with 4×40 ml of tetrachloro-methane. The resinous residue was dissolved in 10 ml of ethanol and mixed with the combined and heated tetrachloro-methane extract. Having filtered, it was dried with anhydrous sodium sulphate and the solvent removed. The residue was dissolved in ethanol and allowed to stand overnight in refrigerator. 5-Nitro-2-hydroxy-benzophenone (0,2 g) crystallized, m. p.: $108-115^\circ \text{C}$. Having recrystallized from ethanol it had a m. p. of $122-124^\circ \text{C}$ (ULLMANN, MALLET found $124-124,5^\circ \text{C}$ [3]). (Found: N 5,65 %, $\text{C}_{13}\text{H}_5\text{O}_4\text{N} = 243,2$ requires: N 5,76 %). The phenylhydrazone was prepared from a 60% ethanol solution by giving a calculated amount of phenylhydrazine to it. The separated brick-red needles melted at $190-191^\circ \text{C}$. (Found: N 12,9 %, $\text{C}_{19}\text{H}_{15}\text{O}_3\text{N}_3 = 333,3$ requires: N 12,9 %). The 2,4-dinitrophenylhydrazone was prepared as in the case of 3-nitro-4-hydroxy-benzophenone-2,4-dinitrophenylhydrazone. Yellow crystals, m. p.: $283-285^\circ \text{C}$. (Found: N 15,7 %, $\text{C}_{19}\text{H}_{13}\text{O}_7\text{N}_5 = 423,3$ requires: N 16,5 %).

The attempted rearrangement of 3-nitrophenyl benzoate

6,6 g of anhydrous aluminium chloride (49,5 millimoles) was dissolved in 40 ml of nitrobenzene, 10 g of 3-nitrophenyl benzoate (41,2 millimoles, prepared from 3-nitro-phenol and benzoyl chloride, m. p.: 93—95° C) was added and kept at 175° C for an hour. Hydrogen chloride evolved during the heating. Working up the mixture was the same as used in the case of 4-nitrophenyl benzoate. Only 3-nitro-phenol and benzoic acid could be isolated.

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ПЕРЕРАСПРЕДЕЛЕНИЕ ФРИЗА МОНОНИТРОФЕНИЛЬНЫХ ЭФИРОВ

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Было осуществлено перераспределение фриза катализовано хлористым алюминием мононитрофенильных бензоатов в нитробензольном растворе. При перераспределении 2- и 4-нитрофенильных эфиров, соответствующие пара- и ортоизомеры были получены и 3-нитро-фенильный бензоат не перераспределился.