FRIES REARRANGEMENT OF SOME NITROPHENOLIC ESTERS IN THE ABSENCE OF SOLVENT

By Á. FURKA and T. SZÉLL

Institute of Applied Chemistry, The University, Szeged

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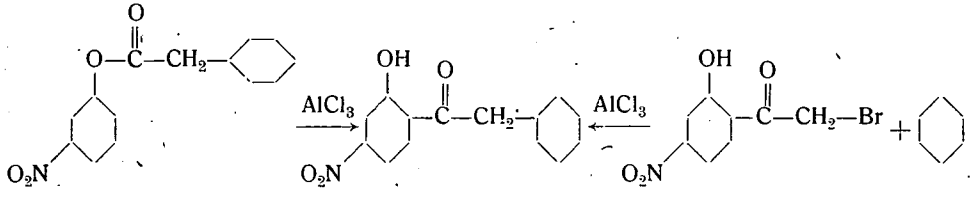
The aluminium chloride catalysed FRIES isomerisation of 4-nitrophenyl acetate, 3- and 4-nitrophenyl phenylacetate was carried out in the absence of a solvent. The products formed were the corresponding ortho hydroxy ketones.

In a previous work [1] it has been found that nitrophenolic esters decompose on heating in the presence of aluminium chloride and the factors having an effect on decomposition determined. These results made possible to choose proper experimental conditions under which, instead of decomposition FRIES rearrangement may take place (if at all). A. S. U. CHOUGHULAY *et al* [2] reported that 4-nitrophenyl acetate, using 2,2 moles of aluminium chloride and no solvent, decomposed instead of rearranging. Our attempt [3] to rearrange 3-nitrophenyl phenylacetate in the presence of 2 moles of aluminium chloride also failed. Using, however, 0,8—0,85 moles of the catalyst the realisation of the FRIES reaction of 4-nitrophenyl acetate, 3-nitrophenyl phenylacetate and that of so far unknown 4-nitrophenyl phenylacetate in the absence of a solvent was successful. Products of these reactions were the known 5-nitro-2-hydroxy-acetophenone [4] (yield*: 28 %), the so far unknown 4-nitro-2-hydroxy-ω-phenyl-acetophenone (yield: 3,5 %), and 5-nitro-2-hydroxy-ω-phenyl-acetophenone (yield: 6 %), respectively. The structure of 4-nitro-2-hydroxy-ω-phenyl-acetophenone was proved by the Friedel-Crafts reaction of 4-nitro-2-hydroxy-ω-bromo-acetophenone [8] with benzene, which gave identical product with that obtained by the FRIES reaction of 3-nitrophenyl phenyl acetate.



* The rearrangement carried out in nitrobenzene gave yields of 24,7 %, [5], 25,1 %, [6], 25 % [2] and 35 %, [7].

It may be concluded that in order to avoid decomposition it is not advisable to use more than one mole of aluminium chloride when rearranging nitrophenolic esters. This is also supported by the fact that we could isomerize 2-nitrophenyl acetate [3] in the presence of one mole of aluminium chloride, while LINDEMAN and ROMANOFF [4] could not, using probably more than one mole of the catalyst.

*Experimental**

Fries reaction of 4-nitrophenyl acetate

Ester prepared according to the method of F. D. CHATTAWAY [9] (10 g, 55,3 millimoles) was thoroughly mixed with anhydrous aluminium chloride (6,2 g, 46,6 millimoles), introduced into a flask provided with a guard tube and kept for 25 minutes at 140—150°C on a sand bath. On heating the ester melted, gas evolved, then it solidified again. The cooled mixture was dissolved in 30 ml of ethanol, made acid by adding 10 ml of concentrated hydrochloric acid and 300 ml of water and allowed to stand in a refrigerator for 2 hours. The black precipitate was filttered off and dissolved in 10 ml of hot ethanol. The filtrate was extracted with 4×40 ml of tetrachloro-methane which was then combined, heated and added to the hot ethanolic solution. Next the solution was cooled, filtered through cotton and shaken with 5×40 ml of 1,5 N sodium hydroxyde solution. On acidifying the alcalic extract a black material separated (6,5 g) which was dissolved in 150 ml of hot ligroin (resins remained undissolved) and allowed to stand in a refrigerator for 3 hours. The separated orange yellow crystals (3,6 g) were recrystallized from ethanol, then from ligroin. The colourless product (2,8 g) melted at 101—102°C and was found to be identical with 5-nitro-2-hydroxy-acetophenone obtained by a different method [5] (Found: N 7,42 %, $C_8H_7O_4N = 181{,}1$ requires: 7,73 %). Phenylhydrazone melted at 224—225°C, 2,4-dinitrophenylhydrazone at 255—258°C.

Fries reaction of 3-nitrophenyl phenylacetate

The ester prepared as described previously [3] (13 g, 50 millimoles) was intimately mixed with aluminium chloride (5,3 g, 40 millimoles) and warmed on a paraffin wax bath for 25 minutes at 140°C (gas evolved). Having decomposed the mixture as described above a black oil and an aqueous layer were obtained. The method of the isolation of the ketone was the same as that of 5-nitro-2-hydroxy-acetophenone, but before extracting the tetrachloromethane solution with aqueous sodium hydroxide, it was shaken with 50 ml of water, filtered through cotton and the organic layer removed.

Yellowish crystals were obtained (0,45 g), m. p.: 152—153°C. (Found: N 5,8 %, $C_{14}H_{11}O_4N = 257{,}24$ requires: 5,44 %). Phenylhydrazone was prepared from the ketone by boiling it with phenylhydrazine in 60 % ethanol for a

* Melting points are uncorrected.

few minutes. Red needles, m. p.: 198—199°C. (Found: N 12,4 %, $C_{20}H_{17}O_3N_3$ = = 347,36 requires: 12,1 %). The ketone was found to be identical with the product obtained by boiling 4-nitro-2-hydroxy-ω-bromo-acetophenone in benzene in the presence of 2 moles of aluminium chloride for an hour.

Preparation of 4-nitrophenyl phenylacetate

Sodium-4-nitrophenolate (8,1 g, 50 millimoles) (prepared from 4-nitrophenol dissolved in benzene by giving ethanolic sodium ethylate to it) was treated with phenylacetyl chloride (7,7 g, 50 millimoles) in benzene (50 ml), the mixture refluxed for 30 minutes and filtered to remove sodium chloride. The solvent from the filtrate was evaporated and the residual oil poured into water (100 ml) while being stirred. The separated oil was then treated with ethanol (5 ml) and petroleum ether (25 ml), and allowed to stand in a refrigerator for 3 days when white platelets of the ester were obtained (9 g), m. p.: 64—65°C. On recrystallizing from ethanol it had a m. p.: 65—66°C. (Found: N 5,80 %, $C_{14}H_{11}O_4N$ = 257,24 requires: 5,44 %).

Fries reaction of 4-nitrophenyl phenylacetate

The mixture of ester (3,7 g, 13,6 millimoles) and aluminium chloride (1,5 g, 11,4 millimoles) was placed into a paraffin wax bath of 105°C, and the temperature raised to 140°C in 12 minutes. On heating a slight explosion was observed at 134°C, dark gases evolved. The ketone (0,22 g) was isolated as desribed in the case of the rearrangement of 3-nitrophenyl phenylacetate. Colourless needles, m. p.: 115—116°C. (Found: N 5,78 %, $C_{14}H_{11}O_4N$ = 257,24 requires: 5,44 %). The yellow phenylhydrazone melted at 185—186°C (Found: N 12,5 %, $C_{20}H_{17}O_3N_3$ = 347,36 requires: 12,1 %).

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ПЕРЕРАСПРЕДЕЛЕНИЕ ФРИЗА НЕСКОЛЬКИХ ЭФИРОВ НИТРОФЕНОЛА В ОТСУТСТВИИ РАСТВОРИТЕЛЯ

А. Фурка и *Т. Селл*

Перераспределение Фриза 4-нитро-фенильного ацетата, 3- и 4-нитро-фенильного-фенильацетата, катализовано хлористым алюминием было исполнено без растворителя. Продукты были соответствующие орто-гидрокси-кетоны.