FRIES REARRANGEMENT OF 3-NITROPHENYL BENZOATE

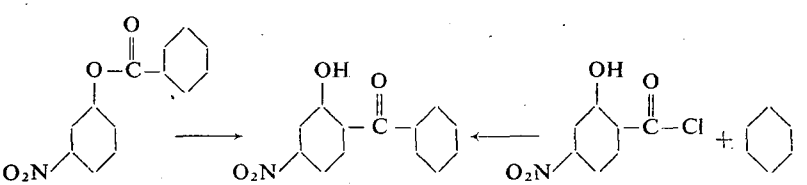
By Á. FURKA and T. SZÉLL

Institute of Applied Chemistry, The University, Szeged

(Received 17 March, 1961)

The aluminium chloride catalised FRIES isomerisation of 3-nitrophenyl benzoate in the absence of a solvent gave the unknown 4-nitro-2-hydroxy-benzophenone, the structure of which was proved by the FRIEDEL—CRAFTS reaction of 4-nitro-2-hydroxy-benzoyl chloride with benzene.

It has been reported [1] that our attempts to realize the FRIES rearrangement of 3-nitrophenyl benzoate in nitrobenzene had been unsuccessful. The isomerisation, however, could be carried out without using a solvent. Thus 3-nitrophenyl benzoate (I) underwent FRIES reaction by fusing it with molar quantity of aluminium chloride at 170—175° C for two hours giving the unknown 4-nitro-2-hydroxy-benzophenone (II) with a yield of 11%, while 23% of the ester remained unchanged. In order to prove the structure, II was synthesized from 4-nitro-2-hydroxy-benzoyl chloride (III) and benzene (IV) by FRIEDEL—CRAFTS reaction, in nitrobenzene at 110° C with a yield of 60%. II was characterized by its sodium salt, phenylhydrazone and 2,4-dinitrophenylhydrazone.



I II III IV

Experimental[1]

FRIES *reaction of 3-nitrophenyl benzoate.* Ester, prepared as previously described [1] (15 g, 62 millimoles) was thoroughly mixed with powdered anhydrous aluminium chloride (8,22 g, 62 millimoles), introduced into a flask equipped with a guard tube and heated in an oil bath. The temperature of the bath was slowly raised to 170° C (during an hour) and kept at it for further two hours. The cooled, solidified mixture was dissolved in 50 ml of hot ethanol, made acid by adding 10 ml of concent-

[1] Melting points are uncorrected.

rated hydrochloric acid and poured into 600 ml of water at 30° C. The oil separated was freed from water and boiled with 250 ml of tetrachloro-ethane for 12 hours, filtered through cotton and shaken with 3 × 40 ml of 4% sodium hydroxyde solution. From the residual tetrachloro-methane solution 3,5 g of 3-nitrophenyl benzoate was recovered. On acidifying the combined alkaline extract a black material has been separated which was extracted with 5 × 10 ml of hot ligroin. By removing ligroin 1,65 g crude 4-nitro-2-hydroxy-benzophenone was obtained (yield: 11%). Recrysotallization from ethanol gave yellow needles melting at 112—113° C. (Found: N 6,0%, $C_{13}H_9O_4N$ = 243,2 calculated: N 5,8%). The yellow sodium salt of this ketone precipitated on adding ethanol solution of sodium ethylate to the benzene-, or nitrobenzene solution of 4-nitro-2-hydroxy-benzophenone. The phenylhydrazine was prepared by boiling the ketone with a calculated amount of phenylhydrazine in 60% ethanol. Orange needles, m. p. 188—189° C (Found: N 12,7, $C_{19}H_{15}O_3N_3$ = = 333,3 calculated: N 12,9%. 2,4-dinitrophenylhydrazine was prepared by adding a solution of 2,4-dinitrophenylhydrazine (1g dissolved in 100ml of concentrated sulphuric acid) to the solution of the ketone in 50% aqueous ethanol. Orange yellow crystals, m. p. 280—283° C (Found: N 16,2%, $C_{19}H_{13}O_7N_5$ = 423,3 calculated: N 16,5%).

The FRIEDEL—CRAFTS *reaction of 4-nitro-2-hydroxy-benzoyl chloride with benzene*

5,5 g of 4-nitro-2-hydroxy-benzoic acid (30 millimoles, m. p. 220—223° C), prepared according to literature [2], and 8,0 g of thionyl chloride (66 millimoles) were dissolved in 30 ml of nitrobenzene, and refluxed for two hours in an oil bath of 120° C. In order to remove thionyl chloride completely, the solution was diluted with 30 ml of benzene and distilled (the endtemperature of the oil bath was 142° C). This operation was repeated twice. To the thionyl chloride free nitrobenzene solution 25 ml of benzene, and 8,0 g of aluminium chloride (60 millimoles) were added, and the solution kept in an oil bath of 100—110° C, for two hours and a half. The excess of the benzene was then removed by distillation continued until the temperature of the oil bath reached 145°, the residue cooled to room temperature and decomposed by pouring it into the mixture of 30 g of ice and 15 ml of concentrated hydrochloric acid. The organic layer was washed successively five times with 70 ml of 2 N hydrochloric acid, five times with 70 ml of cold water and finally with four 50 ml portions of hot water (70° C). From the combined aqueous extract 0,4 g of 4-nitro-2-hydroxy-benzoic acid was extracted with chloroform. The dark nitrobenzene layer was washed four times with 50 ml of 1 N sodium hydroxyde, the combined alkaline extract acidified, cooled in ice, and filtered to give 4,4 g 4-nitro--2-hydroxy-benzophenone, m. p. 99—100° C. Yield: 60%. After recrystallization from 35 ml of ethanol the m. p. was 110—112° C, which was un-depressed on admixture with the ketone, obtained by the FRIES reaction of 3-nitro-phenyl benzoate.

* * *

The present work was supported by the Hungarian Academy of Sciences, which is gratefully acknowledged. The authors are indebted to KORNÉLIA L. LÁNG and GIZELLA B. BOZÓKI (Inst. of Org. Chem. Univ. Szeged) for the microanalyses.

References

[1] *Furka, Á., T. Széll:* Acta Phys. et Chem. Szeged, 6, 113 (1960).
[2] Степанов, Ф. Н., Н. С. Вульфсон, И. А. Микова: Журнал Прикл. Хим. 27, I 332 (1957).

ПЕРЕГРУППИРОВКА 3-НИТРОФЕНИЛ-БЕНЗОАТА ПО ФРИСУ

А. Фурка и Т. Селл

Изомеризация ФРИС без растворителя 3-нитофенилбензоата, катализированная хлористом алюминием, дала неизвестный 4-нитро 2-гидроксибензофенон, структура которого доказывалась реакцией ФРИДЕЛЬ—КРАФТС 4-нитро-2-гидроксихлориотого бензоила и бензола.