

# FRIES REARRANGEMENT OF 3-NITROPHENYL-3-NITROBENZOATE

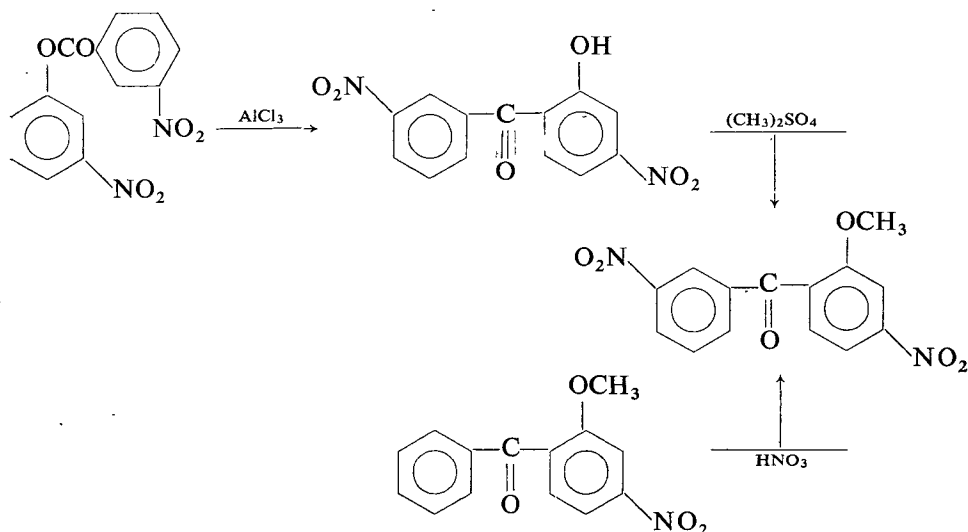
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On subjecting 3-nitrophenyl-3-nitrobenzoate to FRIES rearrangement, the so far unknown 3', 4-dinitro-2-hydroxy-benzophenone was obtained in a poor yield.

In continuation of our earlier work [1, 2], the FRIES rearrangement of 3-nitrophenyl-3-nitrobenzoate was carried out. On keeping the ester and an equivalent amount of aluminium chloride for two hours in an oil bath of 175°, 3,4-dinitro-2-hydroxybenzophenone was formed in a poor yield. The product was characterized by its phenylhydrazone and by its sodium salt.



Though it is known that the successful course of the FRIES reaction is inhibited by the presence of a nitro group substituted in the nucleus of the phenol portion of phenylesters [3], several cases were described [2] where nitro-phenylesters have

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undergone FRIES reaction in rather poor yields. To our knowledge, the present work is, however, the first FRIES rearrangement involving dinitrophenylesters. The poor yield observed may be ascribed to the presence of two nitro groups.

In order to prove the structure of the ketone, it was attempted to nitrate 4-nitro-2-hydroxy-benzophenone [4]. However, the mononitro product obtained in this way was not identical with the ketone formed in the FRIES reaction. (Presumably the nitro group entered the phenol portion.) In order to reduce the effect of the phenolic hydroxyl group, 4-nitro-2-hydroxy-benzophenone was first methylated, and the methyl derivative subjected to nitration. The product thus obtained was identical with the methyl derivative of the compound formed in the FRIES reaction examined, proving that in fact 3', 4-dinitro-2-hydroxy-benzophenone was formed in the FRIES rearrangement.

### *Experimental*

#### *Fries rearrangement of 3-nitrophenol-3-nitrobenzoate*

A mixture of the ester (17,9 g; 62 mmole) and an equivalent amount (8,25 g; 62 mmole) of aluminium chloride (B. D. H.) was placed in a cold oil bath under reflux equipped with a ground calcium chloride tube. The temperature of the oil bath was slowly raised to 175° and kept two hours at a temperature of 173–177°. A hard black blistered melt was obtained.

The melt was boiled 20 minutes with 60 ml of ethanol, the resulting coffee-coloured suspension containing solid undissolved particles was then poured into a mixture of 12 ml of concentrated hydrochloric acid and 600 ml of water, and the mixture allowed to stand overnight. The system separated into two phases: a sharp, slightly brownish aqueous phase and a tar-like organic phase. The aqueous phase was shaken with 6 × 50 ml of carbon tetrachloride, then with 2 × 50 ml of benzene of a temperature of 34–40°. The combined carbon tetrachloride-benzene fractions were washed with 6 × 100 ml of water (in order to remove 3-nitrobenzoic acid), and dried with sodium sulphate. Then a suspension was made of the above mentioned tar-like phase in 50 ml of hot ethanol mixed with the carbon tetrachloride-benzene solution, and the whole system refluxed for 12 hours. After filtering the warm suspension through cotton 200 ml of solvent were removed from the filtrate by distillation, the phenols were extracted from the residue with 4 × 40 ml of 1*N* sodium hydroxide, the alkaline solution acidified with concentrated hydrochloric acid, the system allowed to stand overnight in an ice box, the separated asphalt-like sticky substance filtered through filter paper, dried at room temperature and ground (7,25 g). Subsequently, the product was transferred into a 250 ml round-bottomed flask, boiled with 2 × 100 ml of petroleum ether then with 4 × 15 ml of ligroin (b. p. 112–113°). The combined petroleum ether-ligroin extracts were evaporated to a volume of 25–30 ml, and allowed to stand overnight in an ice box to give 0,4 g of a yellow crystalline substance of m. p. 116–125°. On recrystallizing it from 50% ethanol, then from 96% ethanol the yellow keton melted at 158–159°. (Anal.: Calc.:  $C_{13}H_8O_6N_2 = 288,2$ , C 54,17 H 2,8 N 9,72; Found: C 54,06 H 3,08 N 9,62.)

On adding some phenylhydrazine base to a saturated solution of 3,4'-dinitro-2-hydroxybenzophenone in 60% ethanol, the liquid was boiled 4–5 minutes. On allowing the system to stand in an ice box, dark yellow needles of the phenylhydrazone, m. p. 240–242° separated. (Anal.: Calc.:  $C_{18}H_{14}O_5N_4 = 378,3$  N 14,81; Found: N 14,80.)

From the solution of the ketone in benzene by adding a methanolic solution of sodium methylate (10% in respect to sodium), the orange-red sodium salt of the hydroxy-ketone separated.

#### *Nitration of 4-nitro-2-hydroxybenzophenone*

To the analogy of the nitration of similar compound [5] [6], the nitration of 4-nitro-2-hydroxybenzophenone of authentic structure [4] was carried out as follows. The powdered ketone (1,22 g; 5 mmole) was allowed to stand 3 hours at room temperature with 4 ml of nitric acid of sp. gr. 1,43. Then the mixture was heated two hours at 50–55° on the water bath. The heterogeneous system turned homogeneous, then again heterogeneous. By filtration, a substance melting at 96° while by pouring the mother liquor into 80 ml of water a substance melting at 130 were separated. On repeatedly recrystallizing the latter substance from 60% ethanol, its m. p. rose to 144–146°. The product ( $C_{13}H_8O_6N_2 = 288,2$ ) contained 9,72% of N proving that it was a mononitro product. Neither of the products however, were identical with the ketone obtained by the FRIES reaction of 3-nitrophenyl-3-nitrobenzoate.

#### *Methylation of 4-nitro-2-hydroxybenzophenone*

The solution of 1,22 g of 4-nitro-2-hydroxybenzophenone (5 mmoles) in 2,5 ml of 2N sodium hydroxide was diluted with 7 ml of water. On adding 0,65 g (*i. e.* 0,5 ml) of dimethyl sulphate (5 mmoles) to the bordeaux red solution, its colour gradually turned into dark red, and precipitation of crystals was observed. The system was then stirred for one hour at 40°, its colour turned yellow. Further 0,2 g (1,5 mmoles) of dimethyl sulphate was added to the emulsion and the system allowed to stand overnight. The suspension (pH=2) was treated with 1,2 ml of 2N sodium hydroxide, stirred 25 minutes at 40°, then the pH value adjusted with one drop of 2N sodium hydroxide to 7,5–8,0, the precipitated crystals filtered and washed with water. Yield: 1,18 g (91,4%) of crude methylether, m. p. 112–116°. Recrystallization of the product once from ligroin and once from ethanol gave 0,75 g of white needles, m. p. 130–131°. (Anal.: Calc.:  $C_{14}H_{11}O_4N = 257,24$  C 65,35 H 4,31 N 5,44; Found: C 65,05 H 4,52 N 5,58.)

#### *Nitration of 4-nitro-2-methoxybenzophenone*

2 ml of nitric acid of sp. gr. 1,43 was poured on 0,64 g (2,5 mmoles) of 4-nitro-2-methoxybenzophenone. At first much heat evolved, the substance was instantaneously dissolved and the nitric acid turned brown. On allowing the mixture to

stand an hour, it was kept for another hour on a 55° water bath, then 15 hours at room temperature, and finally poured into 40 ml of ice water. The precipitated product was filtered, dried at room temperature to give a crude product which was boiled with 10 ml of ethanol and filtered hot. In an ice box, 0,25 g of a substance of m. p. 153—158° crystallized from the filtrate. By recrystallizing it from a 3:1 mixture of ethyl acetate and ethanol, white needles of m. p. 159—160° were obtained. (Anal.: Calc.:  $C_{14}H_{10}O_6N_2 = 302,24$  C 55,63 H 3,34 N 9,27; Found: C 55,71 H 3,70 N 8,91.)

#### *Methylation of 4,3'-dinitro-2-hydroxy-benzophenone*

0,15 g of 4,3'-dinitro-2-hydroxy-benzophenone was suspended in 0,3 ml of 2 N sodium hydroxide. The substance was only partially dissolved. Subsequently the suspension was diluted with 0,9 ml of water, 0,1 ml of dimethyl sulphate added, and the suspension stirred at 40° until it turned yellow. On adding 3,3 ml of sodium hydroxide solution and 0,2 ml of dimethyl sulphate, stirring was continued for an hour. The final pH was about 10. White crystals were separated from the yellow solution by filtration, and recrystallized from 8 ml of a 3:1 mixture of ethanol and ethyl acetate. M. p. 158—159°. This white substance proved to be identical with the end product of the preceding experiment.

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#### References

- [1] Furka, Á., T. Széll: Acta Phys. et Chem. Univ. Szeged. 7, 70 (1961).
- [2] Széll, T., J. Egyed: J. Org. Chem. 27, 2225 (1962).
- [3] Blatt, A. H.: Chem. Rev. 27, 429 (1940); Org. Reactions (John Wiley and Sons Inc., New York) 1943. I. 342.
- [4] Furka, Á., T. Széll: Acta Phys. et Chem. Univ. Szeged. 6, 122 (1960).
- [5] Haase, E.: Annalen 283, 167 (1894).
- [6] Neumann, G.: Chem. Ber. 19, 2980 (1886).

#### ПЕРЕГРУППИРОВКА ФРИЗА 3-НИТРОФЕНИЛ-3-НИТРОБЕНЗОАТА

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Подвергая 3-нитрофенил-3-нитробензоат перегруппировке Фриза, авторы получили незнакомый до сих пор 3',4-динитро-2-гидрокси-бензофенон в небольшом выходе.