February, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **55**, *629—630 (1982)* 629

Regioselective Preparation of 2- and 3-Nitrodibenzofurans by the Direct Nitration of Dibenzofuran

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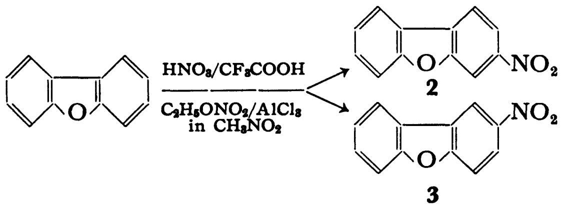
(Received May 21, 1981)

Synopsis. Nitration of dibenzofuran with nitric acid in trifluoroacetic acid gave 3-nitrodibenzofuran selectively under very mild conditions. In contrary, the Friedel-Crafts type nitration using alkyl nitrates and aluminium chloride in nitromethane gave 2-nitrodibenzofuran as the main product.

Nitrodibenzofurans are important precursors for many kinds of dibenzofuran derivatives. Nitration of dibenzofuran (**1**) with mixed acids gives 3-nitrodibenzofuran (**2**) as a main product.[1–3] Yamashiro had reported that the nitration of **1** with 12 equiv. of fuming nitric acid in acetic acid gave **2** in a yield of 70%.[3] As for a synthesis of 2-nitrodibenzofuran (**3**), circuitous processes have been taken due to a difficulty of the preparation from the direct nitration of **1** by the usual methods.[4–6] Cullinane had obtained **3** in a total yield of 16% from **1** by the dinitration of **1**, followed by partial reduction and deamination.[4] On the other hand, Gilman had prepared **3** in the total yield of 13% *via* a process of 6 steps starting from **1**.[5]

By choosing the appropriate nitration method, we have succeeded in controlling the main product to **2** or **3** in the direct nitration of **1**. We would like to report the regioselective nitration of **1** to give **2** or **3**.



Using trifluoroacetic acid in place of acetic acid in Yamashiro's procedure, the mononitration of **1** was attained in a quantitative yield with 1.2 equiv. of 99% nitric acid under very mild conditions, at 0 °C for 0.5 h. In addition, it was observed that **2** was very predominantly formed in the reaction. The GLC analysis of the crude product showed that a mixture of mononitrodibenzofurans was obtained in a quantitative yield and that the distribution of the 1-, 2-, 3-, and 4-nitroisomers in the mixture was 4 : 6 : 90 : trace. By a recrystallization of the crude product, **2** was isolated in a yield of 80%. In contrast, when the nitration in acetic acid was carried out with 1.2 equiv. of 99% nitric acid at 0 °C for 0.5 h, the yield of mononitrodibenzofurans was only 2% and the distribution of the isomers was 1-, 10 : 2-, 26 : 3-, 62 : 4-, 2.

On the other hand, in the Friedel-Crafts type nitration using alkyl nitrate and Lewis acid, the main product significantly changed from **2** to **3**. It was observed from the GLC analysis that the reaction of **1** with 1-cyano-1-methylethyl nitrate (CMN) in the presence of aluminium chloride in nitromethane gave a mixture of mononitrodibenzofurans in a yield of 92%, in which the distribution of the isomers was 1-, 11 : 2-, 51 : 3-, 36 : 4-, 2. For the preparative method, ethyl nitrate was used in place of CMN. Thus, in the reaction of **1** with 1.2 equiv. of ethyl nitrate and aluminium chloride in nitromethane at 25 °C for 1 h, mononitrodibenzofurans were obtained in a yield of 80%, from which **3** was isolated in a yield of 28% by the column chromatograpy on alumina with benzene. This yield is much higher than the total ones for the derivation from **1** by the indirect methods described in literatures.[4,5]

We can prepare **2** or **3** regioselectively by the direct nitration of **1** with either the nitric acid/trifluoroacetic acid system or with the ethyl nitrate-aluminium chloride/nitromethane system. We believe, therefore, the procedures described here should be much simpler and more convenient for the preparation of **2** and **3** than those reported previously.

Experimental

Materials and Measurements. 1-Nitrodibenzofuran (mp 123 °C, lit,[7] 120—121 °C), 4-nitrodibenzofuran (mp 138 °C, lit,[8] 138—139 °C), and CMN (bp 84 °C/34 mmHg,[†] lit,[9] 62—65 °C/10 mmHg) were prepared according to the methods described in the literature. Other chemicals were obtained commercially.

The GLC analysis was carried out on a Hitachi GC 163 Model gas chromatograph using a steel column (length 3 m, i.d. 3 mm) packed with 3% Dexil 300 GC on Chromosorb W and a hydrogen flame ionization detector. Isomer distribution of nitrodibenzofurans was calculated from the peak areas obtained using a Takeda TR 2220A Model integrator after calibration against authentic samples.

2-Nitrodibenzofuran (3). To a solution of **1** (5.00 g, 30 mmol) and ethyl nitrate (3.2 g 36 mmol) in nitromethane (30 ml), a solution of aluminium chloride (4.8 g, 36 mmol) in nitromethane (10 ml) was added at 5 °C over 0.1 h and then, the mixture was stirred at 25 °C for 1 h. After an addition of 0.1 mol dm^{-3} hydrochloric acid (30 ml) to the mixture, the solvent and the unreacted **1** were distilled off with steam to yield a crude product of nitrated dibenzofuran; 6.07 g, mp 102—142 °C. The crude product was treated with boiling ethanol (280 ml) and the insoluble by-product, dinitrodibenzofuran was collected; 0.47 g (6.1%), mp 261—269 °C. Evaporation of the filtrate gave a mixture of mononitrodibenzofurans as a light yellow solid, 5.09 g (80%), mp 108—139 °C. After treatment with hot ethanol (first 45 ml, then 35 ml) as above, the resulted ethanol-soluble component (4.12 g, mp 122—134 °C) was chromatographed on alumina with benzene to afford **3**: 1.76 g (28%), mp 152—153 °C (lit,[4] 151 °C), **2**; 1.08 g (17%), mp 162—174 °C, and 1-nitrodibenzofuran; 0.33 g (5%), mp 123 °C (lit,[7] 120—121 °C).

3-Nitrodibenzofuran (2). To a suspension of **1** (4.00 g, 24 mmol) in trifluoroacetic acid (50 ml), a solution of 99% nitric acid (1.82 g, 29 mmol) in trifluoroacetic acid (10 ml) was added dropwise at a rate such as to maintain the temperature

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[†] 1 mmHg≈133.322 Pa.

at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h and poured into ice–water. The resulted precipitates were filtered and washed thoroughly with alkali and water to give crude nitrodibenzofuran; 5.06 g (100%), mp 168—174 °C. The well refined product was heated with ethanol (50 ml) at 50 °C for 1 h and the insoluble material was recrystallized from acetic acid (29 ml) to give **2** in a almost pure form; 4.07 g (80%), mp 182 °C (lit,[3] 182 °C).

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