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2,5-Diarylfurans are formed along with 2-acetyl-5-arylfurans in the Meerwein arylation of 2-acetylfuran.

We have previously [1] studied the arylation of furfural with arenediazonium salts containing electron-acceptor substituents in the benzene ring. The utilization of arenediazonium salts containing electron-donor substituents in this reaction does not give positive results [2].*

In the present investigation, we have established that the expected 2-acetyl-5-arylfurans (Ia, b) are formed in the reaction of 2-acetylfuran with p-chloro- and p-bromobenzenediazonium chlorides. However, this reaction proceeds in an extremely peculiar manner. Acetylfurans Ia, b are not the only reaction products: under the conditions that we selected, an aryl residue also enters the 2 position of the furan ring, displacing an acetyl group and forming symmetrical 2.5-diarylfurans IIa, b.

$$\frac{p - x C_6 H_4 N_2^+ C \Gamma^-}{0} + \frac{1}{0} COCH_3 - \frac{p - x C_6 H_4}{0} COCH_3 + \frac{p - x C_6 H_4}{0} C_6 H_4 x - p$$

$$\frac{1}{0} COCH_3 + \frac{p - x C_6 H_4}{0} C_6 H_4 x - p$$

$$\frac{1}{0} COCH_3 + \frac{p - x C_6 H_4}{0} C_6 H_4 x - p$$

$$\frac{1}{0} COCH_3 + \frac{p - x C_6 H_4}{0} COCH_3 + \frac{p - x C_6 H_4}{0} C_6 H_4 x - p$$

$$\frac{1}{0} COCH_3 + \frac{p - x C_6 H_4}{0} COCH_3 + \frac{p - x C_6}{0} COCH_3 + \frac{$$

The mechanism of this peculiar reaction is worthy of special study, but arylacetylfurans Ia,b are apparently not intermediates in the formation of diarylfurans IIa,b: specially formulated experiments demonstrated that 2-acetyl-5-arylfurans Ia,b do not undergo arylation.

In conclusion, we note that 2-acetyl-5-(p-nitrophenyl)furan (Ic) is obtained as the only reaction product in high yield in the arylation of 2-acetylfuran with p-nitrobenzenediazonium chloride; the diarylfuran is not formed at all in this case.

The structures of the compounds obtained were confirmed by their IR, UV, and PMR spectra, as well as by independent synthesis of Ib and IIb by acetylation (under severe conditions) and, respectively, by p-chlorophenylation of 2-(p-chlorophenyl)furan.

EXPERIMENTAL

Reaction of p-Bromobenzenediazonium Chloride with Acetylfuran. p-Bromoaniline hydrochloride, obtained from 22.6 g (0.133 mole) of p-bromoaniline, 25 ml of water, and 70 ml of concentrated hydrochloric acid, was diazotized with a solution of 9.2 g (0.12 mole) of sodium nitrite in 40 ml of water. The reaction mixture was stirred at 5° for 20 min, and 13.7 g (0.125 mole) of 2-acetylfuran [3] in 10 ml of acetone and a solution of 2.6 g of cupric chloride in 5 ml of water were added. The reaction mixture was stirred at 20-25° for 4 h, 500 ml of water was added, and the resulting precipitate was washed with water to give 2.6 g (10% based on the converted acetylfuran) of 2,5-di (p-bromophenyl)furan (IIa) with mp 202-203° (from benzene) [4].

^{*}See also the literature review on this problem in [2].

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The IR spectrum did not contain the absorption band of a CO group. UV spectrum, λ_{max} , nm (log ϵ): 335 (4.46), 233 (4.11) (ethanol). The PMR spectrum contained two signals with an intensity ratio of 4:1 at δ 7.56 and 6.74 ppm. Found: C 50.9; H 2.7; Br 42.2%. $C_{16}H_{10}Br_{2}O$. Calculated: C 50.8; H 2.7; Br 42.3%.

The filtrate after separation of IIa was extracted with ether, and the extract was dried with magnesium sulfate and vacuum-distilled to give 3.2 g of 2-acetylfuran and 3.6 g of 1-bromo-4-chlorobenzene (mp 66-67°). The residue began to crystallize on standing to give 7.5 g (30% based on the converted acetylfuran) of Ia with mp 90-91° (from benzene). IR spectrum: 1660 cm⁻¹ (CO). Found: C 54.0; H 3.5; Br 30.6%. $C_{12}H_{9}BrO_{2}$. Calculated: C 54.4; H 3.4; Br 30.1%.

Reaction of p-Chlorobenzenediazonium Chloride with Acetylfuran. This experiment was carried out as described above with 13.7 g (0.125 mole) of acetylfuran. A total of 4.5 g of unchanged 2-acetylfuran, 0.6 g of p-dichlorobenzene (mp 52-53°), and 1.9 g (8% based on the converted acetylfuran) of 2,5-di (p-chlorophenyl)furan (IIb) with mp 168-169° (from hexane) [4] were isolated. Found: C 66.0; H 3.5; Cl 24.8%. $C_{16}H_{10}Cl_2O$. Calculated: C 66.4; H 3.5; Cl 24.6%. The ether extract yielded 9.1 g (52% based on the converted acetylfuran) of 2-acetyl-5-(p-chlorophenyl)furan (Ib) with bp 126-129° (1 mm), mp 60.5-61.5° (from hexane), and R_f 0.5 [hexane-acetone (4:1), Silufol]. Found: C 65.3; H 4.1; Cl 15.7%. $C_{12}H_9ClO_2$. Calculated: C 65.3; H 4.1; Cl 16.1%.

2-Acetyl-5-(p-nitrophenyl)furan (Ic). Furan Ic with mp 164.5-165.5° (from ethyl acetate) was obtained in 80% yield under the conditions described above. The product had R_f 0.42 [chloroform-petroleum ether (1:1), Al₂O₃, colored spot] and 0.67 (chloroform, Silufol). Found: C 62.6; H 3.9; N 6.0%; $C_{12}H_9NO_4$. Calculated: C 62.3; H 3.9; N 6.1%. The thiosemicarbazone had mp 215-216° (from acetic acid). Found: C 51.7; H 4.2; N 18.2; S 10.0%. $C_{13}H_{12}N_4O_3S$. Calculated: C 51.3; H 4.0; N 18.4; S 10.5%.

5-(p-Chlorophenyl)-2-acetylfuran (Ib). Boron trifluoride etherate (0.3 g) was added to a cooled (to 0°) solution of 3.6 g (0.02 mole) of p-chlorophenylfuran [5] in 8 ml of acetic anhydride. The reaction mass was heated to 110°, cooled rapidly to 0°, and stirred at room temperature for 0.5 h.* The reaction mixture was treated with water and extracted with ether. The extract was washed with sodium carbonate solution and water, dried with sodium sulfate, and evaporated. The residue began to crystallize on standing to give 0.24 g (5%) of yellow crystals of Ib with mp 60.5-61.5° (from hexane). The product did not depress the melting point of a sample of Ib obtained by means of the Meerwein reaction. The product had R_f 0.5 (hexane—acetone (4:1), Silufol].

2,5-Di (p-chlorophenyl)furan (IIb). p-Chloroaniline hydrochloride, obtained from 4.5 g (0.035 mole) of p-chloroaniline, 7 ml of water, and 15 ml of concentrated hydrochloric acid, was diazotized with a solution of 2.3 g (0.033 mole) of sodium nitrite in 10 ml of water. The reaction mixture was stirred at 5° for 20 min and 5.9 g (0.033 mole) of 2-(p-chlorophenyl)furan [5] in 40 ml of acetone and a solution of 0.7 g of cupric chloride in 1.5 ml of water were added. The mixture was then stirred at 15-20° for 4 h, 100 ml of water was added, and the resulting precipitate was removed by filtration and washed with water to give 1.2 g (12%) of IIb with mp 167-168° (from ethanol) [4]. The product did not depress the melting point of the previously obtained sample of IIb.

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^{*}The reaction does not proceed under the usual conditions for the acetylation of furan [3].