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SHORT COMMUNICATIONS

Chemistry of Iminofurans. Unusual Reaction of 3-(4-Bromophenylimino)-5-phenyl-2,3-dihydrofuran-2-one with Malononitrile and Ethyl Cyanoacetate

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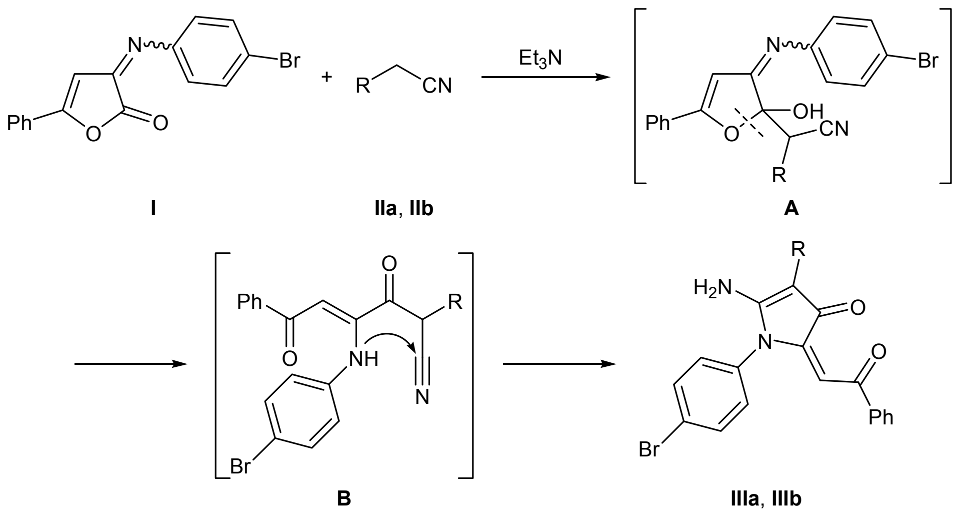
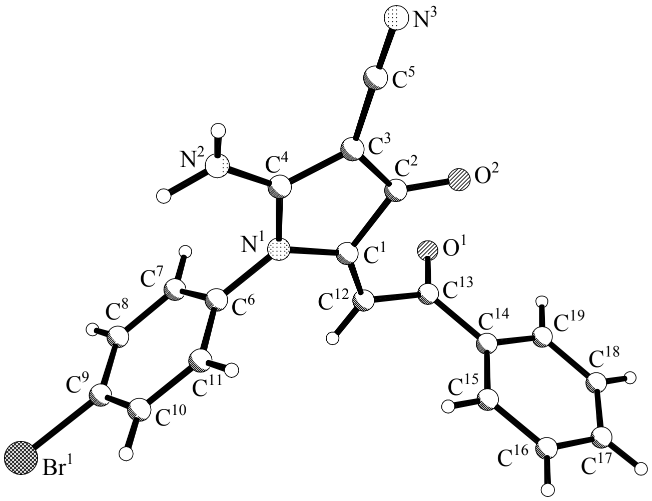
Condensation of 5-aryl-2,3-dihydrofuran-2,3-diones with malononitrile and ethyl cyanoacetate in dioxane in the presence of triethylamine leads to the formation of 6-aryl-3,4-dihydroxy-6-oxohexa-2,4-dienoic acid amides having a cyano or ethoxycarbonyl group, respectively, on C^2 [1]. The reaction involves initial attack by the activated methylene group in malononitrile or ethyl cyanoacetate on the lactone carbonyl group of furandione with formation of acyclic intermediate which undergoes hydrolysis of the cyano group to amide. In the present work, instead of 5-aryl-2,3-dihydrofuran-2,3-dione, we examined the transformation of its 3-arylimino derivative under analogous conditions. This transformation was interesting from the viewpoint of studying chemical properties of 3-imino-2,3-dihydrofuran-2-ones that are reactive compounds and intermediate products in the synthesis of acyclic and heterocyclic compounds possessing biological activity [2].

3-(4-Bromophenylimino)-5-phenyl-2,3-dihydrofuran-2-one (**I**) reacted with malononitrile (**IIa**) in anhydrous dioxane in the presence of triethylamine on heating for a short time to give (5*E*)-2-amino-1-(4-bromophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-4,5-dihydro-1*H*-pyrrole-3-carbonitrile (**IIIa**) whose structure was proved by X-ray analysis. The reaction of compound **I** with ethyl cyanoacetate (**IIb**) followed analogous pattern and afforded pyrrole derivative **IIIb**.



R = CN (**a**), EtOCO (**b**).



Structure of the molecule of (5*E*)-2-amino-1-(4-bromophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-4,5-dihydro-1*H*-pyrrole-3-carbonitrile (**IIIa**) according to the X-ray diffraction data.

Presumably, initial nucleophilic attack on the C^2 atom in the furan ring by the activated methylene group or carbanion generated by the action of triethylamine gives intermediate **A**. The subsequent opening of the furan ring via cleavage of the C^2–O bond produces intermediate **B**, and the latter undergoes intramolecular nucleophilic attack by the NH group on the cyano carbon atom with formation of substituted pyrrole **III**.

(5*E*)-2-Amino-1-(4-bromophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-4,5-dihydro-1*H*-pyrrole-3-carbonitrile (IIIa). A solution of 3.56 g (0.01 mol) of furan-2-one **I**, 0.66 g (0.01 mol) of malononitrile (**IIa**), and 1 g (0.01 mol) of triethylamine in 30 ml of anhydrous dioxane was heated for 1 min and cooled, and the precipitate was filtered off and recrystallized from acetonitrile. Yield 3.51 g (89%), mp 242–243°C (from acetonitrile). IR spectrum, ν, cm^{-1}: 3458, 3280 (NH); 2208 (C≡N); 1687, 1659 (C=O). ^1H NMR spectrum, δ, ppm: 5.57 s (1H, CH), 7.60 m (9H, H_{arom}), 8.16 s and 8.9 s (1H each, NH_2). ^{13}C NMR spectrum, δ_C, ppm: 66.44 (C^3), 109.75 (=CH), 114.63 (CN), 123.32 (C), 128,52 (CH), 128.66 (CH), 131.57 (CH), 131.81 (C), 133.24 (CH), 133.54 (CH), 136.98 (C), 141.41 (C^2), 164.71 (C^5), 177.16 (C^4), 193.0 (CO). Found, %: C 57.92; H 3.06; Br 20.31; N 10.64. $C_{19}H_{12}BrN_3O_2$. Calculated, %: C 57.89; H 3.07; Br 20.27; N 10.66.

Ethyl (5*E*)-2-amino-1-(4-bromophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (IIIb) was synthesized in a similar way from 3.56 g (0.01 mol) of furanone **I** and 1.13 g (0.01 mol) of ethyl cyanoacetate (**IIb**). Yield 3.79 g (86%), mp 264–266°C (from acetonitrile). IR spectrum, ν, cm^{-1}: 3441, 3281 (NH); 1711 (C=O, ester); 1665, 1645 (C=O). ^1H NMR spectrum, δ, ppm: 1.14 t (3H, Me), 4.07 q (2H, OCH_2), 5.55 s (1H, CH), 7.60 m (9H, H_{arom}), 8.15 s and 8.30 s (1H each, NH_2). ^{13}C NMR spectrum, δ_C, ppm: 14.52 (CH_3), 58.36 (CH_2), 85.88 (C^3), 108.53 (=CH), 123.32 (C), 128.44 (CH), 128.50 (CH), 131.36 (CH), 132.05 (C), 132.98 (CH), 133.48 (CH), 137.23 (C), 141.79 (C^2), 164.48 (C^5), 166.08 (CO), 174.68 (C^4), 193.62 (CO). Found, %: C 57.12; H 3.85; Br 18.15; N 6.32. $C_{21}H_{17}BrN_2O_4$. Calculated, %: C 57.16; H 3.88; Br 18.11; N 6.35.

X-Ray analysis of compound IIIa. Single crystals of compound **IIIa** suitable for X-ray analysis were obtained by crystallization from dioxane–acetonitrile (1:9). Compound **IIIa** crystallized as a solvate with dioxane at a ratio of 2:1. $C_{19}H_{12}N_3O_2 \cdot 0.5C_4H_8O_2$. Monoclinic crystal system; unit cell parameters: a = 8.420(2), b = 19.909(4), c = 11.835(2) Å; β = 98.90(3)°; V = 1960.1(7) $Å^3$; M 438.28; d_{calc} = 1.485 g/ cm^3; Z = 4; space group $P2(1)/n$. The unit cell parameters and experimental reflection intensities were measured on a KM-4 (Kuma Diffraction) automatic four-circle diffractometer with χ-geometry (monochromatized MoK_α irradiation; ω–2θ scanning in the range 2.05 < 2θ < 25.01°). Total of 3976 reflections were measured, 3067 of which were independent (R_{int} = 0.0329). No correction for absorption was introduced (μ = 2.124 mm^{-1}). The structure was solved by the direct statistical method using SIR92 program [3], followed by a series of calculations of electron density maps. The positions of hydrogen atoms were set on the basis of geometry considerations. The structure was refined by the least-squares procedure in full-matrix anisotropic approximation using SHELXL-97 software [4]; the final divergence factors were R_1 = 0.0608, wR_2 = 0.1632 for 1799 reflections with $I \geq 2\sigma(I)$ (262 refined parameters); goodness of fit 0.969.

The examined crystals consist of molecules **IIIa** and dioxane molecule located in the crystallographic symmety center, so that a half of dioxane molecule fits one molecule **IIIa**. The structure of molecule **IIIa** is shown in figure. All bond lengths and bond angles do not differ from the corresponding standard values. The plane of the *para*-substituted phenyl ring with the pyrrole ring plane forms a dihedral angle of 79.0°. The orientation of the 2-oxo-2-phenylethylidene substituent is characterized by the torsion angles $N^1C^1C^{12}C^{13}$ 172.9° and $C^1C^{12}C^{13}C^{14}$ 107.5°, and the carbonyl group lies in the plane of the benzene ring which is turned through a dihedral angle of 75.4° with respect to the pyrrole ring plane. Molecules **IIIa** in crystal are related to each other through a glide-reflection plane *n* and are linked by intermolecular hydrogen bonds $N^2–H^{2A}\cdots O^2$ 2.77 Å to form infinite chains. The chains are linked by dioxane molecules into layers via hydrogen bonds $N^2–H^{2B}\cdots O^3$ 2.89 Å.

The IR spectra were measured on an FSM-1201 spectrometer from samples dispersed in mineral oil. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus-300 instrument at 300 and 75 MHz, respectively, using DMSO-d_6 as solvent and hexamethyldisiloxane as internal reference. The elemental compositions were determined on a Leco CHNS-932 analyzer. The purity of the isolated compounds was checked, and the progress of reactions was monitored, by TLC on Silufol UV-254 or Sorbfil plates using diethyl ether–benzene–acetone (10 : 9 : 1) as eluent.

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