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LETTERS TO THE EDITOR

SYNTHESIS OF 3-(2,4-DINITROPHENYL)-HYDRAZONES OF 5-ARYLFURAN-2,3-DIONES

V. O. Kozminykh, A. O. Belyaev, and E. N. Kozminykh

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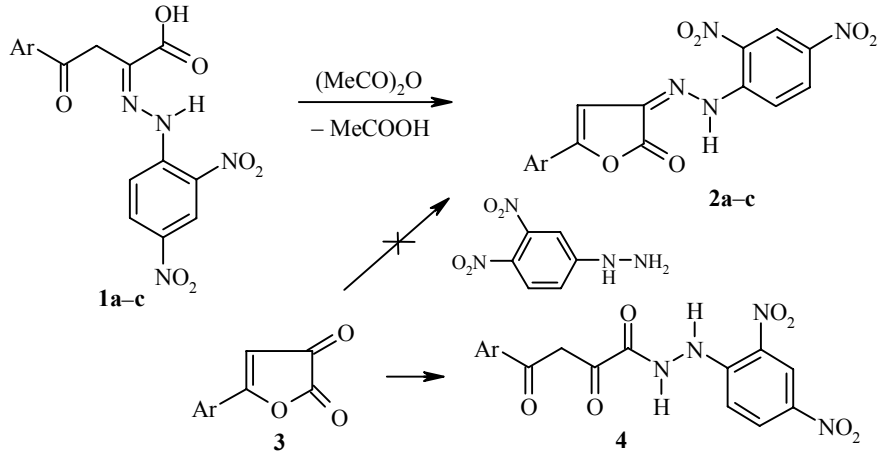
Dehydration of 4-aryl-2-[(1,5-dimethyl-3-oxo-2-phenylpyrazolin-4-yl)amino]-4-oxo-2-butenoic acids in the presence of acetic anhydride leads to 4-[(5-aryl-2-oxofuran-3-ylidene)amino]-1,5-dimethyl-2-phenylpyrazolin-3-ones [1, 2]. In contrast to 2-heterylamino derivatives, no cyclization products can be isolated upon dehydration of 4-aryl-2-arylamino-4-oxo-2-butenoic acids under these conditions. We have established for the first time that 4-aryl-2-[(2,4-dinitrophenyl)hydrazono]-4-oxobutanoic acids **1a-c** [3, 4] when treated with acetic anhydride undergo ring closure to form the previously inaccessible 3-(2,4-dinitrophenyl)hydrazones of 5-arylfuran-2,3-diones **2a-c**. Compounds **2** cannot be obtained directly by reaction of 5-arylfuran-2,3-diones **3** with 2,4-dinitrophenylhydrazine, since (2,4-dinitrophenyl)hydrazides of aroylpyruvic acids **4** [3, 4] are formed as a result.

Hydrazones **2** are bright red crystalline compounds that are stable in storage, are difficultly soluble in conventional organic solvents, and decompose upon heating. In contrast to the starting acids **1**, the IR spectra of compounds **2** have the characteristic band of a lactone carbonyl conjugated with the 3-hydrazone linkage, in the 1791-1808 cm^{-1} region.



1, 2 a Ar = Ph, **b** Ar = *p*-MeC_6H_4, **c** Ar = *p*-Cl C_6H_4

Perm State Pedagogical University, Perm 614990, Russia; e-mail: kvo@pi.ccl.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1263-1264, August, 2003. Original article submitted May 3, 2003.

3-(2,4-Dinitrophenyl)hydrazones of 5-Arylfuran-2,3-diones 2a-c. A solution of the corresponding acid **1a-c** (5 mmol) [3, 4] in acetic anhydride (5-7 ml) was heated at 80-90°C for 15-20 min. After cooling, the precipitate was filtered out and washed with ether.

5-Phenylfuran-2,3-dione 3-(2,4-Dinitrophenyl)hydrazone (2a). Yield 1.63 g (92%); mp 277-278°C (decomposes). IR spectrum (vaseline oil), ν, cm^{-1}: 3215 (NH), 1808 ($CO_{lactone}$), 1668, 1638, 1541, 1462. ^1H NMR spectrum (80 MHz, DMSO-d_6), δ, ppm: 7.15 (1H, s, $C_{(4)}H$); 7.26-8.67 (8H, m, Ph, C_6H_3); 8.82 (1H, s, NH). Found, %: C 53.89; H 3.14; N 15.64. $C_{16}H_{10}N_4O_6$. Calculated, %: C 54.24; H 2.85; N 15.81.

5-*p*-Tolylfuran-2,3-dione 3-(2,4-Dinitrophenyl)hydrazone (2b). Yield 1.71 g (93%); mp 266-267°C (decomposes). IR spectrum (vaseline oil), ν, cm^{-1}: 3223 (NH), 1802 ($CO_{lactone}$), 1665, 1632, 1547, 1460. ^1H NMR spectrum (80 MHz, DMSO-d_6), δ, ppm: 7.13 (1H, s, $C_{(4)}H$); 7.18-8.62 (7H, m, C_6H_4, C_6H_3); 8.88 (1H, s, NH). Found, %: C 55.68; H 3.43; N 15.07. $C_{17}H_{12}N_4O_6$. Calculated, %: C 55.44; H 3.28; N 15.21.

5-*p*-Chlorophenylfuran-2,3-dione 3-(2,4-Dinitrophenyl)hydrazone (2c). Yield 1.70 g (88%); mp 284-285°C (decomposes). IR spectrum (vaseline oil), ν, cm^{-1}: 3251 (NH), 1791 ($CO_{lactone}$), 1644, 1536, 1460. ^1H NMR spectrum (80 MHz, DMSO-d_6), δ, ppm: 7.22 (1H, s, $C_{(4)}H$); 7.10-8.55 (7H, m, C_6H_4, C_6H_3); 9.15 (1H, s, NH). Found, %: C 49.72; H. 2.50; Cl 8.91; N 14.63. $C_{16}H_9ClN_4O_6$. Calculated, %: C 49.44; H 2.33; Cl 9.12; N 14.41.

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