Chemistry of Heterocyclic Compounds, Vol. 41, No. 6, 2005

A NOVEL HETEROCYCLIC SYSTEM: BENZO[*b*]FURO[4,3,2-*ef*][1]BENZOXEPIN

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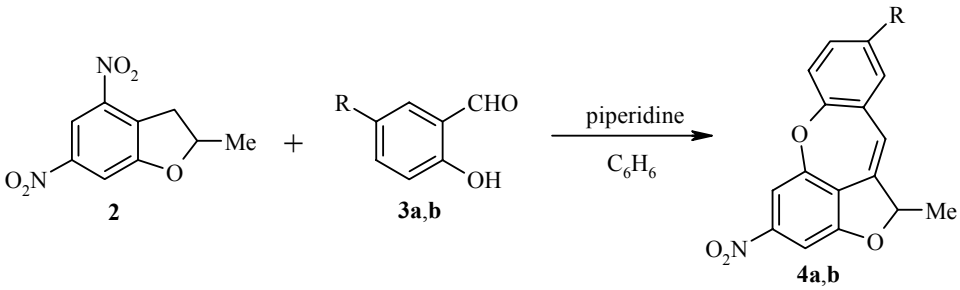
Keywords: 1H-benzo[*b*]furo[4,3,2-*ef*][1]benzoxepin, 2-methyl-4,6-dinitro-2,3-dihydrobenzofuran, salicylic aldehyde, Knoevenagel condensation, nucleophilic substitution of a nitro group.

In one of our previous publications on utilization of trinitrotoluene, we reported on synthesis of the novel heterocyclic system benzoxepinoindole **1** [1] by condensation of 4,6-dinitro-1-tosylindoline with salicylic aldehyde under base catalysis conditions (we obtained 4,6-dinitro-1-tosylindoline earlier from trinitrotoluene [2]).

Accordingly, it seemed of interest to synthesize analogs of compound **1** containing a heteroatom other than nitrogen. With this objective, we reacted salicylic aldehyde with 2-methyl-4,6-dinitro-2,3-dihydrobenzofuran (**2**), the oxygen analog of 4,6-dinitro-1-tosylindoline. We know that reaction of compound **2** with benzaldehyde in the presence of piperidine occurs as a Mannich reaction [3]. However, in this work we have shown that when it is reacted with salicylic aldehyde **3a** under the same conditions (boiling in benzene with addition of an equimolar amount of piperidine), we see formation of a derivative of the novel heterocyclic system benzo[*b*]furo[4,3,2-*ef*][1]benzoxepin **4a**, the oxygen analog of indole **1**.



3, **4 a** R = H, **b** R = Br

Obviously this reaction, in contrast to the reaction of **2** with benzaldehyde, occurs as a Knoevenagel condensation followed by intramolecular nucleophilic substitution of the nitro group. 5-Bromosalicylic aldehyde **3b** reacts similarly to form compound **4b**.

^{1}H NMR spectra were taken on Bruker DRX-500 (500 MHz) in DMSO-d_6, internal standard TMS.

1-Methyl-4-nitro-1H-benzo[*b*]furo[4,3,2-*ef*][1]benzoxepin (4a). Yield 68%; mp 155-156°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.54 (3H, d, J = 7.5, CH_3); 5.56 (1H, m, H-1); 6.35 (1H, s, H-11); 6.99 (1H, d, J = 8.2, H-7); 7.12 (2H, m); 7.27 (2H, m); 7.35 (1H, s, H-3 or H-5). Mass spectrum, m/z (I_{rel}, %): 281 $[M]^+$ (90), 266 (100), 220 (63), 163 (34). Found, %: C 68.22; H 4.06; N 4.88. $C_{16}H_{11}NO_4$. Calculated, %: C 68.32; H 3.94; N 4.98.

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9-Bromo-1-methyl-4-nitro-1H-benzo[*b*]furo[4,3,2-*ef*][1]benzoxepin (4b). Yield 53%; mp 211-214°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.53 (3H, d, *J* = 7.6, CH_3); 5.58 (1H, m, H-1); 6.35 (1H, s, H-11); 6.93 (1H, d, *J* = 8.3, H-7); 7.28 (1H, s, H-10); 7.36 (1H, d, *J* = 1.9); 7.38 (1H, d, *J* = 1.9, H-3 and H-5); 7.42 (1H, dd, *J* = 8.2, *J* = 2.1, H-8). Mass spectrum, *m*/*z* (I_{rel}, %): 361 $[M]^+$ (95), 359 $[M]^+$ (100), 346 (57), 344 (59), 280 (51), 163 (53). Found, %: C 53.76; H 2.50; Br 22.20; N 3.66. $C_{16}H_{10}BrNO_4$. Calculated, %: C 53.36; H 2.80; Br 22.19; N 3.89.

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