

SHORT  
COMMUNICATIONS

## Synthesis of 9-Bromo-3-methoxydibenzo[*c,f*][1,2]oxazepine-11-carbonitrile

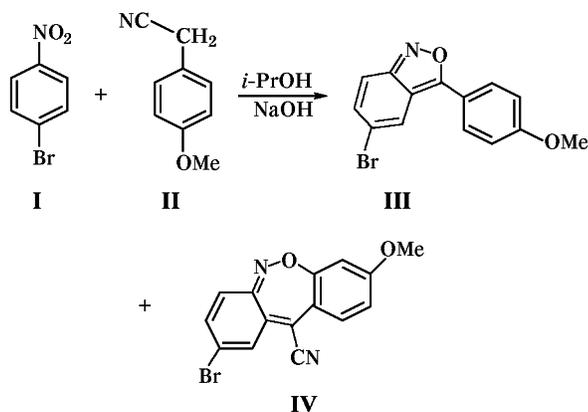
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Reactions of 4-substituted nitroarenes with acylacetonitriles in alcohol in the presence of excess alkali [1, 2] is a convenient procedure for preparation of 2,1-benzisoxazoles (anthranils), synthons for the fine organic synthesis, semiproducts in monomers production [3], and bioactive substances [4].

We found that the reaction of 4-nitrobromobenzene (**I**) with 4-methoxyphenylacetonitrile (**II**) in 2-propanol in the presence of excess sodium hydroxide (molar ratio of the reagents 1:1.2:15 respectively) afforded a mixture of products.



Alongside the main reaction product, 5-bromo-3-(4-methoxyphenyl)-2,1-benzisoxazole (**III**) (synthesized in [1] for the first time), was isolated as an individual compound previously unknown 9-bromo-3-methoxydibenzo[*c,f*][1,2]oxazepine-11-carbonitrile (**IV**). No mention of compound **IV** was also in the other publication dealing with the reactions of this type [2].

**Reaction of 4-nitrobromobenzene (I) with 4-methoxyphenylacetonitrile (II).** To a mixture of 50 ml of 2-propanol and 6 g (150 mmol) of fine powder of sodium hydroxide was added at room temperature 2 g (9.9 mmol) of 4-nitrobromobenzene

(**I**) and 1.6 ml (11.9 mmol) of nitrile **II**. The reaction mixture was stirred for 15 h at 20°C, and then poured into 500 ml of 3% HCl mixed with ice. The separated precipitate was filtered off and dried in air to get 2.8 g of dry mixture of the reaction products.

**5-Bromo-3-(4-methoxyphenyl)-2,1-benzisoxazole (III).** The dry residue obtained above was boiled in 2-propanol and filtered hot. The light-orange crystals precipitated from the filtrate on cooling were filtered off, washed with ethanol, and dried in air for 6 h. We obtained 1.9 g (63%) of compound **III**, mp 128–129°C (134–135°C [1]). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1638 (C=N), 1275 (N-O).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 8.31 d (1H, H<sup>4</sup>), 7.36 d.d (1H, H<sup>6</sup>), 7.52 d (1H, H<sup>7</sup>), 7.96 d (2H, C<sub>6</sub>H<sub>4</sub>), 7.17 d (2H, C<sub>6</sub>H<sub>4</sub>), 3.88 s (3H, OCH<sub>3</sub>). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 303 [ $M$ ]<sup>+</sup> (60), 288 (20), 260 (60), 224 (40), 153 (100), 107 (20), 92 (90), 77 (90), 63 (80). Found, %: C 55.10; H 3.15; N 4.22. C<sub>14</sub>H<sub>10</sub>BrNO<sub>2</sub>. Calculated, %: C 55.29; H 3.31; N 4.61.

**9-Bromo-3-methoxydibenzo[*c,f*][1,2]oxazepine-11-carbonitrile (IV).** The residue retained on the filter after filtration of the hot solution in 2-propanol was crushed into powder and carefully washed on a filter with boiling 2-propanol with benzene added, then it was dried in air for 6 h. We obtained 0.3 g (9.2%) of bright-red compound, mp 233–234°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2219 (C≡N).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 8.62 d (1H, H<sup>3</sup>), 8.37 d (1H, H<sup>4</sup>), 8.25 d.d (1H, H<sup>6</sup>), 7.95 d (2H, H<sup>1</sup>, H<sup>7</sup>), 7.55 d.d (1H, H<sup>2</sup>), 4.10 s (3H, OCH<sub>3</sub>). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 328 [ $M$ ]<sup>+</sup> (100), 312 (40), 298 (20), 283 (30), 269 (30), 190 (45), 178 (50), 163 (30), 151 (40), 113 (30), 74 (30), 63 (20), 50 (20), 40 (40). Found, %: C 54.47; H 2.35; N 8.24. C<sub>15</sub>H<sub>9</sub>BrN<sub>2</sub>O<sub>2</sub>. Calculated, %: C 54.74; H 2.75; N 8.51.

<sup>1</sup>H NMR spectra were registered on spectrometer Bruker AC-300 SE (300.13 MHz) from solutions in DMSO-*d*<sub>6</sub>, internal reference HMDS. IR spectra were recorded on spectrophotometer Specord M-80 from mulls in mineral oil. Elemental analyses were performed on CHN analyzer. The molecular weight was derived from mass spectra obtained on MKh-1310 device. The purity of compounds was checked by GLC on chromatograph LKhM-80 equipped with flame-ionization detector, column 3000×3 mm, stationary phase 3% SKTFT-50 X on Chromaton N-AW DMCS (0.2–0.25 mm), temperature of vaporizer 250°C, of detector 250°C, oven tempera-

ture 230°C, carrier gas nitrogen, flow rate 30 ml min<sup>-1</sup>.

#### REFERENCES

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