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SHORT COMMUNICATIONS

Reaction of 4-Nitrochlorobenzene with 2-Methoxyphenylacetonitrile

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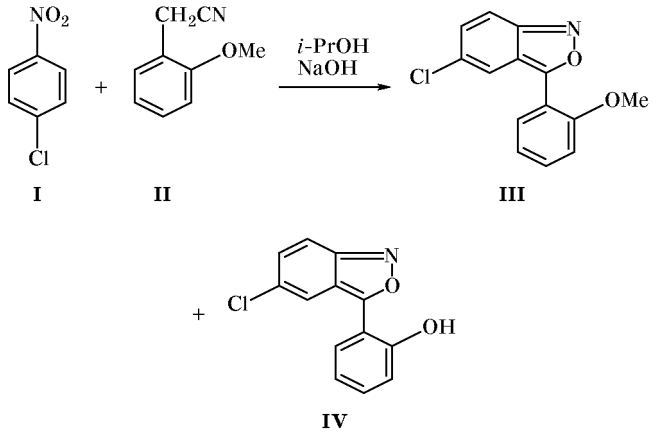
The reaction of 4-substituted nitroarenes with arylacetonitrile in alcoholic medium in the presence of excess alkali provides a convenient method for the preparation of 2,1-benzisoxazoles which are versatile synthons and intermediate products in manufacture of monomers and bioactive substances (tranquilizers) [1–3]. We have found that the reaction of 4-nitrochlorobenzene (**I**) with 2-methoxyphenylacetonitrile (**II**) gives a mixture of methoxy and hydroxy derivatives **III** and **IV**.



I **II** **III** **IV**

The major reaction product is previously unknown 5-chloro-3-(2-hydroxyphenyl)-2,1-benzisoxazole (**IV**) rather than 5-chloro-3-(2-methoxyphenyl)-2,1-benzisoxazole (**III**). By special experiments we showed that replacement of the methoxy group occurs at an intermediate stage of the process, for compound **III** was not converted into **IV** in a mixture of isopropyl alcohol and sodium hydroxide.

To a mixture of 50 ml of isopropyl alcohol and 8 g (0.2 mol) of finely powdered sodium hydroxide we added 2.2 g (15 mmol) of 2-methoxyphenylacetonitrile (**II**) and 2 g (12.7 mmol) of 4-nitrochlorobenzene (**I**). The mixture was stirred for 10 h at room temperature and poured into 500 ml of water, and the precipitate was filtered off, dried, and recrystallized from a 1:1 mixture of alcohol with acetone. We thus isolated 0.7 g (21%) of compound **III**. To the filtrate we added 40 ml of 20% hydrochloric acid. The precipitate was filtered off, dried, and washed with a small amount of cold acetone to obtain 1.6 g (51%) of compound **IV**.

5-Chloro-3-(2-methoxyphenyl)-2,1-benzisoxazole (III). mp 173–174°C; published data [4]: mp 69–70°C. IR spectrum, ν, cm^{-1}: 1638 (C=N), 1275 (N−O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.22 d (1H, 4-H), 7.77 d.d (1H, 6-H), 7.29 d (1H, 7-H), 7.39 m (1H, H_{arom}), 7.83–7.91 m (3H, H_{arom}), 3.89 s (3H, OCH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 259 $[M]^+$ (65), 244 (74), 228 (100), 200 (30), 174 (10), 164 (28), 153 (10), 75 (20), 63 (15). Found, %: C 64.66; H 3.80; N 5.45. $C_{14}H_{10}ClNO_2$. Calculated, %: C 64.75; H 3.88; N 5.39.

5-Chloro-3-(2-hydroxyphenyl)-2,1-benzisoxazole (IV). mp >250°C. IR spectrum, ν, cm^{-1}: 3275 (OH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.21 d (1H, 4-H), 7.73 d.d (1H, 6-H), 8.23 d (1H, 7-H), 7.28 m (1H, C_6H_4), 7.73–7.89 m (3H, C_6H_4), 11.4 s (1H, OH). Mass spectrum, *m*/*z* (I_{rel}, %): 244 $[M-H]^+$ (42), 228 (100), 200 (50), 174 (10), 164 (50), 153 (10), 138 (20), 124 (12), 110 (12), 101 (19), 83 (19), 74 (48), 63 (34), 50 (60), 39 (22). Found, %: C 63.47; H 3.15; N 5.14. $C_{13}H_8ClNO_2$. Calculated, %: C 63.75; H 3.28; N 5.70.

The ^1H NMR spectra were recorded on a Bruker AC-300SF spectrometer (300.13 MHz) in DMSO-d_6 using HMDS as internal reference. The IR spectra were measured on a Specord M-80 instrument from samples dispersed in mineral oil. The elemental

compositions were determined on a CHN-1 analyzer. The mass spectra were run on an MKh-1310 mass spectrometer.

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