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REGIOSELECTIVE ARYLATION OF NH-TETRAZOLES

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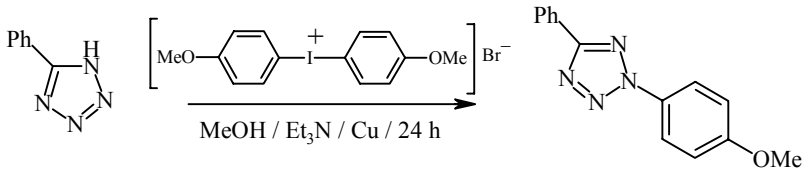
Reactions of 5-substituted tetrazoles with various electrophilic reagents are generally used in synthesis of N-alkyltetrazoles [1]. The use of this route to obtain N-aryltetrazoles does not lead to the desired result, which can be achieved only by more complicated methods [2]. An exception is the attempt to carry out arylation of the sodium salt of 5-phenyltetrazole with diaryliodonium salts, leading to formation of a complex mixture of isomeric products [3]. As noted by the authors themselves of the cited paper, this is a consequence of competing reactions of the diaryliodonium halide with the solvent (*t*-BuOH). Following the patent in [4], we attempted to alter the reaction conditions, using the triethylammonium salt of 5-phenyltetrazole in methanol in the reaction with bis(4-methoxyphenyl)iodonium bromide.



In contrast to [3], in this case we observe selective formation of 2-(4-methoxyphenyl)-5-phenyltetrazole. The method described possibly is competitive with the traditional methods for obtaining N-aryltetrazoles.

2-(4-Methoxyphenyl)-5-phenyltetrazole. A solution of 5-phenyltetrazole (1.45 g, 10 mmol), bis(4-methoxyphenyl)iodonium bromide (8.42 g, 20 mmol), triethylamine (1.4 ml, 10 mmol) and copper powder (0.1 g, 1.5 mmol) in 100 ml anhydrous methanol were stirred for 24 h at 18-20°C. The suspension formed was filtered to remove a small amount of undissolved material, and then the methanol was evaporated under vacuum. The residue was dissolved in chloroform (100 ml), washed with a 5% solution of sodium bicarbonate (3 × 20 ml), distilled water (2 × 25 ml), and dried over sodium sulfate. The chloroform was evaporated under vacuum, and the dry residue was recrystallized from ethanol. Yield 0.40 g (16%) of 2-(4-methoxyphenyl)-5-phenyltetrazole; mp 100.5-101.0°C (according to data in]5], mp 101-102°C; for the analogous 1H-isomer, according to data in [6], mp 130-132°C). R_f 0.75 (Merck 60 F254, 100% chloroform). ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm, *J* (Hz): 8.12 (2H, d, *J* = 4.4, Ph); 8.02 (2H, d, *J* = 8.7, Ar); 7.56 (3H, s, Ph); 7.17 (2H, d, *J* = 8.0, Ar); 3.84 (3H, s, OCH_3). ^{13}C NMR spectrum (DMSO-d_6, 75 MHz), δ, ppm: 165.1 ($C_{(5)}$ in 2,5-tetrazole), 131.6, 130.4, 130.1, 127.4, 122.3, 115.9 (Ph and Ar), 56.5 (OCH_3). IR spectrum (KBr), ν, cm^{-1}: 1609, 1596 (Ph and Ar), 1515, 1450, 1263, 1018 (tetrazole ring), 829, 726, 687. Found, %: C 66.53; H 4.70; N 22.30. $C_{14}H_{12}N_4O$. Calculated, %: C 66.65; H 4.79; N 22.21.

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