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PREPARATION OF (BENZO)ISOQUINOLINES USING *in situ* GENERATED ARYNE INTERMEDIATES

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(Benzo)isoquinoline derivatives are of significant interest in different areas of basic and applied organic chemistry. Of special promise are their biological [1-3], photophysical, and coordination [4-8] properties. Their use as chiral catalysts [9, 10] is also of interest.

The most frequently used methods for preparing (benzo)isoquinoline systems are cross-coupling reactions [11, 12], which demand the use of special catalysts. We propose a method for preparing (benzo)isoquinoline derivatives based on an aza Diels–Alder reaction with 1,2,4-triazines as dienes and the aryne intermediates acting as dienophiles.

The methodology for preparing diverse pyridine derivatives *via* reaction of the corresponding 1,2,4-triazines has long been known [13-15]. However, there are only a few examples of using aryne intermediates in similar reactions. The range of dienophiles in these cases is limited to certain dehydrobenzene derivatives, the generation of which used poorly available anthranilic acids [16, 17] despite the marked growth in the chemistry of arynes in recent years [18, 19].

In our work, we propose a highly efficient method for the preparation of (het)aryl-substituted isoquinoline **1a** and benzo[*h*]isoquinoline **1b**, which involves the reaction of arynes **2a**,**b** with the substituted 1,2,4-triazines **3a**,**b** in anhydrous toluene for 24-36 h at 140°C under an argon atmosphere. The target compounds **1a**,**b** were obtained in 76% and 80% yield, respectively. The corresponding arynes were generated in situ by the action of potassium *tert*-butoxide on the chloro- and bromo-substituted arenes **4a**,**b**.

The structure of the obtained compounds **1a**,**b** was confirmed from the ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and by elemental analysis data. The mass spectra of compounds **1a**,**b** showed the presence of a molecular ion peak.

The compounds obtained are 2,2'-bipyridine type ligands with an extended conjugated system, and are of interest from the viewpoint of complex formation and as luminescent materials.

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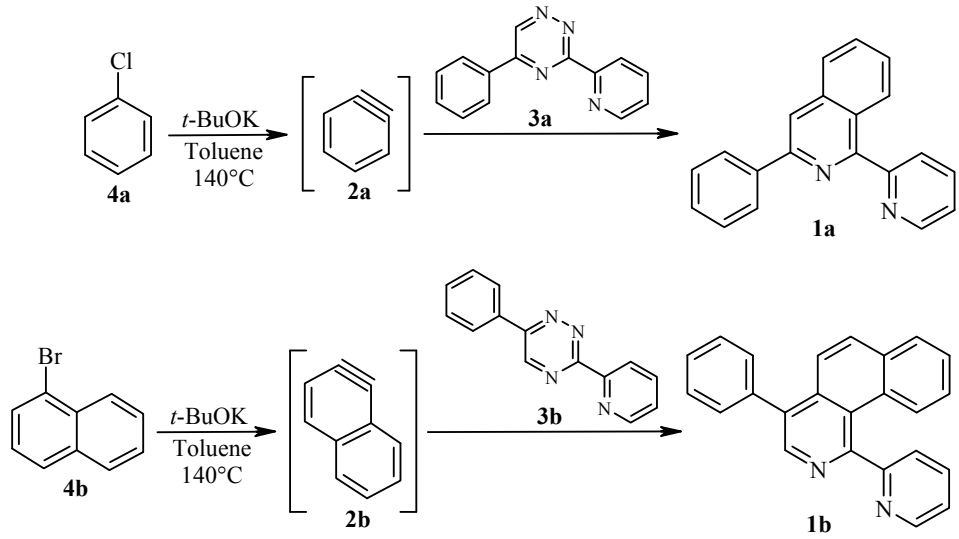

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 and 100 MHz, respectively) using $CDCl_3$ with TMS as internal standard. ESI mass spectra were recorded on a Bruker Daltonics micrOTOF-Q II mass spectrometer. Elemental analysis was conducted on a Perkin-Elmer PE 2400 series II CHN-analyzer. Melting points were determined on a Boetius hot stage apparatus. TLC analysis was performed on Merck 60 F254 silica gel and visualized in UV light. All of the synthetic procedures were carried out under an argon atmosphere.

The 5-phenyl-3-(2-pyridyl)-1,2,4-triazine (**3a**) [20] and 6-phenyl-3-(2-pyridyl)-1,2,4-triazine (**3b**) [15] were synthesized by the reported methods.

Preparation of the Aryne Cycloaddition Products (General Method). A suspension of the triazine **3a**,**b** (0.50 mmol), the haloarene **4a**,**b** (0.50 mmol), and *t*-BuOK (85 mg, 0.75 mmol) in absolute toluene (50 ml) was stirred in an autoclave at 140°C for 24 h. After cooling to room temperature, the reaction mixture was washed with water (2×50 ml), and the organic fraction was dried over anhydrous Na_2SO_4. Toluene was evaporated under reduced pressure, and the residue was purified by column chromatography using CH_2Cl_2 as eluent.

3-Phenyl-1-(2-pyridyl)isoquinoline (1a). Yield 110 mg (80%). Colorless crystals. Mp 107-109°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.41-7.45 (3H, m, H Ph); 7.51-7.53 (2H, m, H isoquinoline); 7.57-7.59 (1H, m, H isoquinoline); 7.68-7.70 (1H, m, H isoquinoline); 7.93-7.95 (2H, m, H Ph); 8.15 (1H, s, H-4); 8.21-8.23 (2H, m, H Py); 8.75 (1H, dd, ^3J = 8.4, ^4J = 1.8, H-3 Py); 8.81 (1H, dd, ^3J = 4.8, ^4J = 1.8, H-6 Py). ^{13}C NMR spectrum, δ, ppm: 117.0; 123.2; 125.6; 127.0; 127.4; 127.5; 128.0; 128.5; 128.6; 128.8; 130.1; 137.0; 138.2; 139.5; 148.3; 149.8; 157.0; 158.8. Mass spectrum, *m/z* (I_{rel}, %): 283.12 $[M+H]^+$ (100). Found, %: C 84.81; H 4.80; N 9.61. $C_{20}H_{14}N_2$. Calculated, %: C 85.08; H 5.00; N 9.92.

4-phenyl-1-(2-pyridyl)benzo[*h*]isoquinoline (1b). Yield 130 mg (76%). Colorless crystals. Mp 202-204°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.29-7.33 (2H, m, H-5 Py, H Ar); 7.49-7.64 (6H, m, H Ph, H Ar); 7.45-7.86 (6H, m, H Ph, H Ar); 8.22-8.24 (2H, m, H-3,6 Py). ^{13}C NMR spectrum, δ, ppm: 120.4; 122.9; 124.5; 126.9; 128.1; 128.4; 128.9; 129.6; 130.1; 131.2; 131.7; 133.2; 133.9; 136.8; 137.7; 142.9; 144.2; 149.2; 149.9; 151.6; 153.7; 160.7. Mass spectrum, *m/z* (I_{rel}, %): 333.15 $[M+H]^+$ (100). Found, %: C 86.55; H 4.76; N 8.21. $C_{24}H_{16}N_2$. Calculated, %: C 86.72; H 4.85; N 8.43.

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