Chemistry of Heterocyclic Compounds, Vol. 44, No. 11, 2008

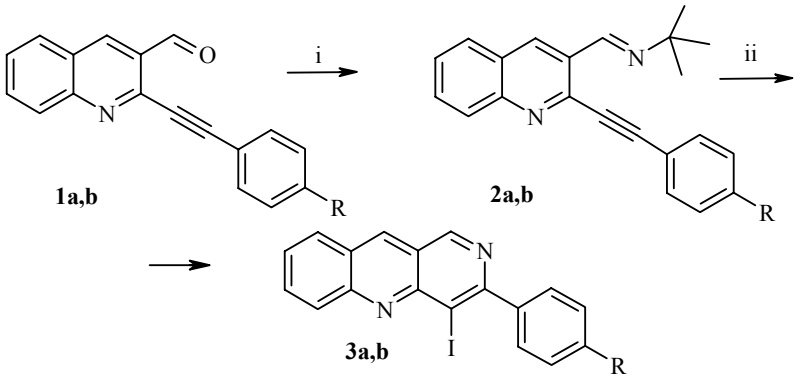
LETTERS TO THE EDITOR

FACILE SYNTHESIS OF 3-ARYL-4-IODOBENZO[*b*][1,6]NAPHTHYRIDINES

S. Rudys and I. Cikotiene

Keywords: alkynes, benzo[*b*][1,6]naphthyridines, *tert*-butylimines, cyclization.

In continuing our research on intramolecular cyclizations of alkynes that possess a nucleophile in close proximity to the carbon-carbon triple bond [1, 2] we have performed a facile synthesis of 3-aryl-4-iodobenzo-[*b*][1,6]naphthyridines. The latter compounds attract our attention as starting materials for preparation of more complex polyaromatic systems which could be of interest for practical applications, especially for OLED (organic light-emitting diode). Thus, reaction of 2-arylethynylquinoline-3-carbaldehydes **1a**,**b** with *tert*-butyl-amine in sealed tubes at 100°C gave the corresponding *tert*-butylimines **2a**,**b**. The latter two compounds underwent smooth iodine-mediated ring closure reaction and the corresponding 3-aryl-4-iodobenzo-[*b*][1,6]naphthyridines **3a**,**b** were formed. In this reaction, the iodine attacks the triple bond of compounds **2a**,**b** first, therefore nucleophilic attack of the neighboring *tert*-butylimino group becomes more favorable [3].



1–3 a R = H; **b** R = Et
Reagents and conditions: i – *t*-$BuNH_2$, sealed tube, 100°C, 24 h;
ii – I_2, $MeCO_2Na$, MeCN, r. t., 5 h

The IR spectra were obtained on a Spectrum BX II FT-IR spectrophotometer (Perkin–Elmer) in KBr disks. The ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Inova (300 and 75 MHz, respectively) in $CDCl_3$, internal standard TMS.

Vilnius University, Faculty of Chemistry, Department of Organic chemistry, Vilnius LT-03225, Lithuania; e-mail: inga.cikotiene@chf.vu.lt. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1739-11740, October, 2008. Original article submitted August 29, 2008, 2008.

 0009-3122/08/4411-1416

The starting 2-arylethynylquinoline-3-carbaldehydes **1a,b** were synthesized according to the method of [4].

N-(*tert*-Butyl)-N-{(1*E*)-[2-(arylethynyl)quinolin-3-yl]methylene}amines (2a,b). A mixture of the corresponding 2-arylethynylquinoline-3-carbaldehyde **1a**,**b** (0.2 mmol) and *tert*-butylamine (3 ml) in a tube was flushed with argon and the tube was carefully sealed. The mixture was heated at 100°C for 24 h. The solvent was evaporated under reduced pressure, and compounds **2a**,**b** were recrystallized.

N-(*tert*-Butyl)-N-{(1*E*)-[2-(phenylethynyl)quinolin-3-yl]methylene}amine (2a). Yield 92%; mp 144-146°C (octane). IR spectrum, ν, cm^{-1}: 2202 (C≡C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.44 (9H, s, $C(CH_3)_3$); 7.43–7.46 (3H, m, ArH); 7.58 (1H, ddd, *J* = 7.5, *J* = 6.0, *J* = 0.9, CH); 7.69–7.72 (2H, m, ArH); 7.94 (1H, d, *J* = 7.5, CH); 8.16 (1H, d, *J* = 8.7, CH); 8.85 (1H, s, CH); 9.08 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 29.7, 58.3, 86.8, 94.3, 122.0, 127.3, 127.5, 128.6, 128.7, 129.1, 129.4, 130.7, 130.8, 132.1, 133.6, 143.4, 148.8, 152.8. Found, %: C 84.68; H 6.34; N 9.02. $C_{22}H_{20}N_2$. Calculated, %: C 84.58; H 6.45; N 8.97.

N-(*tert*-Butyl)-N-{(1*E*)-[2-(4-ethylphenylethynyl)quinolin-3-yl]methylene}amine (2b). Yield 87%; mp 122–124°C (octane). IR spectrum, ν, cm^{-1}: 2204 (C≡C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 (3H, t, *J* = 7.8, CH_3); 1.44 (9H, s, $C(CH_3)_3$); 2.73 (2H, q, *J* = 7.8, CH_2); 7.28 (2H, d, *J* = 8.1, ArH); 7.58 (1H, ddd, *J* = 7.5, *J* = 6.0, *J* = 0.9, CH); 7.62 (2H, d, *J* = 8.1, ArH); 7.78 (1H, ddd, *J* = 7.2, *J* = 6.9, *J* = 1.5, CH); 7.93 (1H, d, *J* = 8.4, CH); 8.15 (1H, d, *J* = 8.4, CH); 8.84 (1H, s, CH); 9.09 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 15.2, 28.9, 29.7, 58.3, 86.4, 94.8, 127.2, 127.3, 128.1, 128.6, 129.0, 130.7, 130.8, 132.1, 133.5, 143.6, 146.1, 148.8, 152.9. Found, %: C 84.55; H 7.04; N 8.09. $C_{24}H_{24}N_2$. Calculated, %: C 84.67; H 7.11; N 8.23.

3-Aryl-4-iodobenzo[*b*][1,6]naphthyridines 3a,b. A mixture of the corresponding N-(*tert*-butyl)-N-{(1*E*)-[2-(arylethynyl)quinolin-3-yl]methylene}amine **2a**,**b** (1 mmol), iodine (1.54 g, 6 mmol), and sodium acetate (0.25 g, 3 mmol) in acetonitrile (5 ml) was stirred at room temperature for 5 h. The reaction mixture was diluted with ether (25 ml), washed with sat. $Na_2S_2O_3$ (25 ml), dried over sodium sulfate and evaporated.

4-Iodo-3-phenylbenzo[*b*][1,6]naphthyridine (3a). Yield 90%; mp 108–110°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.51–7.59 (3H, m, ArH); 7.71 (1H, ddd, *J* = 7.3, *J* = 6.5, *J* = 1.1, CH); 7.80–7.82 (2H, m, ArH); 7.99 (1H, ddd, *J* = 7.3, *J* = 6.8, *J* = 1.2, CH); 8.17 (1H, d, *J* = 8.7, CH); 8.47 (1H, d, *J* = 9.0, CH); 8.99 (1H, s, CH); 9.43 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 101.3, 120.9, 127.3, 127.6, 127.7, 128.7, 128.8, 130.3, 133.1, 138.1, 140.7, 145.1, 149.5, 152.6, 154.2, 159.7. Found, %: C 56.75; H 3.00; N 7.46. $C_{18}H_{11}IN_2$. Calculated, %: C 56.57; H 2.90; N 7.33.

3-(4-Ethylphenyl)-4-iodobenzo[*b*][1,6]naphthyridine (3b). Yield 80%; mp 94–96°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.43 (3H, t, *J* = 7.8, CH_3); 2.80 (2H, q, *J* = 7.8, CH_2); 7.39 (2H, d, *J* = 7.8, ArH); 7.67 (1H, ddd, *J* = 7.3, *J* = 6.5, *J* = 1.1, CH); 7.76 (2H, d, *J* = 7.8, ArH); 7.96 (1H, ddd, *J* = 7.4, *J* = 6.6, *J* = 1.2, CH); 8.12 (1H, d, *J* = 8.7, CH); 8.42 (1H, d, *J* = 9.0, CH); 8.92 (1H, s, CH); 9.38 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 15.4, 28.7, 100.9, 120.7, 127.0, 127.3, 127.4, 128.4, 128.5, 129.9, 132.8, 137.6, 140.3, 144.8, 149.2, 152.3, 153.9, 159.4. Found, %: C 58.77; H 3.58; N 7.00. $C_{20}H_{15}IN_2$. Calculated, %: C 58.55; H 3.69; N 6.83.

The work was supported by the Lithuanian Science and Study Foundation, Reg. *No*. T-08032, Grant No. T-18/08.

REFERENCES

1. I. Cikotiene, M. Morkunas, D. Motiejaitis, and S. Rudys, A. Brukstus, *Synlett*, 1693 (2008).
2. I. Cikotiene, R. Buksnaitiene, and A. Brukstus, *Khim. Geterotsikl. Soed.*, 619 (2007). [*Chem. Heterocycl. Comp*., **43**, 515 3. (2007)].
3. Q. Huang, J. A. Hunter, and R. C. Larock, *Org. Lett*., 2973 (2001).
4. P. Amaury and P. Belmont, *Synthesis*, 2400 (2005).