

[A0028]

Regioselectivity of Arylation of 2,3'-Biquinolyl Dianion

A.V. Aksenov,^{*a} I.V. Aksenova,^a I.V. Borodaev,^a and Yu. I. Smushkevich^b

^a Stavropol State University, Chair of Organic Chemistry, Stavropol 355009, Russia

^b Russian Mendeleev University of Chemical Technology, Chair of Organic Chemistry, 9 Miusskaya sq., 125047 Moscow, Russia. E-mail: sirovsk@cacr.ioc.ac.ru

Received: 30 July 1997 / Uploaded: 30 July 1997

Abstract: Dianion of 2,3'-biquinolyl with aryl- and hetaryl halides forms product of arylation to 4'-position, which on treatment with alkyl halides or water yield 1'-alkyl-1',4'-dihydro-2,3'-biquinolyls or 4'-aryl-1',4'-dihydro-2,3'-biquinolyls respectively. The oxydation of the latter leads to 4'-aryl-2,3'-biquinolyls. The cation dependence of the arylation is shown.

Keywords: Regioselectivity, arylation, 2,3'-biquinolyl dianion.

Recently we have developed the procedure for the generation of 2,3'-biquinolyl dianion (**I**) that allows to study its properties. The present work is devoted to its arylation and heteroarylation.

The studied reactions of such species with aryl halides include, as a rule, the transfer of electrones from the dianion (anion-radical) to halogenated derivative **2-4**. Thus the dianion of diphenyl reacts with halobenzenes yielding benzoic acid after the treatment of the reaction mixture with carbon dioxide **2**. We have supposed that the dianion **I** would also behave as an electron donor respective to aryl halides. However, we have supposed that due to bigger affinity of **I** to electrones comparing with that of diphenyl there can be one-electron transfer leading to the anion-radical (**II**). According to quantum chemical calculations the maximum spin density in **II** is at the 4'-position (see fig 1.).

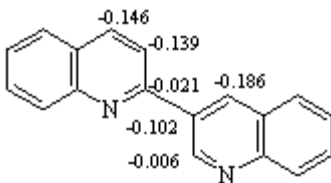
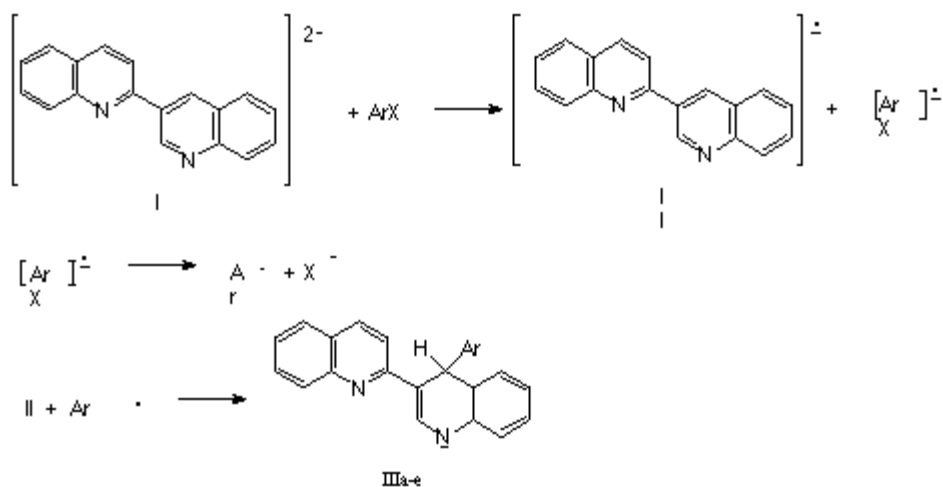


Figure 1. The distribution of the spin density in anion-radical **II** (MNDO calculations).

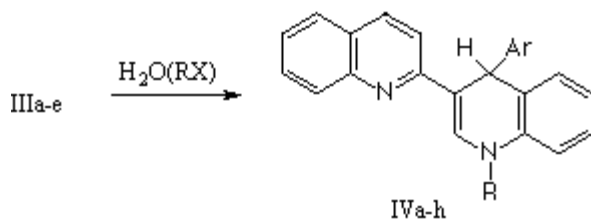
In this case, the aryl radical formed after the elimination of the halide ion would react with the anion radical (**II**) yielding the anion (**III**) (see Scheme 1).



Scheme 1. **III a:** Ar= Ph; **b** Ar= 1-C₁₀H₇; **c** Ar= 2-C₅H₄N; **d** Ar= 1-methyl-2-benzimidazolyl; **e** Ar= 1-isopropyl-2-benzimidazolyl; ArX= PhBr, 1-bromonaphthalene, 2-fluoropyridine, 1-methyl-2-chlorobenzimidazole, 1-*iso*-propyl-2-chlorobenzimidazole.

Indeed, the continuous addition of aryl or hetaryl halides to dianion **I** obtained in the reaction of 2,3'-biquinolyl with metallic lithium in THF¹ with the subsequent treatment of the resulting mixture with water yielded 4'-aryl(hetaryl)-1',4'-dihydro-2,3'-biquinolyls (**IV a-e**) with yields ranging from 64 to 78%. The treatment of the reaction mixture with alkyl halides instead of water results in formation of N-alkylation products, i.e. 1'-alkyl-4'aryl(hetaryl)-1',4'-dihydro-2,3'-biquinolyls (**IV f-h**) with yields being in the range 72-75% (Scheme 2).

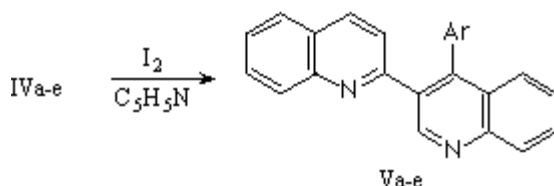
The same results were obtained when dianion **I** was generated using metallic potassium or potassium naphthalide, although their use is less convenient than that of lithium. Our investigations showed that the metal cation plays an important role in the electron transfer. Thus, 2,3'-biquinolyl does not react with potassium naphthalide in absolute THF in the presence of 1.2 molar excess of 18-crown-6 (on potassium) even during long stirring. The reaction begins on addition of dry potassium iodide.



Scheme 2: **IV a** Ar = Ph, R = H; **b** Ar=1-C₁₀H₇, R=H; **c** Ar= 2-C₅H₄N, R=H; **d** Ar = 1-methyl-2-benzimidazolyl, R=H; **e** Ar = 1-isopropyl-2-benzimidazolyl, R = H; **f** Ar= Ph, R= Me; **g** Ar=1-C₁₀H₇, R=Me; **h** Ar=1-C₁₀H₇, R=CH₂Ph; RX= MeI, PhCH₂Cl.

The same results were obtained in the arylation reaction. Thus, dianion **I** obtained from 1.25 mmol 2,3'-biquinolyl and 2.7 mmol potassium does not react with bromobenzene in the presence of 3 mmol 18-crown-6 even after two hours reflux. On addition of 1.5 mmol KI the reaction proceeds in a usual way and results in formation of **IVa**.

Compounds **IV a-e** are readily oxidised by iodine in pyridine to 4'-aryl-2,3'-biquinolyls (**V a-e**) with nearly quantitative yield (Scheme 3).



Scheme 3: **V a** Ar= Ph; **b** Ar=1-C10H7; **c** Ar= 2-C5H4N; **d** Ar = 1-methyl-2-benzimidazolyl; **e** Ar = 1-iso-propyl-2-benzimidazolyl.

The structure of these compounds was confirmed by ¹H NMR spectra. The characteristic feature of **V a-e** spectra is the movement of 3-H signal to the strong field region: **Va** 6.97 ppm, **Vb** 6.83, **Vc** 7.08, **Vd** 7.32, **Ve** 7.43 compared with 8.04 in case of 2,3'-biquinolyl. In our opinion it is explained by the perpendicular position of the aryl substituent shielding the proton in the 3 position.

It is worth noting that protons of two methyl groups in **IVe** and **Ve** are not equivalent (**IVe** 1.73 (1H, d.), 1.85 (1H, d.); **Ve** 0.75 (1H, d.), 1.24 (1H d.) as these groups are diastereotopic. However if **IVe** possess an asymmetric carbon atom in the 4' position, there is no such atom in **Ve**. Nevertheless, **Ve** also has an asymmetric center due to the inhibited rotation about C4-C2 bond of the imidazolic ring owing to the presence of bulky substituents in both quinolyl and benzimidazole fragments.

The direction of arylation was confirmed by experiments with 4'-D-2,3'biquinolyl. In the ¹H NMR spectra of **IV a-e** we have observed the lowering of 4-H signal intensity corresponding to deuterium content in starting biquinolyl. There is no "label" in **V a-e**.

Experimental section

Mass-spectra were registered on Varian MAT 331a mass-spectrometer, NMR spectra at Bruker WP-200 NMR spectrometer. The reactions were monitored by TLC on Silufol UV-254 plates, eluent ethyl acetate - hexane 2:1. THF was purified by distillation over LiAlH₄ and ketine radical, and 2,3'-biquinolyl was recrystallised from benzene and sublimed.

4'-phenyl-1',4'-dihydro-2,3'-biquinolyl (IVa, C₂₄H₁₈N₂): The solution of 0.64 g (2.5 mmol) of 2,3'-biquinolyl and 0.05 g (7 mmol) of powdered lithium in 10 mL of THF is stirred for 3 h at ambient temperature under Ar blanket. After that the solution of 0.71 g (4.5 mmol) bromobenzene in 4 mL THF is added dropwise. The reaction mixture is stirred for 1 hour at ambient temperature and refluxed for 1 h. After that 40 mL of water is added and reaction mixture is extracted with benzene (3 [lozenge] 30 mL). The organic solution is evaporated and resulting yellow oil is crystallized on benzene addition. Yield 0.65 g (78%), m.p. 212-213 deg.C (bnz.). ¹H NMR spectrum (CDCl₃): 5.73 (1H, s, 4'-H); 6.36 (1H, d, J_{NH-2'H}= 5.5 Hz, NH); 6.70 (1H, d, J_{7'8'} = 8.10 Hz, 8'-H); 6.88 (1H, d. d, J_{5'6'} = 7.64, J_{6'7'} = 7.82 Hz, 6'-H); 7.04 (1H, d. d, J_{6'7'} = 7.82, J_{7'8'} = 8.12 Hz, 7'-H); 7.2 (3H, m, 3''-H, 4''-H, 5''-H); 7.23 (1H, d, J_{5'6'} = 7.64 Hz, 5'-H); 7.34 (1H, d. d, J₅₆ = 8.02, J₆₇ = 7.51 Hz, 6-H); 7.38 (1H, d, J₃₄ = 8.91 Hz, 3-H); 7.46 (2H, d, J = 7,1 Hz, 2''-H, 6''-H); 7.61 (1H, d. d, J₆₇ = 7.51, J₇₈ = 8.61 Hz, 7-H); 7.62 (1H, d, J₅₆ = 8.02 Hz, 5-H); 7.77 (1H, d, J_{NH-2'H} = 5.5 Hz, 2'-H); 7.86 (1H, d, J₃₄ = 8.91 Hz, 4-H); 7.98 (1H, d, J₇₈ = 8.61 Hz, 8-H); determined, % C 86.28; H 5.29; N 8.43. C₂₄H₁₈N₂, calculated, % C 86.19; H 5.43; N 8.38.

4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (IVb C₂₈H₂₀N₂): Obtained just as above out of 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li and 0.72 g (3.5 mmol) 1-bromonaphthalene. Yield 0.7 g (73%), m.p. 196-197 deg.C (bnz.). ¹H NMR spectrum (CDCl₃): 6.38 (1H, d, J_{NH-2'H} = 5.7 Hz, NH); 6.64 (1H, s, 4'-H); 6.72 (1H, d. d, J_{5'6'} = 7.72, J_{6'7'} = 7.92 Hz, 6'-H); 6.74 (1H, d, J_{7'8'} = 8.06 Hz, 8'-H); 7.01 (1H, d. d, J_{6'7'} = 7.92, J_{7'8'} = 8.06 Hz, 7'-H); 7.23 (1H, d, J_{5'6'} = 7.72 Hz, 5'-H); 7.27-7.33 (3H, m, 6'-H, 3''-H, 6''-H); 7.49 (1H, d, J₃₄ = 8.83 Hz, 3-H); 7.51-7.8 (7H, m, arom.); 7.81 (1H, d, J₃₄ = 8.83 Hz, 4-H); 7.86 (1H, d, J_{NH-2'H} = 5.7 Hz, 2'-H); 9.01 (1H, d, J = 8.54, 8''-H or 8-H); determined, % C 87.71; H 5.12; N 7.17. C₂₈H₂₀N₂. Calculated, % C 87.46; H 5.25; N 7.29.

4'-(2-pyridyl)-1',4'-dihydro-2,3'-biquinolyl (IVc, C₂₃H₁₇N₃): Just as **IVa** out of 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li and 0.34 g (3.5 mmol) 2-fluoropyridine. Yield 0.56 g (67%), m.p. 219-220deg. C (bnz.). ¹H NMR spectrum (CDCl₃): 5.88 (1H, s, 4'-H); 6.60 (1H, d, J_{NH-2'H} = 5.3 Hz, NH); 6.72 (1H, d, J_{7'8'} = 7.94 Hz, 8'-H); 6.88 (1H, d. d, J_{5'6'} = 7.68, J_{6'7'} = 7.79 Hz, 6'-H); 6.98 (1H, m, 5''-H); 7.07 (1H, d. d, J_{6'7'} = 7.79, J_{7'8'} = 7.94 Hz, 7'-H); 7.34 (1H, d, J_{5'6'} = 7.68 1.63 Hz, 5'-H); 7.38 (1H, d. d., J₅₆ =

7.98, $J_{67} = 7.62$ Hz, 6-H); 7.46 (1H, d, $J_{34} = 8.96$ Hz, 3-H); 7.5 (2H, m, 3''-H, 4''-H); 7.57 (1H, d. d., $J_{67} = 7.62$, $J_{78} = 8.46$ Hz, 7-H); 7.62 (1H, d, $J_{56} = 7.98$ Hz, 5-H); 7.88 (1H, d, $J_{34} = 8.96$ Hz, 4-H); 7.90 (1H, d, $J_{78} = 8.46$, $J_{68} = 1.1$ Hz, 8-H); 7.92 (1H, d, $J_{\text{NH}-2'\text{H}} = 5.3$ Hz, 2'-H); 8.51 (1H, d. d., $J_{5''6''} = 4.7$, $J_{4''6''} = 1.7$ Hz, 6''-H); determined, % C 82.64; H 4.98; N 12.38. C₂₃H₁₇N₃. Calculated, % C 82.36; H 5.11; N 12.53.

4'-(1-methyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl (IVd, C₂₆H₂₀N₄): Just as **IVa** out of 0.64 g (2.5 mmol) 2,3'biquinolyl, 0.05 g (7 mmol) Li and 0.58 g (3.5 mmol) 1-methyl-2-chlorobenzimidazole. Yield 0.66 g (68%), m.p. 266-267 deg.C (bnz). 1H NMR spectrum (CDCl₃): 4.44 (3H, s, Me); 6.36 (1H, s, 4'-H); 6.70 (1H, d, $J_{7'8'} = 8.05$ Hz, 8'-H); 6.81 (1H, d. d., $J_{5'6'} = 7.68$, $J_{6'7'} = 7.34$ Hz, 6'-H); 6.92 (1H, d. d., $J_{6'7'} = 7.34$, $J_{7'8'} = 8.05$, 7'-H); 7.09 (1H, d, $J_{5'6'} = 7.68$ Hz, 5'-H); 7.13 (1H, d. t., $J_{4''5''} = 8.55$, $J_{5''6''} = 7.38$, $J_{5''7''} = 1.63$ Hz, 5''-H); 7.21 (1H, d. t., $J_{5''6''} = 7.38$, $J_{6''7''} = 7.67$, $J_{4''6''} = 2.35$ Hz, 6''-H); 7.29 (1H, d. d., $J_{56} = 8.04$, $J_{67} = 7.31$ Hz, 6-H); 7.38 (1H, d. d., $J_{6''7''} = 7.67$, $J_{5''7''} = 1.63$ Hz, 7''-H); 7.41 (1H, d, $J_{\text{NH}-2'\text{H}} = 5.49$ Hz, 2'-H); 7.43 (1H, d, $J_{34} = 9.14$ Hz, 3-H); 7.53 (1H, d. d., $J_{67} = 7.31$, $J_{78} = 8.04$ Hz, 7-H); 7.59 (1H, d. d., $J_{4''5''} = 8.55$, $J_{4''6''} = 2.35$ Hz, 4''-H); 7.6 (1H, d., $J_{56} = 8.04$ Hz, 5-H); 7.78 (1H, d, $J_{78} = 8.04$ Hz, 8-H); 7.80 (1H, d, $J_{34} = 9.14$ Hz, 4-H); 10.39 (1H, d, $J_{\text{NH}-2'\text{H}} = 5.49$ Hz, NH); determined, % C 80.63, H 5.11, N 14.26, C₂₆H₂₀N₄. Calculated C 80.39, H 5.19, N 14.42.

4'-(1-iso-propyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl (IVe, C₂₈H₂₄N₄): Just as **IVa** out of 0.64 g (2.5 mmol) 2,3'biquinolyl, 0.05 g (7 mmol) Li and 0.68 g (3.5 mmol) 1-iso-propyl-2-chlorobenzimidazol. Yield 0.67 g (64 %), m.p. 206-208deg. C (bnz).). 1H NMR spectrum (CDCl₃): 1.73 (3H, d., $J = 6.95$, Me); 1.85 (3H, d, $J = 6.95$, Me); 5.86 (1H, m, CH); 6.58 (1H, s, 4'-H); 6.81 (1H, d, $J_{7'8'} = 7.98$, Hz, 8'-H); 6.85 (1H, d. d., $J_{5'6'} = 7.58$, $J_{6'7'} = 7.42$ Hz, 6'-H); 7.0 (1H, d. d., $J_{6'7'} = 7.42$, $J_{7'8'} = 7.98$ Hz, 7'-H); 7.1 (2H, m, 5''-H, 6''H); 7.2 (1H, d, $J_{5'6'} = 7.58$ Hz, 5'-H); 7.30 (1H, d. d., $J_{56} = 8.08$, $J_{67} = 7.41$ Hz, 6-H); 7.48 (1H, d, $J_{34} = 9.05$ Hz, 3-H); 7.5 (1H, d, $J_{\text{NH}-2'\text{H}} = 5.49$ Hz, 2'-H); 7.54-7.61 (4H, m, 5-H, 7-H, 4''-H, 7''-H); 7.79 (1H, d, $J_{34} = 9.05$ Hz, 4-H); 7.88 (1H, d, $J_{78} = 8.34$ Hz, 8-H); 10.33 (1H, d, $J_{\text{NH}-2'\text{H}} = 5.49$ Hz, NH); determined, % C 80.95; H 5.68; N 13.37. C₂₈H₂₄N₄. Calculated, % C 80.74; H 5.81; N 13.45.

1'-methyl-4'-phenyl-1',4'-dihydro-2,3'-biquinolyl (IVf, C₂₅H₂₀N₂): The solution of 0.64 g (2.5 mmol) 2,3'-biquinolyl and 0.05 g (7 mmol) of powdered Li in 10 mL THF is stirred under Ar blanket at ambient temperature for 3 h, then the solution of 0.71 g (4.5 mmol) of bromobenzene in 4 mL THF is added dropwise. The reaction mixture is stirred for 1 h at room temperature, than refluxed for 1 h. The mixture is cooled to room temperature 0.71 g MeI in 2 mL THF is added and mixture is stirred for 1 h. The mixture is poured into 50 ml of water and extracted with benzene (3 [lozenge] 30 mL). The organic solution is evaporated and resulting yellow oil is crystallized on hexane addition. Yield 0.65 g (75%), m.p. 173-174 deg.C (EtOH). 1H NMR spectrum (CDCl₃): 3.38 (3H, s, Me); 5.68 (1H, s, 4'-H); 6.84 (1H, d, $J_{7'8'} = 8.12$ Hz, 8'-H); 6.89 (1H, d. d., $J_{5'6'} = 7.61$, $J_{6'7'} = 7.76$ Hz, 6'-H); 7.12 (1H, d. d., $J_{6'7'} = 7.76$, $J_{7'8'} = 8.12$ Hz, 7'-H); 7.19 (3H, m, 3''-H, 4''-H, 5''-H); 7.27 (1H, d, $J_{5'6'} = 7.61$ Hz, 5'-H); 7.35 (1H, d. d., $J_{56} = 7.99$, $J_{67} = 7.56$ Hz, 6-H); 7.42 (1H, d, $J_{34} = 9.01$ Hz, 3-H); 7.48 (2H, d, $J = 7.13$ Hz, 2''-H, 6''-H); 7.64 (1H, d. d., $J_{67} = 7.56$, $J_{78} = 8.53$ Hz, 7-H); 7.67 (1H, d, $J_{56} = 7.99$ Hz, 5-H); 7.81 (1H, s, 2'-H); 7.91 (1H, d, $J_{34} = 9.01$ Hz, 4-H); 7.99 (1H, d, $J_{78} = 8.53$ Hz, 8-H); determined, %: C 86.44; H 5.67; N 7.89. C₂₅H₂₀N₂. Calculated, % C 86.18; H 5.79; N 8.03.

1'-methyl-4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (IVg, C₂₉H₂₂N₂): Just as **IVf** out of 0.64 g (2.5 mmol) 2,3'biquinolyl, 0.05 g (7 mmol) Li, 0.72 g (3.5 mmol) 1-bromonaphthalene and 0.71 g (5 mmol) MeI. Yield 0.73 g (73%), m.p. 151-153 deg.C (benzene-hexane). 1H NMR spectrum (CDCl₃): 3.51 (3H, s, Me); 6.59 (1H, s, 4'-H); 6.77 (1H, d. d., $J_{5'6'} = 7.78$, $J_{6'7'} = 7.62$ Hz, 6'-H); 6.88 (1H, d, $J_{7'8'} = 8.04$ Hz, 8'-H); 7.1 (1H, d. d., $J_{6'7'} = 7.62$, $J_{7'8'} = 8.04$ Hz, 7'-H); 7.23-7.28 (4H, m, 5'-H, 6'-H, 3''-H, 6''-H); 7.49 (1H, d, $J_{34} = 8.79$ Hz, 3-H); 7.51-7.8 (7H, m, arom.); 7.81 (1H, d, $J_{34} = 8.88$ Hz, 4-H); 7.83 (1H, s, 2'-H); 8.99 (1H, d, $J = 8.54$, 8''-H or 8-H); determined, %: C 87.64; H 5.47; N 6.89. C₂₉H₂₂N₂. Calculated, %: C 87.41; H 5.56; N 7.03.

1'-benzyl-4'-(1'-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (IVh, C35H26N2): Just as **IVf** out of 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li, 0.72 g (3.5 mmol) 1-bromonaphthalene and 0.44 g (3.5 mmol) PhCH₂Cl. Yield 0.85 g (72%), m.p. 143-144 (EtOH). ¹H NMR spectrum (CDCl₃): 5.1 (2H, d, J = 4.38 Hz, CH₂); 6.69 (1H, s, 4'-H); 6.77 (1H, d. d., J_{5'6'} = 7.58, J_{6'7'} = 7.36 Hz, 6'-H); 6.78 (1H, d, J_{7'8'} = 7.82 Hz, 8'-H); 6.95 (1H, d. d., J_{6'7'} = 7.36, J_{7'8'} = 7.82 Hz, 7'-H); 7.04 (1H, d, J_{5'6'} = 7.58 Hz, 5'-H); 7.29-7.59 (8H, m, arom.); 7.41 (1H, d, J₃₄ = 8.91 Hz, 3-H); 7.42-7.8 (7H, m, arom.); 7.81 (1H, d, J₃₄ = 8.91 Hz, 4-H); 7.93 (1H, s, 2'-H); 9.03 (1H, d, J = 8.56, 8''-H or 8-H); determined, %: C 88.75; H 5.44; N 5.81 C₃₅H₂₆N₂. Calculated, %: C 88.58; H 5.52; N 5.90.

4'-phenyl -2,3'-biquinolyl (Va, C24H16N2): The solution of 0.42 g (1.25 mmol) 4'-phenyl-1',4'-dihydro-2,3'-biquinolyl (**IVa**) and 0.33 g I₂ in 5 mL pyridine is refluxed for 10 min. The reaction mixture is poured into 100 mL of water containing 1 g Na₂S₂O₃ and 0.5 g NaOH, the forming white precipitate is filtered out and washed with water (3 [lozenge] 30 mL). Yield 0.4 g (95%), m.p. 133-134 deg.C (bnz). ¹H NMR spectrum (CDCl₃): 6.97 (1H, d, J₃₄ = 8.54 Hz, 3-H); 7.35 (5H, m, Ph); 7.52 (1H, d. d., J_{5'6'} = 8.11, J_{6'7'} = 6.95 Hz, 6'-H); 7.56 (1H, d. d., J₅₆ = 8.04, J₆₇ = 7.01 Hz, 6-H); 7.72 (1H, d. d., J_{6'7'} = 6.95, J_{7'8'} = 8.38 Hz, 7'-H); 7.74 (1H, d. d., J₆₇ = 7.01, J₇₈ = 8.31 Hz, 7-H); 7.76 (1H, d., J₅₆ = 8.04 Hz, 5-H); 7.79 (1H, d, J_{5'6'} = 8.11 Hz, 5'-H); 7.84 (1H, d, J₃₄ = 8.54 Hz, 4-H); 8.19 (1H, d, J_{7'8'} = 8.38 Hz, 8'-H); 8.25 (1H, d, J₇₈ = 8.31 Hz, 8-H); 9.40 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 332 (M⁺), determined, %: C 86.92; H 4.75; N 8.33. C₂₄H₁₆N₂. Calculated, %: C 86.71; H 4.86; N 8.43.

4'-(1-naphthyl)2,3'-biquinolyl (Vb, C28H18N2): Just as 4'-phenyl-2,3'-biquinolyl (**Va**), out of 0.48 g (1.25 mmol) 4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (**IVb**) and 0.33 g (1.3 mmol) I₂. Yield 0.44 g (92%), m.p. 158-159 deg.C (benzene-hexane). ¹H NMR spectrum (CDCl₃): 6.83 (1H, d, J₃₄ = 8.55 Hz, 3-H); 7.31 (3H, m, 2''-H, 3''-H, 6''-H); 7.39 (1H, d, J₃₄ = 8.55 Hz, 4-H); 7.43-7.48 (3H, m, 7''-H, 8''-H, 6'-H); 7.63 (2H, d, J = 8.04 Hz, 4''-H, 5''-H); 7.68 (1H, d. d., J₅₆ = 8.04, J₆₇ = 7.03 Hz, 6-H); 7.71 (1H, d. d., J_{6'7'} = 6.95, J_{7'8'} = 8.34 Hz, 7'-H); 7.73 (1H, d. d., J₆₇ = 7.03, J₇₈ = 8.28 Hz, 7-H); 7.89 (1H, d, J₅₆ = 8.04 Hz, 5-H); 7.92 (1H, d, J_{5'6'} = 8.11 Hz, 5'-H); 8.10 (1H, d, J_{7'8'} = 8.34 Hz, 8'-H); 8.28 (1H, d, J₇₈ = 8.28 Hz, 8-H); 9.55 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 382 (M⁺), determined, %: C 88.17; H 4.53; N 7.3. C₂₈H₁₈N₂. Calculated, %: C 87.92; H 4.75; N 7.33.

4'-(2-pyridyl)-2,3'-biquinolyl (Vc, C23H15N3): Just as 4'-phenyl-2,3'-biquinolyl (**Va**), out of 0.42 g (1.25 mmol) 4'-(2-pyridyl)-1',4'-dihydro-2,3'-biquinolyl (**IVc**) and 0.33 g (1.3 mmol) I₂. Yield 0.4 g (94 %), m.p. 93-94 deg.C (bnz). ¹H NMR spectrum (CDCl₃): 7.08 (1H, d, J₃₄ = 8.54 Hz, 3-H); 7.18 (1H, d. d., J_{3'4'} = 7.69, J_{3''5''} = 1.28 Hz, 3''-H); 7.31 (1H, d. t., J_{4''5''} = 7.54, J_{5''6''} = 4.7, J_{3''5''} = 1.28 Hz, 5''-H); 7.55 (1H, d. d., J₅₆ = 8.04, J₆₇ = 7.01 Hz, 6-H); 7.59 (1H, d. t., J_{3'4'} = 7.69, J_{4''5''} = 7.54, J_{4''6''} = 1.7 Hz, 4''-H); 7.71 (1H, d. d., J_{6'7'} = 6.95, J_{7'8'} = 8.34 Hz, 7'-H); 7.73 (1H, d. d., J_{5'6'} = 8.11, J_{6'7'} = 6.95 Hz, 6'-H); 7.74 (1H, d. d., J₆₇ = 7.01, J₇₈ = 8.32 Hz, 7-H); 7.76 (1H, d, J₅₆ = 8.04 Hz, 5-H); 7.79 (1H, d, J_{5'6'} = 8.11 Hz, 5'-H); 7.91 (1H, d, J₃₄ = 8.54 Hz, 4-H); 8.11 (1H, d, J_{7'8'} = 8.34 Hz, 8'-H); 8.26 (1H, d, J₇₈ = 8.32 Hz, 8-H); 8.81 (1H, d. d., J_{5''6''} = 4.7, J_{4''6''} = 1.7 Hz, 6''-H); 9.43 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 333 (M⁺), determined, %: C 82.89; H 4.47; N 12.64. C₂₃H₁₅N₃. Calculated, %: C 82.85; H 4.54; N 12.61.

4'-(1-methyl-2-benzimidazolyl)-2,3'-biquinolyl (Vd, C26H18N4): Just as 4'-phenyl-2,3'-biquinolyl (**Va**), out of 0.48 g (1.25 mmol) 4'-(1-methyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl (**IVd**), and 0.33 g (1.3 mmol) I₂. Yield 0.46 g (95 %), m.p. 338-340 deg.C (EtOH). ¹H NMR spectrum (CDCl₃): 3.25 (1H, s, Me); 7.31 (1H, d, J_{5'6'} = 8.1 Hz, 5'-H); 7.32 (1H, d, J₃₄ = 8.4 Hz, 3-H); 7.38 (1H, d. t., J_{4''5''} = 8.52, J_{5''6''} = 7.41, J_{5''7''} = 1.61 Hz, 5''-H); 7.51 (1H, d. d., J_{5'6'} = 8.1, J_{6'7'} = 6.94 Hz, 6'-H); 7.53 (1H, d. d., J_{6''7''} = 7.65, J_{5''7''} = 1.61 Hz, 7''-H); 7.55 (1H, d. d., J₅₆ = 8.06, J₆₇ = 7.14 Hz, 6-H); 7.58 (1H, d. t., J_{5''6''} = 7.41, J_{6''7''} = 7.61, J_{4''6''} = 2.23 Hz, 6''-H); 7.68 (1H, d. d., J_{6'7'} = 6.94, J_{7'8'} = 8.32 Hz, 7'-H); 7.73 (1H, d, J₅₆ = 8.06 Hz, 5-H); 7.82 (1H, d. d., J₆₇ = 7.14, J₇₈ = 8.21 Hz, 7-H); 7.87 (1H, d. d., J_{4''5''} = 8.52, J_{4''6''} = 2.23 Hz, 4''-H); 7.93 (1H, d, J_{7'8'} = 8.32 Hz, 8'-H); 7.94 (1H, d, J₃₄ = 8.4 Hz, 4-H); 8.29 (1H, d, J₇₈ = 8.21

Hz, 8-H); 9.61 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 386 (M+), determined, %: C 80.94; H 4.59; N 14.47. C₂₆H₁₈N₄. Calculated, %: C 80.81; H 4.69; N 14.5.

4'-(1-*iso*-propyl-2-benzimidazolyl)-2,3'-biquinolyl (Ve, C₂₈H₂₂N₄): Just as 4'-phenyl-2,3'-biquinolyl (**Va**), out of 0.52 g (1.25 mmol) 4'-(1-*iso*-propyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl (**Ive**) and 0.33 g (1.3 mmol) 12. Yield 0.47 g (91 %), m.p. 221-222 deg.C (bnz). ¹H NMR spectrum (CDCl₃): 0.72 (3H, d, J= 6.83, Me); 1.24 (3H, d, J= 6.83, Me); 4.16 (1H, m, CH); 7.31 (1H, d, J_{5'6'} = 8.14 Hz, 5'-H); 7.36 (1H, d. t., J_{4''5''} = 8.55, J_{5''6''} = 7.38, J_{5''7''} = 1.63 Hz, 5''-H); 7.43 (1H, d, J₃₄ = 8.78 Hz, 3-H); 7.5 (1H, d. d., J_{6''7''} = 7.67, J_{5''7''} = 1.63 Hz, 7''-H); 7.52 (1H, d. d., J_{5'6'} = 8.14, J_{6'7'} = 6.97 Hz, 6'-H); 7.55 (1H, d. d., J₅₆ = 8.04, J₆₇ = 7.11 Hz, 6-H); 7.59 (1H, d. t., J_{5''6''} = 7.38, J_{6''7''} = 7.67, J_{4''6''} = 2.25 Hz, 6''-H); 7.7 (1H, d. d., J_{6'7'} = 6.97, J_{7'8'} = 8.31 Hz, 7'-H); 7.74 (1H, d, J₅₆ = 8.04 Hz, 5-H); 7.81 (1H, d. d., J₆₇ = 7.11, J₇₈ = 8.21 Hz, 7-H); 7.92 (1H, d. d., J_{4''5''} = 8.55, J_{4''6''} = 2.25 Hz, 4''-H); 7.93 (1H, d, J₃₄ = 8.78 Hz, 4-H); 8.06 (1H, d, J_{7'8'} = 8.31 Hz, 8'-H); 8.28 (1H, d, J₇₈ = 8.21 Hz, 8-H); 9.57 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 414 (M+), determined, %: C 81.24; H 5.27; N 13.49. C₂₈H₂₂N₄. Calculated, %: C 81.13; H 5.35; N 13.52.

Acknowledgement: The work was supported by Russian Foundation of Basic Research (RFBR), grant No. 96-03-32036a.

References

- . Aksenov, A.V.; Aksenova, I.V.; Borovlev, I.V.; Bumber, A.A.; Pozharskii, A.F.; Smushkevich, Yu.I. *Khim Geterotsikl Soed.* [*Heterocycl. Cpd.*] 1996, p. 1391
- . Eisch, J. J. *J. Org. Chem.*, 1963, p. 707.
- . Banerji, A.; Maiti, S. *Tetrahedron*, 1994, p. 9079.
- . Holy, N. L. *Chem. Rev.*, 1974, p. 243

Comments

During 1-30 September 1997, all comments on this poster should be sent by e-mail to ecsoc@listserv.arizona.edu with **A0028** as the message subject of your e-mail. After the conference, please send all the comments and reprints requests to the author(s).
