Chemistry of Heterocyclic Compounds, Vol. 42, No. 2, 2006

INVESTIGATIONS ON 2,3'-BIQUINOLINE SERIES. 19*. REGIOSELECTIVITY OF THE REACTION OF 1,1'-DIALKYL-3,3'-DI(2-QUINOLYL)-1,1',4,4'-TETRAHYDRO-4,4'-BIQUINOLINES WITH ORGANOMAGNESIUM AND ORGANOLITHIUM COMPOUNDS

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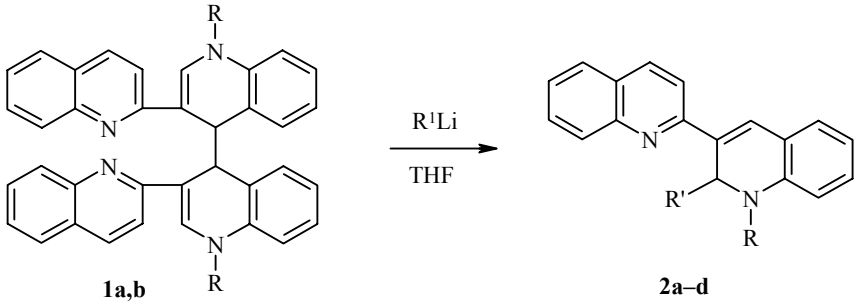
1,1'-Dialkyl-3,3'-di(2-quinolyl)-1,1',4,4'-tetrahydro-4,4'-biquinolines react with organolithium and organo-magnesium compounds to form 1'-alkyl-2'-R-1',2'-dihydro-2,3'-biquinolines.

Keywords: 1,1'-dialkyl-3,3'-di(2-quinolyl)-1,1',4,4'-tetrahydro-4,4'-biquinolines, 1',2'-dihydro-2,3'-biquinolines, organolithium compounds, nucleophilic substitution, Grignard reagents.

We have developed a new method for the synthesis of 1,1'-dialkyl-3,3'-di(2-quinolyl)-1,1',4,4'-tetrahydro-4,4'-biquinolines **1** [2], which has allowed us to study their properties. In this paper we report their reactions with organometallic compounds.

We have shown that the reaction of a diastereomeric mixture of compound **1** with organolithium compounds in THF at room temperature gave the 1',2'-dihydro-2,3'-biquinolines **2** in close to quantitative yield.



1a,b **2a–d**

1 a R = Me, **b** R = Et; **2 a** R = R^1= Me, **b** R = Me, R^1 = Ph, **c** R = Et, R^1 = Me, **d** R = Et, R^1 = Ph

It is likely that the reaction occurs as shown in the scheme below. In the first stage the organolithium behaves as a nucleophilic reagent towards compound **1**. As a result of nucleophilic substitution with allylic rearrangement compound **2** and the anion **3** are formed. It is probable that the anion loses an electron to form the radical **4**. Recombination of the latter leads to the tetraquinoline starting material **1**.

* For part 18 see [1].

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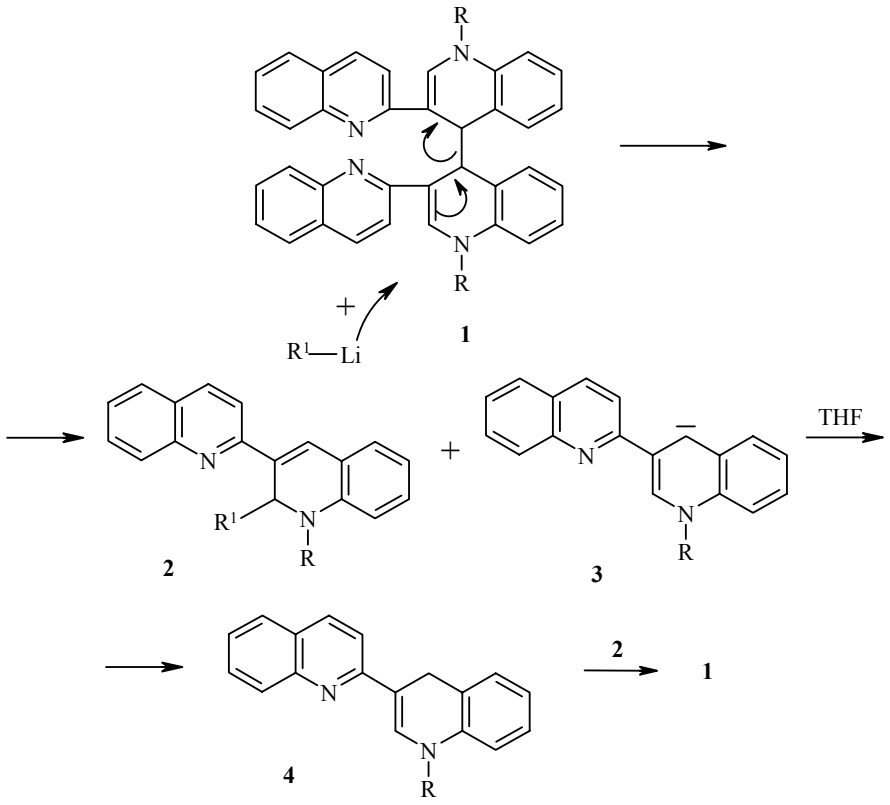
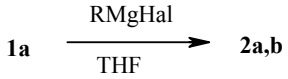


The reaction of compound **1** with Grignard reagents occurs analogously. The yield of compound **2** in this case is also close to quantitative.



EXPERIMENTAL

^{1}H NMR spectra of $CDCl_3$ solutions with TMS as internal standard were recorded on a Bruker WP-200 (200 MHz) machine. Tetrahydrofuran was dried by distillation from $LiAlH_4$. Course of reactions and purity of synthesized compounds were monitored on Silufol UV-254 strips, 1:1 ethyl acetate-hexane as solvent. Flash chromatography was carried out by a know method [3] (column: d = 60 mm, l = 50 mm) with benzene as solvent of low polarity and ethyl acetate as the polar solvent.

Synthesis of 1'-R-2'-R-1',2'-Dihydro-2,3'-biquinolines (2) (General Method). A solution of the corresponding organolithium compound or Grignard reagent (8 mmol) was added cautiously to a solution of a 1,1'-dialkyl-3,3'-di(2-quinolyl)-1,1',4,4'-tetrahydro-4,4'-biquinoline **1** (1.25 mmol) in THF (10 ml). The reaction mixture was stirred under argon at room temperature of 1 h, poured into water, and extracted with benzene (3 × 20 ml), and the solvent evaporated. The residue was purified by flash chromatography, collecting the first colored fraction.

1',2'-Dimethyl-1',2'-dihydro-2,3'-biquinoline (2a). From 1,1'-dimethyl-3,3'-di(2-quinolyl)-1,1',4,4'-tetrahydro-4,4'-biquinoline **1a**. Yield 94 (MeLi), 97% (MeMgCl); mp 168-169°C (benzene–hexane). According to [4,5], mp 168-169°C. R_f 0.88 (Silufol UV-254, 1:1 ethyl acetate–hexane). A mixed melting point with a known sample gave no depression. The ^{1}H NMR spectra were identical.

1'-Methyl-2'-phenyl-1',2'-dihydro-2,3'-biquinoline (2b). From compound **1a**. Yield 98 (PhLi), 97% (PhMgBr); mp 138-139°C (ethanol), lit. data 138-139°C [4,5]. R_f 0.77 (Silufol UV-254, 1:2 ethyl acetate–hexane). A mixed melting point with a known sample gave no depression. The ^{1}H NMR spectra were identical.

1'-Ethyl-2'-methyl-1',2'-dihydro-2,3'-biquinoline (2c). From 1,1'-diethyl-3,3'-di(2-quinolyl)-1,1',4,4'-tetrahydro-4,4'-biquinoline **1b** and MeLi. Yield 97%. Yellow oil. R_f 0.92 (Silufol UV-254, ethyl acetate–hexane 1:2. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.22 (3H, d, J = 6.41, 2'-CH_3); 1.47 (3H, t, J = 6.95, 1'-$CH_2\underline{CH_3}$); 4.06 (2H, m, J_{gem} =14.99, J_{cis} = 6.95, 1'-$\underline{CH_2}CH_3$); 5.27 (1H, q, J = 6.41, H-2'); 6.59 (1H, d, $J_{7'8'}$ = 8.10, H-8'); 6.70 (1H, dd, $J_{5'6'}$ = 7.52, $J_{6'7'}$ = 7.37, H-6'); 7.13 (1H, d, $J_{5'6'}$ = 7.61, H-5'); 7.19 (1H, dd, $J_{6'7'}$ = 7.37, $J_{7'8'}$ = 8.16, H-7'); 7.29 (1H, s, H-4'); 7.48 (1H, dd, J_{56} = 8.09, J_{67} = 7.14, H-6); 7.68 (1H, dd, J_{67} = 7.14, J_{78} = 8.41, H-7); 7.77 (1H, d, J_{56} = 8.09, H-5); 7.83 (1H, d, J_{34} = 9.04, H-3); 8.05 (1H, J_{78} = 8.41, H-8); 8.09 (1H, d, J_{34} = 9.04, H-4). Found, %: C 84.08; H 6.64; N 9.28. $C_{23}H_{22}N_2O$. Calculated, %: C 83.96; H 6.71; N 9.33.

1'-Ethyl-2'-phenyl-1',2'-dihydro-2,3'-biquinoline (2d). From compound **1b**. Yield 94%. Yellow oil. R_f 0.85 (Silufol UV-254, ethyl acetate–hexane 1:2. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.38 (3H, dd, $J_{CH_a\text{-}CH_3}$ = 7.26, $J_{CH_bCH_3}$ = 6.83, CH_3); 3.75 (1H, dq, $J_{CH_a\text{-}CH_3}$ = 7.26, $J_{CH_a\text{-}CH_b}$ = 14.94, $\underline{CH_a}CH_bCH_3$); 3.88 (1H, dq, $J_{CH_b\text{-}CH_3}$ = 6.83, $J_{CH_a\text{-}CH_b}$ = 14.94, $CH_a\underline{CH_b}CH_3$); 6.34 (1H, s, H-2'); 6.50 (1H, d, $J_{7'8'}$ = 8.13, H-8'); 6.70 (1H, dd, $J_{5'6'}$ = 7.53, $J_{6'7'}$ = 7.33, H-6'); 7.12 (1H, d, $J_{5'6'}$ = 7.53, H-5'); 7.15 (1H, dd, $J_{6'7'}$ = 7.33, $J_{7'8'}$ = 8.13, H-7'); 7.17 (3H, m, H-3,4,5 Ph); 7.42 (1H, s, H-4'); 7.44 (2H, d, J = 7.14, H-2,6 Ph); 7.45 (1H, dd, J_{56} = 8.22, J_{67} = 7.04, H-6); 7.65 (1H, dd, J_{67} = 7.04, J_{78} = 8.51, H-7); 7.71 (1H, d, J_{56} = 8.22, H-5); 7.76 (1H, d, J_{34} = 8.85, H-3); 8.00 (1H, d, J_{34} = 8.85, H-4); 8.03 (1H, d, J_{78} = 8.51, H-8). Found, %: C 86.32; H 6.04; N 7.64. $C_{23}H_{22}N_2O$. Calculated, %: C 86.158; H 6.12; N 7.73.

This work was carried out with a financial support grant from the President of the Russian Federation for the support of young Russian scientists and for the advancement of the scientific schools of the Russian Federation (grant No. MD-51.2003.03).

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