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INVESTIGATIONS OF 2,3'-BIQUINOLYL.

9.* REACTION OF 1',4'-DIHYDRO-2,3'-BIQUINOLYL WITH ORGANOLITHIUM COMPOUNDS

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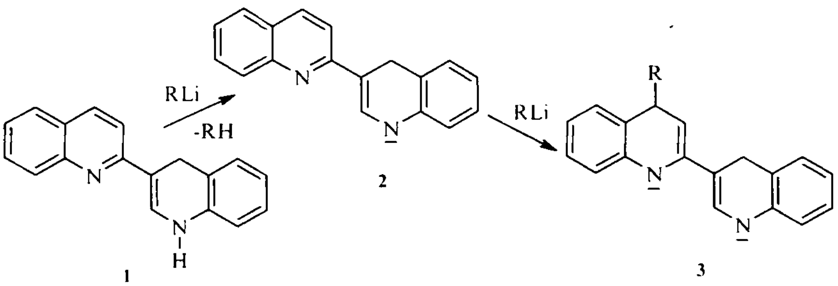
The 1',4'-dihydro-2,3'-biquinolyl reacts with organolithium compounds to form the mixture of 4'-R-1',4'-dihydro-2,3'-biquinolyls and 2'-R-1',2'-dihydro-2,3'-biquinolyls in the ratio analogous to the conversion in the series of 2,3'-biquinolyl. The utilization of the complex, the organolithium compound–TMEDA, in this process leads, after treatment of the reaction mixture with water, exclusively to 2'-R-1',2'-dihydro-2,3'-biquinolyls. Treatment with methyl iodide leads to 1'-methyl-2'-R-1',2'-dihydro-2,3'-biquinolyls.

Keywords: 2,3'-biquinolyl, 1',4'-dihydro-2,3'-biquinolyls, 1',2'-dihydro-2,3'-biquinolyls, organometallic compounds, nucleophilic substitution, regioselectivity.

We previously [2-4] reported that 1',4'-dihydro-2,3'-biquinolyl **1** reacts with organolithium compounds with the formation of anion **2**. The broad possibility of the delocalization of the negative charge and the conformational rotation round the $C_{(2)}$–$C_{(3)}$ bond provides the basis of the assumption that anion **2** will react with excess of the organometallic compound to form adducts at the position 4.



Unexpectedly, the compound **1** reacts with organolithium compounds leading, with the total yield of >90%, to the mixture of 2'-R-1',2'-dihydro-2,3'-biquinolyls **7** and 4'-R-1',4'-dihydro-2,3'-biquinolyls **8** in the same ratio that 2,3'-biquinolyl **4** gives under the given conditions [5]. Utilization of Grignard reagents instead of organolithium compounds does not lead to the formation of any products besides the anion **2**.

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* For Communication 8, see [1].

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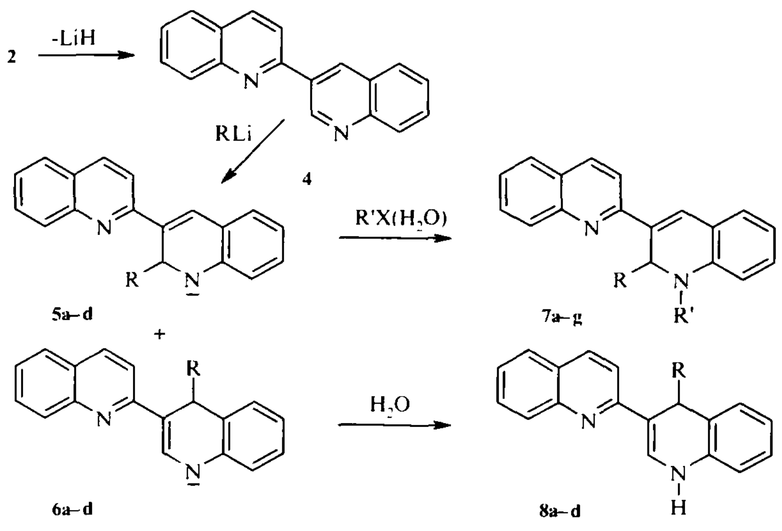

5-8a R = Me; **b** R = Bu; **c** R = Ph; **d** R = 1-$C_{10}H_7$; **e** R = Me; **f** R' = Ph; **g** R = Bu;
7a-d R' = H; **e-g** R' = Me

The data obtained can be explained having assumed a mechanism including the stage of the loss of the hydride ion from anion **2** and the subsequent addition of the organolithium compound to biquinolyl **4**. In fact, when the compound **7** or **8** is utilized instead of compound **1**, the reaction stops at the stage of deprotonation, and the TMEDA employed in the addition of organolithium compounds to 2,3'-biquinolyl leads to an increase in the share of the product **7**. This was explained by the higher inflexibility of the organolithium compound under the given conditions [5]. We proposed that the utilization of the complex organolithium compound–TMEDA in the case of dihydrobiquinolyl **1** also leads to the preferred formation of anions **5**. In fact, when compound **1** reacts with organolithium compounds in the presence of TMEDA, anion **5** is obtained. Treatment of the last with water gives the 2'-R-1',2'-dihydro-2,3'-biquinolyls **7a-d**, and treatment with methyl iodide gives the 1'-methyl-2'-R-1',2'-dihydro-2,3'-biquinolyls **7e-g** with the yield of 81-89%. The compounds **8** were not isolated in marked amounts.. The reaction proceeds with significantly more selectivity than with the compound **4** [5]. The increase in the share of the products **7** when the compounds **1** are utilized can be explained by the lower concentration of compound **4** in the reaction mixture in the given case, which decreases the probability of its complexation with the organolithium compound, and consequently the SET-process.

EXPERIMENTAL

The ^1H NMR spectra were recorded on Bruker WP-200 instruments with the utilization of TMS as the internal standard. The monitoring of the course of reactions and the purity of the compounds synthesized was accomplished on plates of Silufol UV-254 with the 1:1 solvent system of ethyl acetate–hexane, and column chromatography was performed on silica gel L 40/100. The THF was purified by distillation over $LiAlH_4$, and further over benzophenoneketyl. Diethyl ether was purified by distillation over benzophenoneketyl. The concentration of the organolithium compounds was determined by the method of the work [2].

General Method for the Alkylation (Arylation) of 1',4'-Dihydro-2,3'-biquinolyl by Organolithium Compounds. To a solution of the organolithium compound (3.6 mmol) in ether (10 ml) at 0°C TMEDA (0.92 g, 8 mmol) is added.* The mixture is stirred for 10 min prior to the careful addition of crystalline 1',4'-dihydro-2,3'-biquinolyl (0.32 g, 1.25 mmol). The reaction mixture is stirred in an atmosphere of argon for 2 h at room temperature,

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* TMEDA was not utilized in the first series of experiments.

after which THF (10 ml) is added, and the mixture is boiled for 30 min more. Water (50 ml) is added carefully, and the mixture is extracted with benzene (3×20 ml). The benzene extracts are combined, dried over sodium sulfate, and concentrated. The residue is dissolved in benzene (5 ml) and subjected to column chromatography utilizing the 10:1 solvent system of benzene–ethyl acetate. The first colored fraction is collected, and the solvent is evaporated to give the compounds **7a-d**. Further elution is performed with ethyl acetate with collection of the second colored fraction, the evaporation of which leads to the isolation of the compounds **8a-d**. The compounds **8** are not formed in marked amounts in the presence of TMEDA, and were therefore not isolated.

2'-Methyl-1',2'-dihydro-2,3'-biquinolyl (7a) ($C_{19}H_{16}N_2$). Yield 0.048 g (14%). In the presence of TMEDA, yield 0.29 g (87%); mp 138-139°C (alcohol). According to the data of [5], mp 138-139°C; R_f 0.44 (Silufol UV-254, 1:1 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [5].

2'-Butyl-1',2'-dihydro-2,3'-biquinolyl (7b) ($C_{22}H_{22}N_2$). Yield 0.047 g (12%). In the presence of TMEDA, yield 0.33 g (85%); mp 108-109°C (alcohol). According to the data of [5], mp 108-109°C; R_f 0.94 (Silufol UV-254, 1:1 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [5].

2'-Phenyl-1',2'-dihydro-2,3'-biquinolyl (7c) ($C_{24}H_{18}N_2$). Yield 0.18 g (44%). In the presence of TMEDA, yield 0.37 g (89%); mp 207-209°C (alcohol). According to the data of [5], mp 207-209°C; R_f 0.90 (Silufol UV-254, 1:1 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [5].

2'-(1-Naphthyl)-1',2'-dihydro-2,3'-biquinolyl (7d) ($C_{28}H_{20}N_2$). Yield 0.055 g (12%). In the presence of TMEDA, yield 0.39 g (81%); mp 166-167°C (alcohol). According to the data of [5], mp 166-167°C; R_f 0.86 (Silufol UV-254, 1:1 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [5].

4'-Methyl-1',4'-dihydro-2,3'-biquinolyl (8a) ($C_{19}H_{16}N_2$). Yield 0.26 g (77%); mp 148-149°C (benzene). According to the data of [4], mp 148-149°C; R_f 0.44 (Silufol UV-254, 1:1 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [1].

4'-Butyl-1',4'-dihydro-2,3'-biquinolyl (8b) ($C_{22}H_{22}N_2$). Yield 0.34 g (86%). The product is a yellow oil. According to the data of [5], the product is a yellow oil. R_f 0.62 (Silufol UV-254, 1:1 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [5].

4'-Phenyl-1',4'-dihydro-2,3'-biquinolyl (8c) ($C_{24}H_{18}N_2$). Yield 0.2 g (47%); mp 213-214°C (benzene). According to the data of [6], mp 213-214°C; R_f 0.32 (Silufol UV-254, 1:1 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [6].

4'-(1-Naphthyl)-1',4'-dihydro-2,3'-biquinolyl (8d) ($C_{28}H_{20}N_2$). Yield 0.4 g (82%); mp 196-197°C (benzene). According to the data of [6], mp 196-197°C; R_f 0.27 (Silufol UV-254, 1:1 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [6].

General Method for the Synthesis of 1'-Methyl-2'-R-1',2'-dihydro-2,3'-biquinolyls. To the solution of the organolithium compound (3.6 mmol) in ether (10 ml) TMEDA (0.92 g, 8 mmol) is added at 0°C, and the mixture is stirred for 10 min prior to the careful addition of crystalline 1',4'-dihydro-2,3'-biquinolyl (0.32 g, 1.25 mmol). The reaction mixture is stirred in an atmosphere of argon for 2 h at room temperature, after which THF (10 ml) is added, and the mixture is boiled for 30 min more. Methyl iodide (0.35 g, 2.5 mmol) is further added carefully and the reaction mixture is boiled for 1 h more, after which it is poured into water (50 ml). Extraction is performed with benzene (3×20 ml). The benzene extracts are combined, dried over sodium sulfate, and concentrated. The residue is dissolved in benzene (5 ml) and subjected to column chromatography. The first colored fraction is collected utilizing the 10:1 solvent system of benzene–ethyl acetate. The solvent is evaporated to give the compounds **7e,f**.

1',2'-Dimethyl-1',2'-dihydro-2,3'-biquinolyl (7e) ($C_{20}H_{18}N_2$). Yield 0.29 g (83%); mp 168-169°C (benzene–hexane). R_f 0.88 (Silufol UV-254, 1:2 ethyl acetate–hexane). According to the data of [7], mp 168-169°C. The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [7].

1'-Methyl-2'-phenyl-1',2'-dihydro-2,3'-biquinolyl (7f) ($C_{25}H_{20}N_2$). Yield 0.36 g (84%); mp 138-139°C (alcohol). According to the data of [7], mp 138-139°C. R_f 0.77 (Silufol UV-254, 1:2 ethyl acetate–hexane). The mixed test with a known sample does not give a depression of the melting temperature, and the ^{1}H NMR spectrum is identical to that presented in the work [7].

1'-Methyl-2'-butyl-1',2'-dihydro-2,3'-biquinolyl (7g) ($C_{23}H_{24}N_2$). Yield 0.34 g (83%). The product is a yellow oil. R_f 0.98 (Silufol UV-254, 1:1 ethyl acetate–hexane). ^{1}H NMR spectrum ($CDCl_3$): 0.82 (3H, t, J = 7.12 Hz, 2'-$CH_2CH_2CH_2\underline{CH}_3$); 1.28 (2H, m, 2'-$CH_2CH_2\underline{CH}_2CH_3$); 1.36 (2H, m, 2'-$CH_2\underline{CH}_2CH_2CH_3$); 1.64 (2H, m, 2'-$\underline{CH}_2CH_2CH_2CH_3$); 3.12 (3H, s, Me); 5.31 (1H, t, J = 7.21 Hz, 2'-H); 6.53 (1H, d, $J_{7'8'}$ = 8.12 Hz, 8'-H); 6.64 (1H, dd, $J_{5'6'}$ = 7.51 Hz, $J_{6'7'}$ = 7.34 Hz, 6'-H); 7.10 (1H, d, $J_{5'6'}$ = 7.51 Hz, 5'-H); 7.15 (1H, dd, $J_{6'7'}$ = 7.34 Hz, $J_{7'8'}$ = 8.12 Hz, 7'-H); 7.28 (1H, s, 4'-H); 7.45 (1H, dd, J_{56} = 8.11 Hz, J_{67} = 6.93 Hz, 6-H); 7.66 (1H, dd, J_{67} = 6.93 Hz, J_{78} = 8.47 Hz, 7-H); 7.74 (1H, d, J_{56} = 8.11 Hz, 5-H); 7.81 (1H, d, J_{34} = 8.71 Hz, 3-H); 8.02 (1H, d, J_{78} = 8.47 Hz, 8-H); 8.07 ppm (1H, d, J_{34} = 8.71 Hz, 4-H). Found, %: C 84.19; H 7.31; N 8.50. $C_{23}H_{24}N_2$. Calculated, %: C 84.11; H 7.37; N 8.53.

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