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UNUSUAL METHOD FOR BROMINATION OF 2,3'-BIQUINOLYL

N. V. Demidova, O. P. Demidov, and A. V. Aksenov

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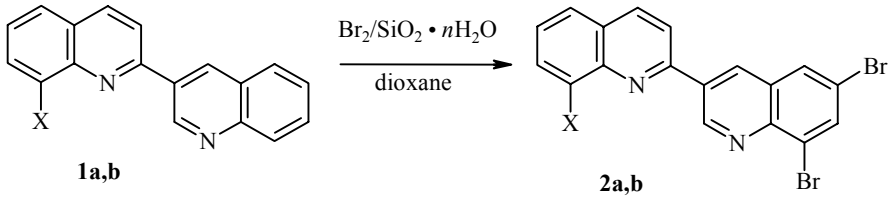
In studying electrophilic substitution in the 2,3'-biquinolyl series, we unexpectedly observed that bromination of compounds **1** can be easily accomplished by using dioxane dibromide in dioxane on Silochrome. As a result of the reaction, the bromo derivatives **2** are formed in 71% to 76% yield. The result is similar to bromination of 1',4'-dihydro-2,3'-biquinolyl in [1].



1a,b **2a,b**

1, **2 a** X = H; **b** X = Br

It is interesting that the reaction does not proceed in the absence of Silochrome. This bromination method has not been known previously.

Compound **1** (3.9 mmol) was dissolved in dioxane (20 ml), and Silochrome was added until a pasty consistency was obtained. Then Br_2 (20 mmol) was added and the mixture was heated with stirring in a boiling water bath for 1 h. Then the reaction mixture was treated with a 15% ammonia solution and a 20% sodium thiosulfate solution (20 ml). This was filtered and dried. The reaction product was extracted with ethanol in a Soxhlet apparatus.

6',8'-Dibromo-2,3'-biquinolyl (2a). Yield 76%; mp 220-222°C (alcohol). According to data in [1], mp 220-222°C. ^{1}H NMR spectrum (200 MHz; $CDCl_3$), δ, ppm, *J*, Hz: 7.61 (1H, dt, J_{56} = 8.25, J_{67} = 7.15, J_{68} = 1.1, 6-H); 7.81 (1H, dt, J_{67} = 7.15, J_{78} = 8.35, J_{57} = 1.65, 7-H); 7.91 (1H, dd, J_{56} = 8.25, J_{57} = 1.65, 5-H); 8.02 (1H, d, J_{34} = 8.50, 3-H); 8.14 (1H, d, $J_{5'7'}$ = 1.65, 7'-H); 8.20 (1H, d, $J_{5'7'}$ = 1.65, 5'-H); 8.22 (1H, d, J_{78} = 8.35, J_{68} = 1.1, 8-H); 8.35 (1H, d, J_{34} = 8.50, 4-H); 8.89 (1H, d, $J_{2'4'}$ = 2.20, 4'-H); 9.83 (1H, d, $J_{2'4'}$ = 2.20, 2'-H). Mass spectrum, *m*/z (70 eV): 414 [M^+] (82.7), 335 [M^+-Br] (6.9), 253 (17.2). Found, %: C 52.38; H 2.37; N 6.71. $C_{18}H_{10}Br_2N_2$. Calculated, %: C 52.21; H 2.43; N 6.76.

Stavropol State University, Stavropol 355009, Russia; e-mail: nauka@stavsu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 557-558, April, 2001. Original article submitted December 28, 2000.

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6',8,8'-Tribromo-2,3'-biquinolyl (2b). Obtained similarly to compound **2a** from starting material **1b**. Yield 71%; mp 300-302°C (alcohol). ^{1}H NMR spectrum (200 MHz; $CDCl_3$), δ, ppm, *J*, Hz: 7.45 (1H, t, J = 7.7, 6-H); 7.85 (1H, dd, J_{67} = 7.7, J_{57} = 1.1, 7-H); 8.10 (1H, d, J_{34} = 8.8, 3-H); 8.13 (1H, dd, J_{56} = 7.7, J_{57} = 1.1, 5-H); 8.15 (1H, d, $J_{5'7'}$ = 2.2, 7'-H); 8.21 (1H, d, $J_{5'7'}$ = 2.2, 5'-H); 8.34 (1H, d, J_{34} = 8.8, 4-H); 8.92 (1H, d, $J_{2'4'}$ = 2.2, 4'-H); 10.01 (1H, d, $J_{2'4'}$ = 2.2, 2'-H). Found, %: C 43.94; H 1.81; N 5.63. $C_{18}H_9Br_3N_2$. Calculated, %: C 43.85; H 1.84; N 5.68.

REFERENCES

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