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UNUSUAL REACTION OF 1,1'-DIALKYL-3,3'-DI(2-QUINOLYL)-1,1',4,4'-TETRAHYDRO-4,4'-BIQUINOLINES WITH ETHYL CHLOROFORMATE

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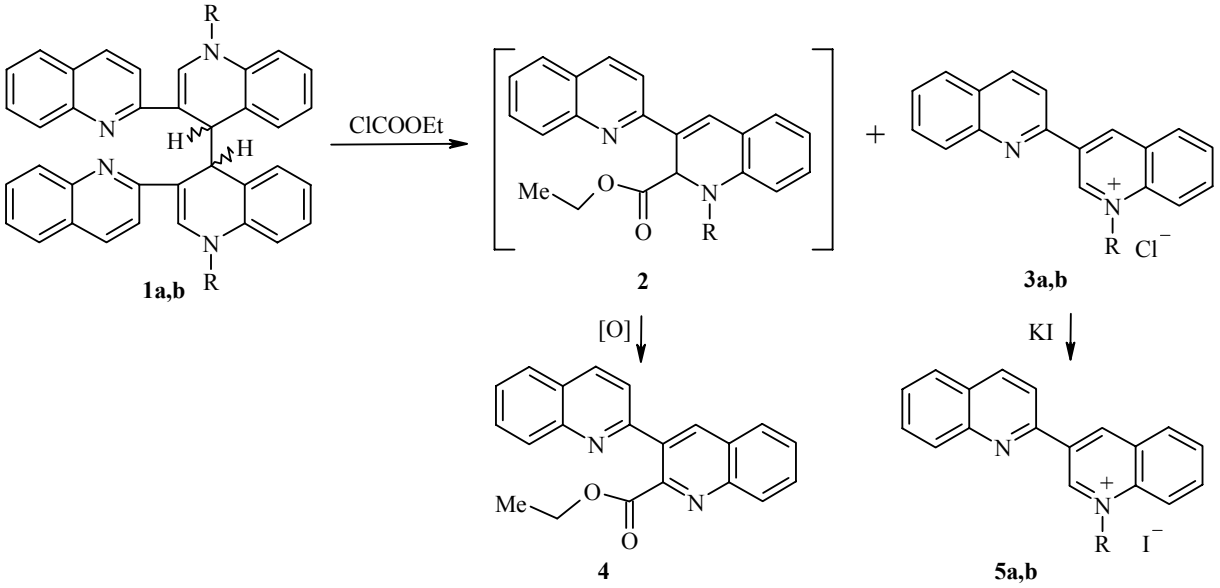
Earlier [1] we developed a method for synthesis of 1,1'-dialkyl-3,3'-di(2-quinolyl)-1,1',4,4'-tetrahydro-4,4'-biquinolines **1a,b** (the dimerization products of 2,3'-biquinolinium salts) and studied their reactions with organometallic compounds [2]. In this paper, we report on the reaction with ethyl chloroformate. We have established that with ethyl chloroformate at room temperature in chloroform, compounds **1** form a mixture of salts **3** and 2,3'-biquinoline-2'-carboxylic acid ethyl ester (**4**), independently of the nature of the group on the nitrogen atom in compound **1**. The reaction probably includes intermediate formation of dihydro derivatives **2**, which enter into the reaction of oxidative dealkylation.



1a,b **2** **3a,b** **4** **5a,b**

1, **3**, **5 a** R = Me, **b** R = Et

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A mixture of compound **1** (0.5 mmol) and ethyl chloroformate (0.15 g, 1.38 mmol) in chloroform (20 ml) was stirred for 3 h at ~20°C, triethylamine (0.5 ml) was added, and the mixture was filtered. The filtrate was evaporated down. The residue was recrystallized from methanol. Compound **4** was obtained. The precipitate obtained by filtering the reaction mixture was salt **3**, which was dissolved in water (5 ml), and then a solution of KI (0.17 g, 1 mmol) in water (5 ml) was added. The precipitated iodide was filtered out.

2,3'-Biquinoline-2'-carboxylic Acid Ethyl Ester (4). Yield 0.07 g (44%); mp 139-140°C (methanol). According to the data in [3], mp 140°C. ^{1}H NMR spectrum, (200 MHz; DMSO-d_6), δ, ppm (*J*, Hz); 1.24 (3H, t, *J* = 7.0, CH_2); 4.41 (2H, q, *J* = 7.0, CH_3); 7.3 (2H, m, H-6',7'); 7.7 (1H, dd, $J_{5'6'}$ = 8.0, $J_{5'7'}$ = 1.5, H-5'); 7.75 (1H, ddd, J_{56} = 7.63, J_{67} = 7.0, J_{68} = 0.9, H-6); 7.91 (1H, ddd, J_{67} = 7.0, J_{78} = 8.2, J_{57} = 1.53, H-7); 7.72 (1H, dd, J_{56} = 7.6, J_{57} = 1.5, H-5); 8.15 (1H, d, J_{34} = 8.8, H-4); 7.33 (1H, dd, J_{78} = 8.2, J_{68} = 0.9, H-8); 8.45 (1H, dd, $J_{7'8'}$ = 8.2, $J_{6'8'}$ = 0.94, H-8'); 8.58 (1H, d, J_{34} = 8.8, H-3); 9.10 (1H, s, H-4'). IR spectrum (KBr disks), ν, cm^{-1}: 1614 (C=O). Mass spectrum (70 eV), *m*/*z* (*I*, %): 300 [M-28] (64), 172 [M-156] (100). Found, %: C 76.92; H 4.83; N 9.03. $C_{21}H_{16}N_2O_2$. Calculated, %: C 76.81; H 4.91; N 8.53.

1-Methyl-3-(2-quinolyl)quinolinium Iodide (5a). Yield 54%; mp 288-290°C. According to the data in [4, 5], mp 288-290°C. The ^{1}H NMR spectrum matches the spectrum given in [5].

1-Ethyl-3-(2-quinolyl)quinolinium Iodide (5b). Yield 56%; mp 278-280°C. According to the data in [4, 5], mp 278-280°C. The ^{1}H NMR spectrum matches the spectrum in [5].

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