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REACTION OF 1'-ALKYL-1',4'-DIHYDRO-2,3'-BIQUINOLYLS WITH SINGLET OXYGEN

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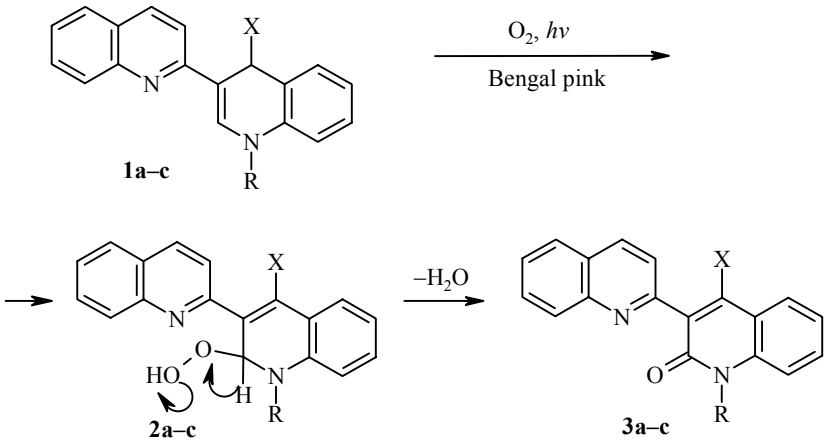
In previous work [1, 2], we developed a series of methods for the synthesis of 1'-R-1',4'-dihydro-2,3'-biquinolyls **1**, which permitted us to study the properties of these compounds. In the present work, we report the reaction of **1** with singlet oxygen.

We have found that the oxidation of 1'-alkyl-1',4'-dihydro-2,3'-biquinolyls **1** by singlet oxygen at room temperature yields 1'-alkyl-1',2'-dihydro-2,3'-biquinolyl-2'-ones **3**. The mechanism of this reaction probably involves formation of hydroperoxide **2** in the first step with subsequent loss of water.



1-3 a X = H, R = Me; **b** X = CN, R = Me; **c** X = CN, R = Bu

A stream of air was usually passed through a mixture of 2.5 mmol of **1** and 2 mg Bengal pink in 40 ml methanol in a quartz flask irradiated by a high-pressure lamp until the starting compound disappeared as indicated by thin-layer chromatography (0.5-1.5 h). The solvent was evaporated and the reaction product was purified by recrystallization.

1'-Methyl-1',2'-dihydro-2,3'-biquinolyl-2'-one (3a) was obtained in 77% yield; mp 174-175°C (ethanol) (174-175°C [3]). IR spectrum (neat), ν, cm^{-1}: 1602 (C=O). A mixed probe with an authentic sample gave an undepressed melting point.

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1'-Methyl-4'-cyano-1',2'-dihydro-2,3'-biquinolyl-2'-one (3b) was obtained in 81% yield; mp 221-222°C (benzene). IR spectrum (neat), ν, cm^{-1}: 1612 (C=O). ^1H NMR spectrum at 200 MHz (acetone-d_6), δ, ppm, *J* (Hz): 3.87 (3H, s, Me); 7.54 (1H, dd, J_{56} = 8.23, J_{67} = 7.88, 6-H); 7.72 (1H, dd, $J_{5'6'}$ = 7.91; $J_{6'7'}$ = 7.88; 6'-H); 7.77 (1H, d, $J_{7'8'}$ = 8.41, 7-H); 8.00 (1H, d, J_{34} = 8.54, 3-H); 8.07 (1H, d, $J_{5'6'}$ = 7.91, 5'-H); 8.11 (1H, d, J_{56} = 8.23, 5-H); 8.17 (1H, d, J_{78} = 8.41, 8-H); 8.47 (1H, d, J_{34} = 8.54, 4-H). Mass spectrum, *m/z* (70 eV): 311 [M^+] (100%). Found, %: C 77.34; H 4.16; N 13.45. $C_{20}H_{13}N_3O$. Calculated, %: C 77.16; H 4.21; N 13.50.

1'-Butyl-4'-cyano-1',2'-dihydro-2,3'-biquinolyl (3c) was obtained in 78% yield; mp 208-209°C (benzene). IR spectrum (neat), ν, cm^{-1}: 1618 cm^{-1} (C=O). ^1H NMR spectrum at 200 MHz ($CDCl_3$), δ, ppm, *J* (Hz): 1.18 (3H, t, *J* = 7.68, 1'-$CH_2CH_2CH_2\underline{CH_3}$); 1.53 (2H, m, 1'-$CH_2CH_2\underline{CH_2}CH_3$); 1.79, m, 1'-$CH_2\underline{CH_2}CH_2CH_3$); 4.39 (2H, t, *J* = 7.69, 1'-$\underline{CH_2}CH_2CH_2CH_3$); 7.42 (1H, dd, $J_{5'6'}$ = 7.91, $J_{6'7'}$ = 7.88, 7'-H); 7.48 (1H, d, $J_{7'8'}$ = 7.96, 8'-H); 7.62 (1H, dd, J_{56} = 7.88, J_{78} = 8.41, 7-H); 7.90 (1H, d, $J_{5'6'}$ = 7.91, 5'-H); 7.94 (1H, d, J_{34} = 8.54, 3-H); 8.19 (1H, d, J_{56} = 8.23, 5-H); 8.23 (1H, d, J_{78} = 8.41, 8-H); 8.30 (1H, d, J_{34} = 8.54, 4-H). Mass spectrum, *m/z* (70 eV): 353 [M^+] (88%). Found, %: C 78.34; H 5.32; N 11.69. $C_{23}H_{19}N_3O$: C 78.16; H 5.42; N 11.89.

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