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INVESTIGATIONS ON 2,3'-BIQUINOLINES
22*. NOVEL AND CONVENIENT METHOD FOR THE SYNTHESIS OF BENZO[5,6]INDOLIZINO-[2,1-*b*]QUINOLINIUM-13-THIOLATES AND BENZO-[5,6]INDOLIZINO[1,2-*c*]QUINOLINE-6(5H)-THIONES

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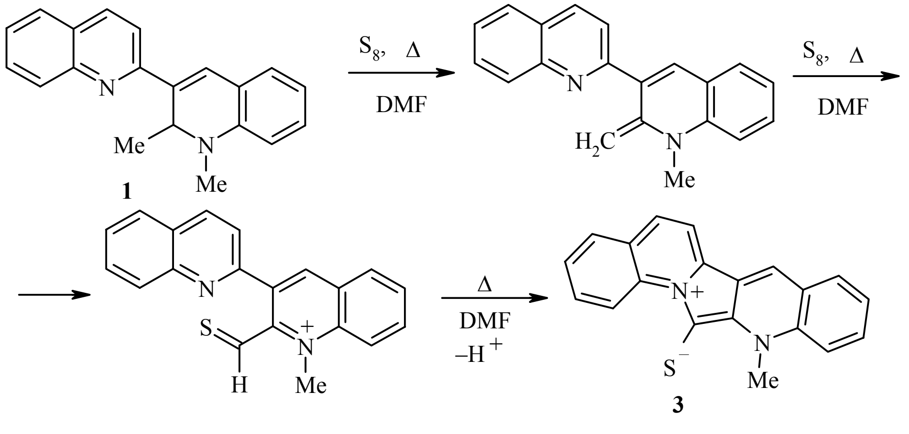
We have developed a method of synthesis of benzo[5,6]indolizino[2,1-b]quinolinium-13-thiolates and 5,6-dihydrobenzo[5,6]indolizino[1,2-c]quinoline-6-thiones based on the reaction of the corresponding 1',2'-dialkyl-1',2'-dihydro-2,3'-biquinolines and 1',4'-dialkyl-1',4'-dihydro-2,3'-biquinolines with sulfur in DMF.

Keywords: benzo[5,6]indolizino[2,1-*b*]quinolinium-13-thiolates, benzo[5,6]indolizino[1,2-*c*]quinoline-6(5H)-thiones, 2,3'-biquinolines, 1',2'-dihydro-2,3'-biquinolines, 1',4'-dihydro-2,3'-biquinolines, sulfur, cyclization.

We have previously studied the reaction of 1'-alkyl- [2], 1'-alkyl-2'- and 4'-aryl- [1], and 4'-alkyl-1',4'-dihydro-2,3'-biquinolines [3] with sulfur. It was found that thiolation, desalkylation, and in the case of the 4'-methyl-1',4'-dihydro-2,3'-biquinoline cyclization to form benzo[5,6]indolizino[1,2-*c*]quinoline can occur depending on the structure of the starting dihydro derivative reacting with the sulfur. For 1',2'-dialkyl-1',2'-dihydro-2,3'-biquinoline **1** and 1',4'-dialkyl-1',4'-dihydro-2,3'-biquinoline **2** any of these reaction routes might be expected hence we have studied the reaction of compounds **1** and **2** with sulfur.



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* For Communication 21 see [1]

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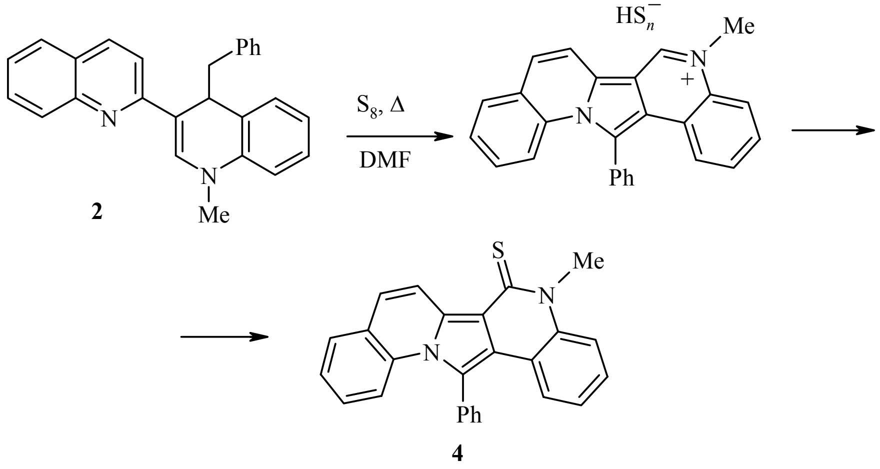
It is known that sulfur reacts with enamines to form the corresponding thiocarbonyl compounds (e.g. see [4]). We have suggested that reaction of the dimethyl derivative **1** with sulfur proceeds *via* the corresponding enamine and thioformyl derivative to the zwitterion **3**.

The reaction of compound **1** with sulfur does, in fact, give this 12-methylbenzo[5,6]indolizino[2,1-*b*]-quinolinium-13-thiolate (**3**) in 73% yield.

It was of interest that selenium did not react with compound **1** when refluxed for more than 20 h in DMF. In our view this is due to steric factors.



The reaction of dihydrobiquinoline **2** with sulfur might also be expected to occur *via* cyclization. The azinium cation produced under these conditions undergoes thiolation to give 5-methyl-14-phenyl-5,6-dihydrobenzo[5,6]indolizino[1,2-*c*]quinoline-6-thione (**4**). We found that compound **4** is formed in 62% yield in this reaction.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker WP-200 (200 MHz) instrument using TMS as internal standard. Mass spectra were taken on a MAT-311A instrument with ionizing voltage 70 eV. Monitoring of the reaction course and purity of the synthesized compounds was carried out on Silufol UV-254 plates with ethyl acetate–petroleum ether (1 : 1) as eluent.

Compounds **1** and **2** were prepared by methods [5, 6].

12-Methylbenzo[5,6]indolizino[2,1-*b*]quinolinium-13-thiolate (**3**). A mixture of 1',2'-dimethyl-1',2'-dihydro-2,3'-biquinoline (**1**) (0.86 g, 3 mmol) and elemental sulfur (0.24 g, 7.5 mmol) in DMF (5 ml) was refluxed for 1 h. The reaction mixture was cooled and the precipitated solid was filtered off and washed with hot benzene. Yield 0.7 g (74%); mp > 300ºC (DMF). ^{1}H NMR spectrum (DMF-d$_7$), δ, ppm (*J*, Hz): 4.09 (1H, s, CH$_3$); 7.34 (1H, ddd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 7.1, $J_{2,4}$ = 3.0, H-2); 7.72 (1H, dd, $J_{8,9}$ = 8.5, $J_{9,10}$ = 8.25, H-9); 7.80 (2H, m, H-3,4); 7.90 (1H, dd, $J_{9,10}$ = 8.25, $J_{10,11}$ = 8.5, H-10); 7.96 (1H, d, $J_{5,6}$ = 9.4, H-6); 8.16 (1H, d, $J_{8,9}$ = 8.5, H-8); 8.84 (1H, s, H-7); 9.20 (1H, d, $J_{1,2}$ = 8.1, H-1); 9.78 (1H, d, $J_{5,6}$ = 9.4, H-5). Mass spectrum, *m/z* (I_{rel}, %): 314 [M]$^+$ (100). Found, %: C 76.54; H 4.46; N 8.81. $C_{20}H_{14}N_2S$. Calculated, %: C 76.40; H 4.49; N 8.91.

5-Methyl-14-phenyl-5,6-dihydrobenzo[5,6]indolizino[1,2-*c*]quinoline-6-thione (**4**). A mixture of 4'-benzyl-1'-methyl-1',2'-dihydro-2,3'-biquinoline (**2**) (1.09 g, 3 mmol) and elemental sulfur (0.24 g, 7.5 mmol) in DMF (5 ml) was refluxed for 3 h. The reaction mixture was cooled and poured into 1% KOH solution (100 ml).

The precipitated solid was filtered off to give orange crystals of raw material. Yield 0.73 g (62%); mp 161-163ºC (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 4.48 (1H, s, CH_3); 6.98 (1H, dd, $J_{1,2}$ = 8.8, $J_{2,3}$ = 7.1, H-2); 7.21 (3H, m); 7.39 (3H, m); 7.62 (3H, m); 7.71 (3H, m); 7.83 (1H, d, $J_{3,4}$ = 8.25, H-4); 10.10 (1H, d, $J_{7,8}$ = 9.9, H-7). Mass spectrum, *m/z* (I_{rel}, %): 390 $[M]^+$ (100). Found, %: C 80.08; H 4.59; N 7.19. $C_{26}H_{18}N_2S$. Calculated, %: C 79.97; H 4.65; N 7.17.

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