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DIFFERENCE IN THE BEHAVIOR OF 1'-METHYL-1',4'-DIHYDRO-2,3'-DIQUINOLYL IN ITS REACTIONS WITH SULFUR AND SELENIUM

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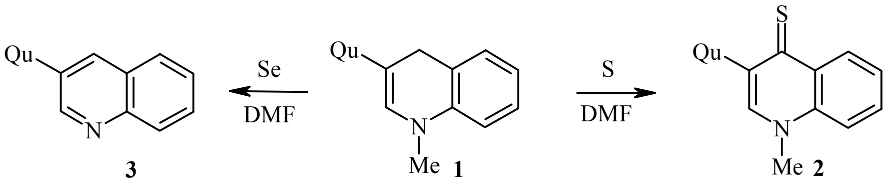
Sulfur converts the active methylene group into thiocarbonyl group [1]. Thus, the thiolation of 1'-methyl-1',4'-dihydro-2,3'-diquinolyl (**1**) to give the corresponding 4'-thione **2** in close to quantitative yield was not unexpected. However, 2,3'-diquinolyl **3** was obtained in an attempt to effect selenation by elemental selenium under the same condition in 81% yield.



Qu = 2-quinolyl

The sharp change in the direction of the reaction may be attributed to formation of a "substrate–chalcogen" radical–ion pair. Recombination within this pair in the reaction with sulfur leads to thione **2**. We note that the nucleophilic thiolation of 1-methyl-3-(2-quinolyl)quinolinium cation gives thione **2** in 30% yield [1]. This reaction competes with demethylation leading to 2,3'-diquinolyl **3**. This difference in the thiolation of dihydro derivative **1** and its corresponding cation indirectly supports our proposed mechanism.

The large radius of the selenium radical permits it to extrude from the cage and attack the sterically available methyl group, leading finally to 2,3'-diquinolyl **3**. As expected, our attempt to effect the selenation of 1-methyl-3-(2-quinolyl)quinolinium iodide by the selenium–KOH–DMF system analogous to the thiolation procedure [1] was unsuccessful and 2,3'-diquinolyl was formed.

1'-Methyl-1',4'-dihydro-2,3'-diquinolyl-4'-thione (2). Mixture of diquinolyl **1** (0.816 g, 3 mmol) [2] and sulfur (0.240 g, 7.5 mmol) in DMF (5 ml) was heated at reflux for 3 h. The reaction mixture was poured into 1% aqueous KOH (100 ml) and filtered. The precipitate was dried to give crude thione **2** as orange crystals. The product yield was 0.87 g (96%); mp 180-181°C (ethanol, benzene, or ethyl acetate) (179-180°C [1]). The ^{1}H NMR spectrum was identical to a reported spectrum [1].

2,3'-Diquinolyl (3). Mixture of diquinolyl **1** (0.816 g, 3 mmol) and selenium (0.593 g, 7.5 mmol) in DMF (5 ml) was heated at reflux for 6 h. The reaction mixture was poured into 1% aqueous KOH (100 ml) and filtered. The precipitate was dried, dissolved in benzene, and passed through 20-30-mm silica gel layer. The solution was evaporated to give 0.62 g (81%) of crystalline compound **3**; mp 175-176°C (ethanol, benzene, or toluene) (175-176°C [2]). The ^{1}H NMR spectrum of this product was identical to a reported spectrum [3].

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REFERENCES

1. L. I. Belen'kii, V. M. Bzhezovskii, N. N. Vlasova, M. G. Voronkov, E. N. Deryagina, G. N. Dolenko, M. A. Ibragimov, G. A. Kalabin, I. I. Kandror, B. V. Kopylova, A. V. Mashkina, E. M. Nanobashvili, R. G. Petrova, A. A. Polyakova, V. A. Smit, F. M. Stoyanovich, V. A. Usov, V. M. Fedoseev, R. Kh. Freidlina, Yu. L. Frolov, and T. D. Churkina, *Chemistry of Organic Sulfur Compounds. General Questions* [in Russian], Khimiya, Moscow (1988), p. 13.
2. A. V. Aksenov, D. V. Moiseev, I. V. Borovlev, and O. N. Nadein, *Khim. Geterotsikl. Soedin.*, 1084 (2000).
3. A. V. Aksenov, I. V. Magedov, and Y. I. Smushkevich, *J. Chem. Soc., Perkin Trans. 1*, 759 (1992).