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SHORT COMMUNICATIONS

Reductive Heterocyclization of 2,2-Dichloro-1,4-naphthoquinone into Naphtho[2,3-f][1,2,3,4,5]pentathiepine-6,11-diol under the Action of Sodium Hydrosulfide in DMF

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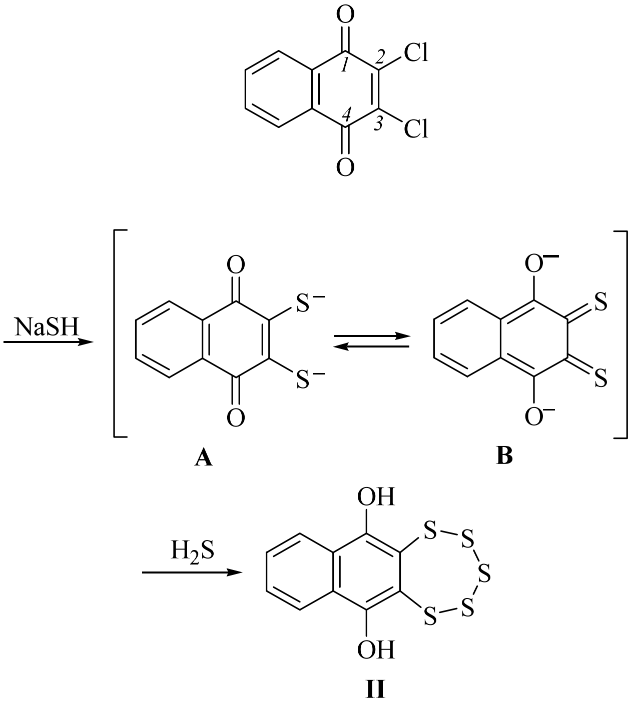
Pentathiepines, heterocyclic compounds containing a double carbon-carbon bond and five sulfur atoms in the ring, are known since their first preparation in 1971 [1]. Later from sea ascidias were isolated several annelated pentathiepines of high biological activity [2–3], and this attracted attention to the synthesis of analogous compounds [4–6]. A recent review summarized the studies in this field performed within the last three decades [7].

The nucleophilic substitution of chlorine in 2,3-dichloro-1,4-naphthaquinone (**I**) with thiol nucleophiles is well studied and occurs with high yields of the final products [8]. Yet the reaction of quinone **I** with NaSH was not investigated. In order to prepare 2,3-dimercapto-1,4-naphthoquinone of **A** type we brought into the condensation with chloroquinone **I** NaSH in DMF solution at various molar ratios quinone–hydrosulfide, 1:4–10. The prosess proceeded with self-heating of the mixture up to ~40°C and change in the color of the solution from light-yellow to blue and further to green. According to TLC the conversion of chloroquinone **I** was complete within 3–4 min. On completion of the process the reaction mixture was diluted with water.

The arising colored reaction products were well soluble in water and insoluble in ethyl acetate. Due to NaSH hydrolysis the water phase had alkaline reaction. On acidifying with diluted HCl till pH ~2–3 the reaction mixture turned from green to bright yellow, and the reaction products were extracted into ethyl acetate. As shown by TLC a yellow substance **II** was present in the extract having R_f 0.78 , and also some more polar light-yellow reaction products that during the workup in air quickly darkened and turned into a difficultly soluble grey-blue solid.

The structure of compound **II** was deduced from IR, ^{1}H NMR, and mass spectra. The homogeneity of isolated pentathiepine **II** was confirmed by HPLC data that revealed the lack of possible homologs containing four or three sulfur atoms. The reduction of the carbonyl groups in the initial 1,4-naphthoquinone was apparently caused by the rearrangement of the formed in the first stage 2,3-



dimercapto-1,4-naphthoquinone of **A** type into isomeric 1,4-dihydroxy-2,3-dithioquinone **B** which in its turn by reaction with H_2S arising on acidifying with HCl afforded pentathiepine **II**.

Naphtho[*2,3-f*][1,2,3,4,5]pentathiepine-6,11-diol (**II**). To a solution of 0.222 g (1.0 mmol) of dichloronaphthoquinone (**I**) in 8 ml of DMF was added at stirring in one portion 4–10 mmol of finely dispersed NaSH (Aldrich), the mixture was stirred for 10–12 min, the reaction mixture was placed into a separatory funnel, diluted with 20 ml of water, acidified with diluted HCl till pH 2–3, and extracted with ethyl acetate (3×15 ml). The extract was washed with water, with a saturated solution of NaCl, dried with Na_2SO_4, evaporated, and pentathiepine **II** was isolated by preparative TLC on SiO_2 in a system hexane–benzene–acetone, 2:1:1. Yield 18–25%, mp 313–316°C (hexane–acetone). IR spectrum, cm^{-1}: 3456 (OH), 1565, 1429, 1247, 1167,1151, 1085. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 6.80 s (2H, 2OH), 7.61–7.69 m (2H, $H^{7,10}$), 8.18–8.26 m (2H, $H^{8,9}$). Mass spectrum, *m/z* (I_{rel}, %): 318 (36) $[M]^+$, 317 (14) $[M-1]^+$, 284 (9), 256 (16), 255 (16), 254 (100), 252 (12), 223 (9), 222 (37), 221 (53), 220 (12), 190 (11), 189 (61). Found *M* 317.8951. $C_{10}H_6O_2S_5$. Calculated *M* 317.8971.

HPLC was carried out on a liquid chromatograph LaChrom (Merck–Hitachi), equipped with a pump L-7400, thermostat L-7300, and integrator D-7500. Column Agilent Technologies Zorbax Eclipse x D3-C-18 (4.6–75 mm, 3.5 μ), protection column Hypersil ODS (4.0 cm × 4.0 mm). Retention time of pentathiepine **II** was 18.70 min. Mass spectra of low resolution were taken on a mass spectrometer LKB-9000S in the mode of direct sample admission at 70 eV. High resolution mass spectrum of electron impact was measured on AMD 604S instrument, accelerating voltage 8 kV, and ionizing electrons energy 70 eV.

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