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UNUSUAL REACTION OF 2,3-DIMERCAPTOQUINOXALINE WITH 4-HYDROXY-4-METHYL-2-PENTYNONITRILE

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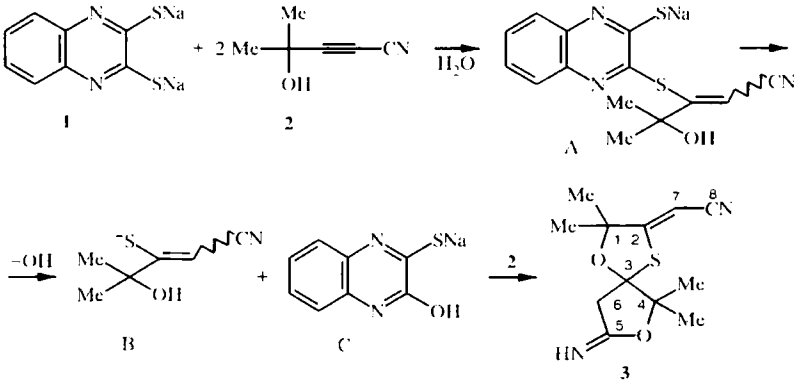
Keywords: 4-hydroxy-4-methyl-2-pentynonitrile, 2,3-dimercaptoquinoxaline, 8-imino-2,2,6,6-tetramethyl-1,7-dioxa-4-thiaspiro[4.4]nonane, intramolecular cyclization.

In reaction of disodium salt of 2,3-dimercaptoquinoxaline (**1**) with 4-hydroxy-4-methyl-2-pentynonitrile (**2**) in water, unexpectedly 3-cyanomethylene-8-imino-2,2,6,6-tetramethyl-1,7-dioxa-4-thiaspiro[4.4]nonane (**3**) was formed in one step instead of the probable S-mono- or S,S-diadducts.



The spirocyclic compound **3** was obtained previously by the reaction of acetylene **2** with sulfide anion [1]. Probably its formation goes through the stage of adding quinoxaline to the triple bond of alcohol **2** with subsequent fission of adduct **A** by hydroxide ion to the vinylthio anion **B** and probably hydroxy derivative **C**. The interaction of the resulting thio anion **B** with a second molecule of alcohol **2** leads to intramolecular cyclization to the thiaspirocyclic compound **3**.

3-Cyanomethylene-8-imino-2,2,6,6-tetramethyl-1,7-dioxa-4-thiaspiro[4.4]nonane (3). A mixture of disodium salt of 2,3-dimercaptoquinoxaline **1** (0.24 g, 1 mmol) and acetylene **2** (0.22 g, 2 mmol) in water (10 ml) was stirred at 20-25°C for 20 h. The water was evaporated and compound **3** (0.37 g, 74%) was isolated by column chromatography (eluent chloroform–benzene–ethanol 20 : 4 : 1); mp 65-67°C (reprecipitation from chloroform with hexane) (literature [1] mp 64-65°C). IR spectrum, cm^{-1}: 750, 800, 890, 940, 980, 1100, 1130, 1200, 1210, 1300, 1380, 1430, 1620, 1640, 2210, 2850, 2930, 2970, 3040, 3310. ^1H NMR spectrum ($CDCl_3$): 1.62, 1.64, 1.66,

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1.74 (12H, s, $4CH_3$); 3.44 (2H, s, CH_2); 5.17 (1H, s, =CH); 7.34 ppm (1H, s, =NH). ^{13}C NMR spectrum ($CDCl_3$): 21.49, 26.63, 29.75, 30.26 (Me); 29.33 ($C_{(6)}$); 84.84 ($C_{(7)}$); 90.77 ($C_{(4)}$); 94.98 ($C_{(1)}$); 101.07 ($C_{(9)}$); 119.75 ($C_{(8)}$); 169.85 ($C_{(2)}$); 171.04 ppm ($C_{(5)}$). The numbering of the carbon atoms in compound **3** is shown in the scheme.

The presumed second reaction product, sodium derivative of 2-hydroxy-3-mercaptoquinoxaline (**C**), was firmly retained by the sorbent.

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REFERENCE

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