CROSS CYCLIZATION OF TERTIARY CYANOACETYLENIC ALCOHOLS WITH SULFIDE ION

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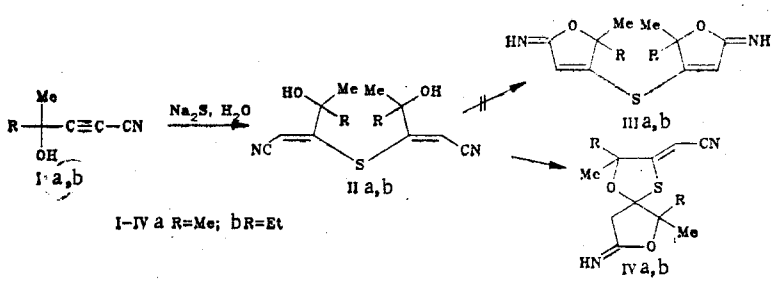
UDC 547.362'642'727.07

When tertiary cyanoacetylenic alcohols, I, react with the $Na_2S \cdot 9H_2O$—KOH—dioxane system at 20°, they undergo intramolecular cyclization, and instead of the disubstituted vinyl sulfide to be expected according to [2], they form 2,2-dialkyl-3,4-di(cyanomethylene)oxetanes.

When we carried out this reaction in aqueous medium without KOH, we encountered an unexpected fact: the sulfide ion adds easily and practically quantitatively to two molecules of acetylene I, but neither divinyl sulfide II nor the most likely product of its cyclization [3], bis-(iminodihydrofuryl) sulfide III, were isolated. It turned out that in this case there is a double cross-over unsymmetrical heterocyclization of the intermediate sulfide II, that gives a new spiroheterocyclic system IV.



The reason for such a reaction path is the Z-configuration of sulfide II, which is the result of concerted trans-addition of sulfide ion to the activated acetylenes [2], and is unfavorable for II → III heterocyclization.

8-Imino-2,2,6,6-tetramethyl-3-cyanomethylene-1,7-dioxa-4-thiaspiro[4,4]nonane (IVa). This was synthesized from a mixture of 5 mmole of hydroxynitrile Ia and 2.87 mmole of $Na_2S \cdot 9H_2O$ (85% pure) in 10 ml of water (5-20°, 2 h). Yield 92%, mp 64-65°. PMR spectrum ($CDCl_3$): 1.41, 1.57, 1.63, 1.72 (12H, s), 3.20 (2H, s), 5.17 (1H, s), 7.35 ppm (1H, s). IR spectrum ($CHCl_3$): 3310, 1660 (=NH), 2218 (CN), 3060, 1620 (C=CH), 1100-1200 cm^{-1} (C—O—C). found, %: C 57.0, H 6.3, N 11.0, S 12.5. $C_{12}H_{16}N_2O_2S$. Calculated, %: C 57.1, H 6.3, N 11.0, S 12.7; M^+ 252.

8-Imino-2,6-dimethyl-3-cyanomethylene-2,6-diethyl-1,7-dioxa-4-thiaspiro[4,4]nonane (IVb). This was synthesized analogously. Mp 68-70°. PMR spectrum ($CDCl_3$): 1.34, 1.62 (12H, s), 0.81, 1.02 (4H, t), 3.14 (2H, s), 5.12 (1H, s), 7.22 ppm (1H, s). IR spectrum ($CHCl_3$): 3310, 1660 (=NH); 2220 (CN); 1100-1200 cm^{-1} (COC). Found, %: C 60.4, H 7.0, N 9.8, S 11.4. $C_{14}H_{20}N_2O_2S$. Calculated, %: C 60.0, H 7.1, N 10.0, S 11.4; M^+ 280.

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, p. 854, June, 1987. Original article submitted December 23, 1986.

 0009-3122/87/2306-0706$12.50