AUTOHETEROCYCLIZATION OF CYANOACETYLENIC CARBINOL IN THE PRESENCE OF SODIUM SULFIDE

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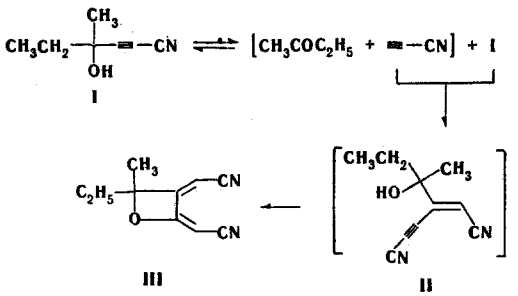
During the reaction of 1-cyano-3-methyl-3-hydroxy-1-pentyne (I) with $Na_2S \cdot 9H_2O$ in the presence of potassium hydroxide (in the ratio of 0.4:1:1; 20°C, dioxane), 2-methyl-2-ethyl-3,4-di(cyanomethylene)oxetane (III), a product of the autoheterocyclization of carbinol I, was obtained instead of the expected sulfide according to [1]. It is possible that cyanoethylene, formed as the result of the inverse Favorski reaction, is added in the form of an anion to the triple bond of the initial carbinol, which is very electrophilic in character. Then, the intermediate carbinol II cyclizes into III in a yield of 55%, mp 89°C (from ether). IR spectrum (KBr): 1650 (C=CH), 2220 cm^{-1} (CN); PMR spectrum (100 MHz, $CDCl_3$): 1.65 (s, 2-CH_3); 1.20 (t, 2-CH_2-CH_3) and 1.88 (qu, 2-CH_2); 5.55 (s, 3'-CH); 5.13 ppm (s, 4'-CH), $f_{3',4'}$ = 0.6 Hz.



The final accepted structure was confirmed by ^{13}C NMR spectra: 100.1 C_2; 156.3 C_3; 166.9 C_4; 22.9 (2-CH_3); 30.9 (2-CH_2); 7.3 (2-CH_2-CH_3); 91.7 (3-CH); 113.3 (3-CN, 4-CN); 70.1 ppm (4-CH).

The signals were assigned on the basis of the observation of direct and long-range $^{13}C-^{1}H$ spin-spin coupling constant interaction (SSCC) in the ^{13}C NMR spectrum without proton decoupling, in which the C_2, C_3, and C_4 signals are broadened due to SSCC with alkyl protons through two or three bonds, and the 3-CH and 4-CH signals are split J = 180 ±2 Hz. The signals from the C_3 and C_4 nuclei and also from 3-CH and 4-CH were assigned by using the additive calculation of δ ^{13}C of these carbon atoms from known values of sp^2 screening of the carbon atom in alkenes, alkyl vinyl ethers, and acetonitrile [2].

The data of elementary analysis for C, H, N correspond to the calculated values.

LITERATURE CITED

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2. G. B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York (1972), p. 156.

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