CYANOACETYLENES IN A REACTION WITH BENZOXAZOLE-2-THIONE AND BENZOXAZOL-2-ONE

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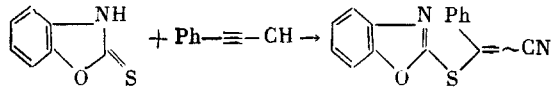
The reaction of benzoxazole-2-thione and benzoxazol-2-one with substituted cyanoacetylenes was studied. 2-[(3-Phenyl-2-propenenitrile)thio]benzoxazole was obtained by the reaction of benzoxazole-2-thione with phenylcyanoacetylene. Benzoxazol-2-one with phenylcyanoacetylene and a tertiary cyanoacetylenic alcohol gave the corresponding N-adducts.

Reactions of azolethiones and azolones with substituted cyanoacetylenes open up new possibilities for the synthesis of both cyanovinyl derivatives and condensed sulfur- and nitrogen-containing heterocyclic systems [1-4]. Continuing investigations of the reaction of activated acetylenes with nucleophiles, in the present paper we studied the reaction of benzoxazole-2-thione (I) and benzoxazol-2-one (II) with 1-phenyl-2-cyanoacetylene (III) and 4-hydroxy-4-methyl-2-pentynenitrile (IV).

It is known that thione (I) reacts with acetylene with the formation of 2-benzoxazolyl vinyl sulfide [5]. In the reaction of (I) with acetylene (III), we also recovered the S-adduct, 2-[(3-phenyl-2-propenenitrile)thio]benzoxazole (V).

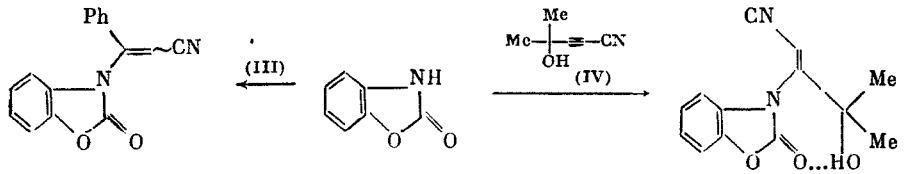


(I) (III) (V)

The reaction occurred in the absence of a catalyst in dioxane at 100°C. The recovery of the S-adduct (V) was 76%. In DMSO, the reaction occurred at room temperature with 73% yield. The use of an alkaline catalyst (KOH) in this reaction increased the yield of the final product insignificantly (85%). The presence of one singlet of the olefinic proton in the PMR spectrum of (V) indicated that the reaction occurred stereospecifically with the formation of only one isomer.

The reaction of thione (I) with cyanoacetylenic alcohol (IV) did not stop at the step of the formation of the S-adduct. Thus, we determined that the reaction of thione (I) with tertiary cyanoacetylenic alcohols was accompanied by further transformations of the S-adduct, as a result of which substituted 1,4-oxathianylthiobenzoxazoles were formed [4].

Unlike its thio analog (I), benzoxazol-2-one (II) does not react with cyanoacetylenes (III) and (IV) in the absence of a catalyst. In addition, the reaction must be carried out in a bipolar aprotic solvent, which, as is known, accelerates the reaction of nucleophilic addition to the activated triple bond. When the reaction of (II) with (III) was carried out in the presence of KOH in CH_3CN, the N-adduct, 3-(3-phenyl-2-propenenitrile)benzoxazol-2-one (VI), was recovered.



(VI) (II) (VII)

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The reaction of (II) with (IV) in the presence of LiOH in DMSO afforded 3-(4-hydroxy-4-methyl-2-pentene-3-nitrile)benzoxazole-2-one (VII). The presence of a wide band with frequency 3270 cm^{-1} in the IR spectrum (in a dilute CS_2 solution) indicated that the hydroxyl group located at the cyanovinyl substituent was bonded by an intramolecular hydrogen bond to the carbonyl group. The nonequivalence of the methyl groups due to retardation of rotation about the C–C bond in adduct (VII) was confirmed by PMR spectroscopy. Thus, the PMR spectrum of (VII) contained two peaks of methyl groups at 1.66 and 1.67 ppm, which coalesced into one singlet at 1.66 ppm as the temperature was increased to 50-60°C.

As in [6], an attempt to obtain a dihydrofuran ring from cyanovinyl derivative (VII) did not give a favorable result. Apparently, the intramolecular hydrogen bond promoted spatial separation of the hydroxyl and cyano groups.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in tablets with KBr. The PMR spectra were recorded on a Tesla BS-497 spectrometer (100 MHz) for 10% solutions in DMSO-d_6, and the internal standard was HMDS. Cyanoacetylenic alcohol (IV) was obtained according to [7].

2-[(3-Phenyl-2-propenenitrile)thio]benzoxazole (V). A mixture of 0.3 g (2 mmoles) of thione (I), 0.25 g (2 mmoles) of acetylene (III), and 0.03 g of KOH in 10 ml of dioxane was boiled for 6 h. The reaction mixture was passed through a short column with Al_2O_3 for removal of the alkali. The solvent was driven off, and the liquid residue was triturated in hexane into a yellow powder. We obtained 0.47 g (85%) of (V) with mp 154-156°C (ethanol). Found, %: C 69.25; H 3.75; N 9.99; S 11.19. $C_{16}H_{10}N_2OS$. Calculated, %: C 69.04; H 3.62; N 10.07; S 11.52. IR spectrum (ν, cm^{-1}): 2210 (CN), 1595, 690 (SC=CH). PMR spectrum (δ, ppm): 65.96 s (=CHCN), 7.12-7.62 m (H aromatic).

3-(3-Phenyl-2-propenenitrile)benzoxazol-2-one (VI). A mixture of 0.27 g (2 mmoles) of (II), 0.25 g (2 mmoles) of (III), and 0.03 g of KOH in 10 ml of CH_3CN was stirred for 10 h at 20-25°C. The reaction mixture was passed through Al_2O_3 for removal of the alkali, and the eluent was ethanol. The solvents were driven off, and 0.51 g (98%) of (VI) was obtained with mp 140-142°C (ethanol). Found, %: C 73.38; H 4.20; N 10.68. M^+ 262. $C_{16}H_{10}N_2O_2$. Calculated, %: C 73.27; H 3.84; N 10.68. M 262.25. IR spectrum (ν, cm^{-1}): 2210, (CN), 1780 (C=O), 3060, 1630 (NC=CH). PMR spectrum (δ, ppm): 6.02 s (=CHCN), 6.52-7.25 m (H aromatic), 7.43 br. s (5H in C_6H_5).

3-(4-Hydroxy-4-methyl-2-pentene-3-nitrile)benzoxazol-2-one (VII). A mixture of 1.35 g (10 mmoles) of (II), 1.1 g (10 mmoles) of (IV), and 0.14 g of LiOH in 15 ml of DMSO was stirred for 14 h. The reaction mixture was poured into ice water with stirring, and the precipitate was filtered and washed with water to pH 7. We obtained 1.74 g (71%), mp 242-243°C (ethanol). Found, %: C 64.16; H 5.17; N 11.60. M^+ 244. $C_{13}H_{12}N_2O_3$. Calculated, %: C 63.93; H 4.95; N 11.47. M 244.24. IR spectrum (ν, cm^{-1}): 2205 (C≡N), 1760 (C=O), 1650 (NC=CH), 2985, 2930 (CH_3), 3270 (intramolecular hydrogen bond). PMR spectrum (δ, ppm): 1.66 s, 1.67 s (CH_3), 4.86 s (=CHCN), 6.75-7.38 m (H aromatic).

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