LITERATURE CITED

1. V. V. Dovlatyan, K. A. Éliazyan, and A. V. Azatyan, *Khim. Geterotsikl. Soedin.*, No. 7, 978 (1987).
2. V. V. Dovlatyan, K. A. Éliazyan, and L. G. Agadzhanyan, *Khim. Geterotsikl. Soedin.*, No. 2, 262 (1977).
3. V. V. Dovlatyan, V. A. Pivazyan, K. A. Éliazyan, and R. G. Mirzoyan, *Khim. Geterotsikl. Soedin.*, No. 8, 1125 (1985).
4. V. V. Dovlatyan and A. V. Dovlatyan, *Khim. Geterotsikl. Soedin.*, No. 1, 124 (1979).
5. V. V. Dovlatyan, K. A. Éliazyan, S. M. Saakyan, and R. G. Mirzoyan, *Khim. Geterotsikl. Soedin.*, No. 9, 1275 (1981).
6. V. V. Dovlatyan, K. A. Éliazyan, V. A. Pivazyan, and A. G. Akopyan, *Khim. Geterotsikl. Soedin.*, No. 5, 657 (1989).

REACTION OF ALKENYNYLAMINES WITH 2-AMINORESORCINOL AS A METHOD FOR THE SYNTHESIS OF 2-(2-ALKENYL)-4-HYDROXYBENZOXAZOLES

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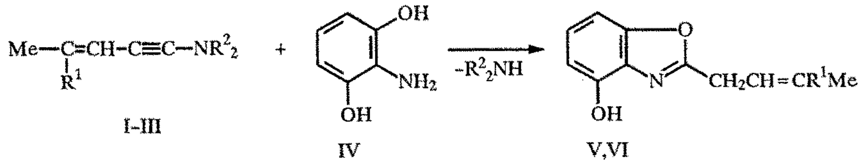
The reaction of 1-diethylamino-(4-methyl)-3-penten-1-ynes with 2-aminoresorcinol leads to the formation of 2-(2-alkenyl)-4-hydroxybenzoxazoles.

A considerable number of papers (e.g., [1,2]) have been devoted to the synthesis of benzoxazoles. Earlier we developed methods for the production of heterocycles of the benzoxazole [3], 1,3-benzodioxole [4], and benzimidazole [5] series by the reaction of 1-dialkylamino-(4-methyl)-3-penten-1-ynes with bifunctional aromatic compounds. A special feature of the reaction is that it takes place by twofold attack at the $C_{(1)}$ carbon atom of the acetylene bond with the formation of condensed heterocycles containing an unconjugated unsaturated fragment at the second position of the ring. By monitoring the reaction between 1-diethylamino-4-methyl-3-penten-1-yne and o-aminophenol it was noticed that the reaction begins at the hydroxy group [3].

It could be supposed that if derivatives of dihydroxyaniline, containing amino and hydroxy groups in the ortho position to each other, were used instead of o-aminophenol the hydroxyl derivatives of benzoxazole would be obtained in the reaction with ynamines. However, investigation of the reaction showed that the reaction only took place with the unambiguous formation of the 2-(2-alkenyl)-4-hydroxybenzoxazoles in the case of 2-aminoresorcinol, whereas 2-amino-4-hydroxyphenol and 3-amino-2-hydroxyphenol gave a complex mixture of reactions of cyclic and noncyclic structure involving one and both hydroxy groups.

In the case of 2-aminoresorcinol, the molecule of which is strictly symmetrical, after addition at the triple bond the reaction can only develop with the participation of the amino group. After the elimination of the dialkylamine the 2-(3-methyl)-2-butenyl-4-hydroxybenzoxazoles (V, VI) are formed.



I R^1=H, R^2=Et; II R^1=Me, R^2=Et; III R^1=Me, R^2=Pr; V R^1=H; VI R^1=Me

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Saint Petersburg Technological Institute, Saint Petersburg 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 231-232, February, 1992. Original article submitted July 31, 1990.

0009-3122/92/2802-0191$12.50

The PMR spectrum of compound (V) contains signals for the protons of the benzene ring (6.48-7.12), the hydroxyl group (10.3), and the unsaturated fragment in the regions of 1.86 (3H, d, J 7.0 Hz) and 3.66 (2H, d, J 7.0 Hz) and in the regions of 1.88 (3H, d, J 7 Hz), 3.66 (2H, d, J 7 Hz), and 5.32-5.81 ppm (2H, m, CH═CH).

The reaction takes place similarly in the series of simple ynamines.

EXPERIMENTAL

The PMR spectra of compounds (V, VI) were recorded on a Tesla BS-487C instrument at 80 MHz for 15% solutions in carbon tetrachloride with HMDS as internal standard. The IR spectra were recorded on an IKS-29 spectrophotometer for 1% solutions in carbon tetrachloride. The elemental analyses for C, H, and N agreed with calculated data.

2-(2-Butenyl)-4-hydroxybenzoxazole (V) ($C_{11}H_{11}NO_2$). To a solution of 1.4 g of 2-aminoresorcinol hydrochloride in 20 ml of absolute ethanol, with the constant passage of nitrogen, we added 0.7 g of sodium bicarbonate. The mixture was stirred for 40 min, and sodium sulfate was then added as drying agent. The mixture was stirred for a further 30 min, and 1.2 g of 1-diethylamino-3-penten-1-yne was added drop by drop. Slight but prolonged heating was observed. At the end of the reaction (monitored by the band at 2200 cm^{-1} in the IR spectrum) the precipitated salt was filtered off. The solvent was removed, and the residue was passed through a column of silica gel. The impurities were first eluted with pentane, and the product was then eluted with a 1:10 mixture of ethanol and hexane. It was recrystallized from heptane; mp 84°C. IR spectrum: 3480 (OH), 1625 cm^{-1} (C═C). The yield was 70%.

2-(3-Methyl-2-butenyl)-4-hydroxybenzoxazole (VI) ($C_{12}H_{13}NO_2$). The compound was obtained by the method above from 2-aminoresorcinol and 1-diethylamino-4-methyl-3-penten-1-yne (II) or 1-dipropylamino-4-methyl-3-penten-1-yne (III); mp 94°C. The yields were 73 and 75%.

2-Ethyl-4-hydroxybenzoxazole. The compound was obtained by the method above from 1-diethylamino-1-propyne and 2-aminoresorcinol; mp 124°C. The yield was 84%.

LITERATURE CITED

1. S. Fujita, K. Koyama, and J. Inagaki, *Synthesis*, No. 1, 68 (1982).
2. K. Hayamizu and O. Yamamoto, *Japanese Patent No. 8221377; Chem. Abs.*, **97**, 23776 (1982).
3. S. E. Tolchinskii, M. V. Kormer, I. A. Maretina, and A. A. Petrov, *Inventor's Certificate No. 910626; Byull. Izobret.*, No. 9 (1982).
4. S. E. Tolchinskii, M. V. Kormer, I. A. Maretina, and A. A. Petrov, *Inventor's Certificate No. 998464; Byull. Izobret.*, No. 7 (1983).
5. E. A. Sokolova, I. A. Maretina, and A. A. Petrov, *Inventor's Certificate No. 1081163; Byull. Izobret.*, No. 11 (1984).