LETTERS TO THE EDITOR

A Convenient Route to Functionalized Derivatives of Pyrrolo[2,1-b][1,3]benzothiazole

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Accessible products of cyclocondensation of *o*-aminothiophenol I with chlorine-containing unsaturated azlactones II [1] can be readily subjected to interesting transformations $III \rightarrow IV \rightarrow V \rightarrow VI \rightarrow VII$ presented in the Scheme 1.

Cyanomethylation of compound III occurs at the

nitrogen atom of the thiazoline fragment, because the IR spectra indicate that the azlactone ring in the reaction products IV is preserved. This ring is capable of further opening with methanol in the presence of sodium methylate. The possibility of easy annelation $V \rightarrow VI$ evidently arises from the formation of Z isomers of the intermediate products V in which the

Scheme 1.



Ar = Ph (**a**), 4-MeC₆H₄ (**b**).

active methylene group and methoxycarbonyl residue are sterically proximate. Numerous examples of such intramolecular cyclizations were reported previously (see, e.g., [2]). Elimination of methanol from intermediates V may probably lead to the corresponding keto nitriles with the characteristic COCHCN group, but we failed to identify this group by comparative analysis of the IR and ¹H NMR spectra of related compounds VI and VII. In this case, formation of enol group is favorable because it does not distort the aromaticity of the pyrrole fragment. Finally, it should be noted that accessible condensed substrates VI appeared to be suitable for preparing not only O-methylation products VII, but also a series of other functional derivatives of pyrrolo[2,1-b][1,3]benzothiazole which will be considered in further papers.

2-[5(4H)-Oxo-2-phenyl-1,3-oxazol-4-ylidene]-2,3-dihydrobenzo[1,3]thiazole (IIIa) was prepared as described previously [1] for **IIIb** and was recrystallized from DMF. Yield 78%, mp 270–272°C. IR spectrum, v, cm⁻¹: 1715 (C=O), 3100–3280 (NH_{ass}). Found, %: N 9.47; S 10.85. $C_{16}H_{10}N_2O_2S$. Calculated, %: N 9.51; S 10.89.

2-[2-Aryl-5(4*H*)-oxo-1,3-oxazol-4-ylidene]-2,3-dihydrobenzo[1,3]thiazol-3-ylacetonitriles IVa and IVb. To a suspension of 0.03 mol of IIIa or IIIb in 80 ml of DMF, 0.04 mol of anhydrous potassium carbonate and 0.04 mol of chloroacetonitrile were added, and the mixture was heated at 100–110°C with stirring for 5 h. After cooling, 200 ml of water was added. The precipitate was filtered off, dried, and purified by crystallization from DMF. Yield of **IVa** 89%, mp 283–285°C. IR spectrum, ν , cm⁻¹: 1730 (C=O). Found, %: N 12.34; S 9.57. C₁₈H₁₁N₃O₂S. Calculated, %: N 12.60; S 9.62. Yield of **IVb** 89%, mp 273–275°C. Found, %: N 11.99; S 9.20, C₁₉H₁₃ · N₃O₂S. Calculated, %: N 12.10; H 9.23.

3-Acylamino-2-hydroxypyrrolo[**2**,**1**-*b*][**1**,**3**]**benzothiazole-1-carbonitriles VIa and VIb.** A solution of 0.019 mol of sodium methylate in 7 ml of methanol was added to a suspension of 0.015 mol of IVa or **IVb** in 50 ml of absolute methanol, and the mixture was refluxed for 10 h. The hot solution was quickly filtered to remove a small amount of a precipitate, the solvent was removed in a vacuum, and the residue was treated with 5 ml of 2% hydrochloric acid. The precipitate thus obtained was filtered off and recrystallized from acetic acid. Yield of VIa 73%, mp 308-310°C. IR spectrum, v, cm⁻¹: 1630 (C=O), 2220 (C=N), 3000-3350 (N-H, O-H_{ass}). ¹H NMR spectrum, δ, ppm: 7.29-8.02 m (9H, C₆H₅, C₆H₄), 9.91 s (1H, NH), 10.67 br.s (1H, OH). Found, %: C 64.78; H 3.39; N 12.35; S 9.50. C₁₈H₁₁N₃O₂S. Calculated, %: C 64.85; H 3.33; N 12.60; S 9.62. Yield of VIb 79%, mp 259–261°C. Found, %: N 12.01; S 9.19. C₁₉H₁₃. N₃O₂S. Calculated, %: N 12.10; S 9.23.

3-Benzoylamino-2-methoxypyrrolo[**2**,**1**-*b*][**1**,**3**]**benzothiazole-1-carbonitrile** (**VIII**). To a suspension of 0.003 mol of **VIa** in 25 ml of acetone, 0.004 mol of anhydrous potassium carbonate and 0.004 mol of methyl iodide were added, and the mixture was refluxed with stirring for 10 h. After cooling, 100 ml of water was added, and the precipitate thus formed was filtered off, dried, and recrystallized from acetonitrile; yield 82%, mp 243–244°C. ¹H NMR spectrum, δ , ppm: 4.15 s (3H, CH₃O), 7.35–8.02 m (9H, C₆H₅, C₆H₄), 10.06 s (1H, NH). Found, %: N 11.99; S 9.18. C₁₀H₁₃N₃O₂S. Calculated, %: N 12.10; S 9.23.

The IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets. The ¹H NMR spectra were taken on a Varian VXR-300 spectrometer (solutions in DMSO- d_6 , internal reference TMS).

REFERENCES

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