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SYNTHESIS OF 2,4-DICHLORO-3-CYANOPYRIDO[2,3-b]-[1,4]BENZOXAZINE BY REACTION OF 3-CYANOTETRA-CHLOROPYRIDINE WITH o-AMINOPHENOL

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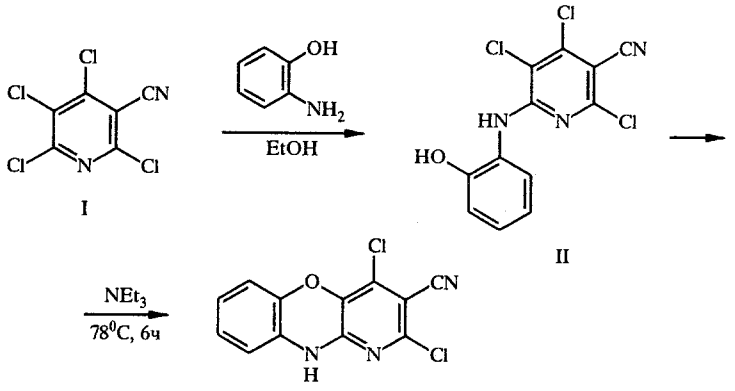
The synthesis of aza-analogs of phenoxazine is in general carried out under rigorous conditions using difficult to obtain catalysts and does not ensure high yields of the desired end products [1, 2]. At the same time it is known that the reactions of polychlorinated pyridines with anilines proceed effectively even under mild conditions and with fairly high yields [3]. It was therefore interesting to study the possibility of the preparation of azaphenoxazine derivatives in the reaction of 3-cyanotetra-chloropyridine with o-aminophenol. It was found that the first stage of this reaction comprises a nucleophilic substitution of the chlorine atom at the 6-position of compound I by the amino group of o-aminophenol with the formation of the corresponding arylaminopyridine II in a yield of 78%. Boiling of the alcoholic solution of compound II in the presence of triethylamine leads to the formation of the corresponding pyrido[2,3-b][1,4]benzoxazine III in a yield of 90%.



It is of interest to note that one of the main paths of the mass-spectral fragmentation of compound II is also an intramolecular heterocyclization giving the fragmentary ion $[M-HCl]^{+\cdot}$ with m/z 277 (50%), the further fragmentation of which is similar to the fragmentation of compound III. The discovered ability of compound II to enter readily into reactions with binucleophilic agents may find significant application in the synthesis of aza-analogs of other known polynuclear heterocycles.

2-(2-Hydroxyphenylamino)-3,4,6-trichloro-5-cyanopyridine (II, $C_{12}H_6Cl_3N_3O$), mp 295-297°C, IR spectrum: 3360 (OH); 3300 (NH); 2240 cm^{-1} (C≡N). PMR spectrum (DMFA-D_7): 10.55 (1H, s, OH); 9.04 (1H, s, NH); 7.94 (1H, d, J = 4 Hz, 6-H); 7.14 (1H, t, J = 4 Hz, 4-H); 7.08 (1H, d, J = 4 Hz, 3-H); 6.94 ppm (1H, t, J = 4 Hz, 5-H). ^{13}C NMR spectrum (DMFA-D_7): 98.6 ($C_{(5)}$); 113.0 (C≡N); 113.2 ($C_{(3)}$); 115.0 ($C_{(1)}$); 118.9 ($C_{(6)}$); 122.7 ($C_{(5)}$); 125.2 ($C_{(1)}$); 125.8 ($C_{(4)}$); 143.0 ($C_{(4)}$); 149.3 ($C_{(2)}$); 149.9 ($C_{(6)}$); 152.8 ppm ($C_{(2)}$).

2,4-Dichloro-3-cyanopyrido[2,3-b][1,4]benzoxazine (III, $C_{12}H_5Cl_2N_3O$), mp 254-255°C. IR spectrum: 3200 (NH); 2215 cm^{-1} (C≡N). PMR spectrum (DMFA-D_7): 8.52 (1H, s, NH); 8.15 (1H, d, J = 3.8 Hz, 6-H); 7.07 (1H, d, J = 3.8 Hz, 9-H); 7.05 (1H, t, J = 3.8 Hz, 7-H); 6.94 ppm (1H, t, J = 3.8 Hz, 8-H). ^{13}C NMR spectrum (DMFA-D_7): 101.8 ($C_{(3)}$); 114.5

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(C≡N); 114.6 ($C_{(6)}$); 116.5 (O−C=CCl); 118.9 ($C_{(9)}$); 121.1 ($C_{(8)}$); 124.2 ($C_{(7)}$); 126.3 (NH−C=CH); 143.5 ($C_{(4)}$); 147.9 (O−C=CH); 151.2 ($C_{(2)}$); 159.5 ppm (NH−C=N).

REFERENCES

1. Y. Ito and Y. Hamada, Chem. Pharm. Bull., **26**, 1375 (1978).
2. R. G. Sutherland, A. Piorko, Choi Chuck Lee, S. H. Simonsen, and V. M. Lynch, J. Heterocycl. Chem., **25**, 1911 (1989).
3. S. V. Chapyshev, Khim. Geterotsikl. Soedin., No. 2, 200 (1991).