TYPICAL ELECTROPHILIC REACTIONS OF FUROPYRIDINES

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In order to reveal the reactivities of furopyridines, we have undertaken the bromination and the nitration of furo[2,3-b]-,(1), furo[3,2-b]-,(2), furo[2,3-c]-,(3) and furo[3,2-c]pyridine (4) whose chemical properties had been almost unknown.

Bromination of 1, 2, 3 and 4 with 3 moles of Br_2 in CCl_4 afforded the corresponding trans-2,3-dibromo-2,3-dihydro derivatives (5, 6, 7 and 8) in 95, 92, 20 and 52% yield, respectively, which were derived to 3-bromofuropyridines (9, 10, 11 and 12) by treatment with NaOH in MeOH-H_2O in almost quantitative yield.

Nitration of 1 with a mixture of fuming HNO_3 and H_2SO_4 afforded a mixture of cis-,(13) and trans-2-nitro-2,3-dihydrofuro[2,3-b]pyrid-3-yl nitrate (14) and 2-nitrofuro[2,3-b]pyridine (15). Both 13 and 14 were easily converted to 15 by treatment with $NaHCO_3$ solution. Compound 2 was nitrated to give a mixture of cis-,(16) and trans-2,3-dihydrofuro[3,2-b]pyridin-3-ol (17) and 2-nitro derivative (18). Compound 16 was transformed to 17 by refluxing on silica gel in AcOEt. The trans isomer 17 was dehydrated with Ac_2O to give 18. Reaction of 3 with a mixture of fuming HNO_3 and H_2SO_4 gave a nitrolic acid derivative 19 in 46% yield. Nitration of 4 gave a mixture of 3-(trinitromethyl)-pyridin-4-ol (20) (yield: 30%) and 2-nitrofuro[3,2-c]pyridine (21) (yield: 32%).

The structure of 19 and 20 were established by X-ray analysis. The differences of behavior observed in these reactions are discussed in connection with the results of the determination of basicities and the relative reactivities of H-D exchange reaction of these furopyridines.