

S_NAr REACTIONS IN PYRIDINE-CONTAINING DIOXINS AND PREDIOXINS

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Introduction

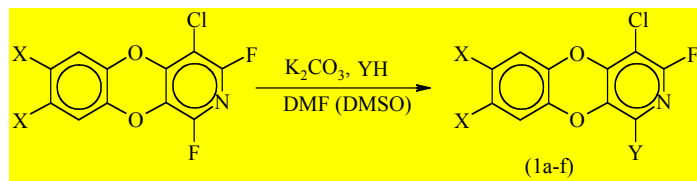
Dioxins and predioxins containing the pyridine ring with the labile fluorine atoms are convenient objects for preparing various derivatives. The presence of the pyridine ring can impact interesting and, probably, useful properties to such derivatives. Some alternatives of modifications of dioxins and predioxins have been proposed in this work.

Materials and Methods

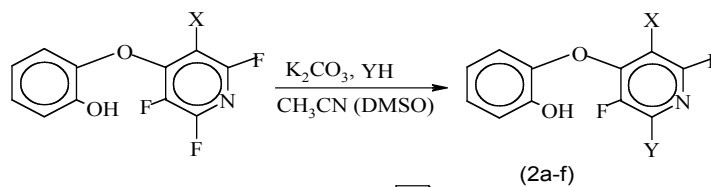
A mixture of dioxin (2g), nucleophile, and calcinated potash (molar ratio, 1:n:1.2, where n increased from 1 to 6 with a decrease of the strength of nucleophile) was added to 10 ml DMSO or DMF. The reaction mixture was stirred in DMSO at 20°C for 30 min (2.5 h for ammonia). In the case of DMF, the reactions were carried out at 20°C for 20 min (propylenediamine), at 70°C for 20 min (di-*n*-propylamine), and at 150°C for 10 h (aniline). The substitution in predioxins was carried out in DMSO at 20°C for 10-30 min or in acetonitrile at 60-70°C for 3 h using the components molar ratio 1:1:1.2 for all nucleophiles. After completion of the reactions, the mixtures were diluted with water. The products were extracted by chloroform and purified by recrystallization from propanol, acetone, or ethanol. The structure of compounds was proved by the element analysis and IR and ¹H, ¹⁹F, and ¹³C NMR-spectroscopy.

Results and Discussion

Reactions of dioxins and predioxins with nucleophiles of medium strength occur under rather mild conditions giving the products of substitution of one fluorine atom (in *p*-position to C1 atom) with high yields (70-95%). Although the interaction with aniline, a weak nucleophile, requires more stringent conditions, the yield of reaction products is still acceptable (50%). One can predict successful reactions of dioxins and predioxins with strong nucleophiles. There is also a possibility of substitution of the second fluorine atom in the dioxine and predioxin molecules. Thus, numerous derivatives of dioxins and predioxins can be synthesized among which the compounds with useful properties can be found.



- (1a) X = H, Y = -OH
 (1b) X = H, Y = -N \square O
 (1c) X = H, Y = -NH₂
 (1d) X = H, Y = -NHPPh
 (1e) X = H, Y = -N(CH₂CH₂CH₃)₂
 (1f) X = Br, Y = -NH(CH₂)₃NH₂



- (2a) X = F, Y = \square N-
 (2b) X = F, Y = \square N-
 (2c) X = F, Y = \square N-
 (2d) X = Cl, Y = \square N-
 (2e) X = Cl, Y = \square N-
 (2f) X = Cl, Y = \square N-