SYNTHESIS OF NEW DIOXINS

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Introduction

There are no data concerning the synthesis of pyridine-containing dioxins widely represented among different physiologically active compounds. It is expedient, at least for this reason, to develop methods of synthesis of such kind of dioxins. A special attention should be paid to the design of tricyclic systems on the basis of perfluoroarenes and, particularly, perfluoropyridines. The pyridine ring of such dioxins can be easily and selectively modified due to a high lability of fluorine atoms activated by nitrogen for the S_NAr processes.

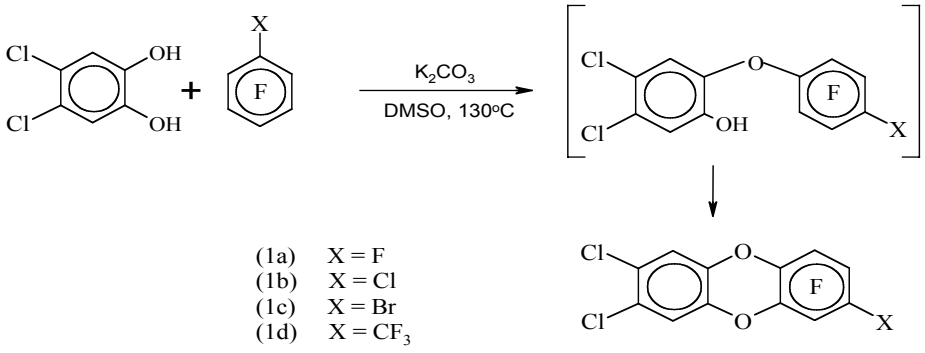
Materials and Methods

One-stage synthesis of dioxins (1a-d). A mixture of substrate (2g), nucleophile, and caltinated potash (molar ratio, 1:1:1.2) in 10 ml of DMSO was stirred at 120-130°C during 30-60 min. The reaction mixtures were diluted by water; the products were extracted by chlorophorm and purified by sublimation or recristallization from ethanol. The structure of compounds was proved by the element analysis and IR and ^1H, ^{19}F, and ^{13}C NMR-spectroscopy.

Synthesis of dioxins from predioxins (2a-g). A solvent (50 ml of DMF or DMSO) containing potash was heated at 100-120°C and added gradually during 1 hour with 2g of predioxin obtained as described in[1)]. The products were isolated, purified and identified as described above.

Results and Discussion

Formation of dioxins by the reaction of substituted pentafluorobenzenes with dichloropyrocatechin occurs readily with a high yield (70-85%).



(1a) X = F
(1b) X = Cl
(1c) X = Br
(1d) X = CF_3

(1a-d)

Dioxins containing polyfluorinated pyridine ring, however, cannot be modified in the same manner because the intermolecular reaction of intermediate predioxins with corresponding

pyrocatechin leads to the complex mixture of products. It is reasonable, therefore, to perform the synthesis by two stages first of which is the formation and isolation of predioxins. The second stage should be cyclization under conditions excluding an intermolecular reaction. For this purpose, predioxins obtained as described in[1)] were added gradually into a big volume of an aprotic solvent conatining anhydrous potash. In this case, pyridine-containing dioxins are formed with a high yield (60-90%).

(2a -g)

(2a)	X = H,	Y = F,	Z = F
(2b)	X = H,	Y = Cl,	Z = F
(2c)	X = H,	Y = Cl,	Z = Cl
(2d)	X = Cl,	Y = F,	Z = F
(2e)	X = Cl,	Y = Cl,	Z = F
(2f)	X = Cl,	Y = Cl,	Z = Cl
(2g)	X = Br,	Y = Cl,	Z = F

References

1. Litvak V.V.; Litvak A.V.; and Saikovich E.G. *Organohalogen Compounds*, **1999**, this issue.