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PREPARATION OF PENTAFLUOROPHENOL AND OTHER POLYFLUOROPHENOLS AND POLYFLUORODIHYDROXYBENZENES FROM POLYFLUOROAROMATIC ACIDS

V.E. Boyko, V.L. Don, S. M. Igoumnov

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St. 28, Moscow, 119991, Russian Federation
e-mail: boykii@mail.ru

NPO PIM-INVEST LLC, Leninsky Prospect, 47, Moscow, 119991, Russian Federation

Abstract: A process developed for the preparation of pentafluorophenol and other polyfluorophenols and polyfluorodihydroxybenzenes from corresponding aromatic acids by oxidation of organozinc compounds, obtained by decarboxylation of trimethylsilyl esters of these acids. The reactions of preparing zinc-organic compounds and their oxidation were carried out without isolation of intermediates.

Keywords: pentafluorophenol, pentafluorobenzoic acid, oxidation, polyfluorophenol, polyfluordihydroxibenzene, perfluorobenzoic acid (trimethyl)silyl ester.

Fluorinated phenols are widely used for producing polymers possessing unique properties [1] and as components of metallocene catalyst systems for olefin polymerization [2-4].

Pentafluorophenyl esters's formation is broadly applied in peptide synthesis since pentafluorophenol readily reacts with amines to form amide bonds, thus, pentafluorophenol is used in the synthesis of peptides and nucleosides, that are intermediates in the synthesis of antitumor agents, inhibitors of HIV [5-7].

Most of known methods for preparing pentafluorophenol involves substituting of fluorine atom in hexafluorobenzene for OH-group by reacting it with alkalis, or preparing phenyl-alkyl ethers by reacting hexafluorobenzene with metal alcoholates and their further decomposition to pentafluorophenol.

A major obstacle to the industrial use of these methods is that hexafluorobenzene is not a commercially available product now in connection with that hexachlorobenzene from which it has

and the reaction mixture was stirred for 1 hr. The content of the flask was then poured into hydrochloric acid (0,51 of 10% solution), the mixture was stirred for 10 minutes, the lower layer was separated and refluxed with concentrated hydrochloric acid for 2 hr, and then again separated and steam distilled over concentrated hydrochloric acid to obtain 2,4,5,6-tetrafluorophenol of 99% purity.(The yield 76%)

NMR ^{19}F δ, ppm.: 141,7m. (2F), -161,7m. (2F).

Tetrafluoroterephthalic acid bis (trimethylsilyl) ester

Trimethylchlorosilane (182 g, 1,69 mol) was added to tetrafluoroterephtalic acid (50 g, 0,21 mol), the reaction mixture was refluxed to the completion of the gas evolution, then an excess of trimethylchlorosilane was distilled off. Tetrafluoroterephthalic acid bis-(trimethyl)silyl ester (80,2 g, 0,21 mol) was obtained.

^{19}F NMR($CDCl_3$), δ, ppm.:-141м (4F), ^{1}H NMR($CDCl_3$) δ, м.д.: 0,78с.

Tetrafluorohydrohinone

DMF (250 ml) and anhydrous zinc acetate (38,5 g) were added to tetrafluoroterephthalic acid bis (trimethylsilyl) ester (80,2 g, 0,21 mol) and the reaction mixture was heated while distilling off trimethylsilyl acetate and decarboxilation. After the completion of the gas evolution the reaction mixture was cooled to 0°C, CuCl (0,2 g) was added and tert-butylperoxybenzoate (81 g , 0,42 mol) was added dropwise. The reaction mixture was stirred for additional 2 hr at 0 °C and 6 hr at ambient temperature, poured on ice mixed with 10% HCl solution, a lower layer was separated. Two volumes of hydrochloric acid were added to the lower layer, the resulting mixture was refluxed for 3 hr, and then cooled, the water (upper) layer was decanted, the lower layer was distilled to yield tetrafluorohydrohinone (30 g) of 99% purity. The yield 80%.

NMR ^{19}F δ, ppm.: 165,3m (4F).

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