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NEW METHODS FOR THE PREPARATION OF HIGHLY FLUORINATED PHENOLS AND THIOPHENOLS.

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Highly fluorinated phenols and thiophenols have been prepared by the replacement of fluorine in polyfluoroaromatic compounds C_6F_5X (X = F-,[1] H,[1] CF_3-[2]) using potassium hydroxide in t-butanol[3] and sodium hydrogen sulphide[1] in ethylene glycol as nucleophilic reagents. However, in each case where X = H-, CF_3-, the fluorine para to the group X was removed - no ortho-substitution products were isolated. We have now synthesised the previously inaccessible 1,2,3,4-tetrafluorophenol and 1,2,3,4-tetrafluorothiophenol using the monolithium derivative of 1,2,3,4-tetrafluorobenzene in tetrahydrofuran recently described by Tamborski.[4]

Earlier work on the preparation of pentafluorophenol[3,5] from pentafluorophenylmagnesium bromide,[6] by reaction with trimethylborate, hydrolysis

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of the ester groups by dilute acid, and subsequent oxidation of the intermediate pentafluorophenylboronic acid (which was not isolated) by 30% hydrogen peroxide,[7] a method used successfully in the hydrocarbon field,[8] gave very poor yields. Pentafluorophenylboronic acid has since been isolated by another method[9] and gave pentafluorophenol in high yield using 85% hydrogen peroxide, presumably because there was little competition from the hydrolytic cleavage of the C-B bond.

We have now prepared pentafluorophenol in 39% yield by making pentafluorophenyl-lithium in tetrahydrofuran and treating this at -65° with trimethyl borate followed by reaction of the dimethyl ester of the boronic acid (not isolated) with 85% hydrogen peroxide. When the monolithium reagents derived from 1,2,3,4-tetrafluorobenzene and 1,2,4,5-tetrafluorobenzene were treated in the same way, 1,2,3,4-tetrafluorophenol and the previously prepared 2,3,5,6-tetrafluorophenol[10] were obtained in 47 and 55% yields respectively.

Thiophenols have been prepared by the reaction of elemental sulphur on Grignard reagents.[11] When pentafluorophenylmagnesium bromide in tetrahydrofuran was treated with sulphur at 0°, pentafluorothiophenol was obtained in 67% yield. Pentafluorophenyl-lithium[4] gave pentafluorothio-

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phenol in 46% yield, while the monolithium reagent at -65°, derived from 1,2,3,4-tetrafluorobenzene gave 1,2,3,4-tetrafluorothiophenol in 67% yield and a small amount of a high boiling fraction which contained bis(1,2,3,4-tetrafluorophenyl)disulphide. This was shown to be the disulphide compound by reduction to the thiophenol with zinc and acetic acid, and by synthesis from the parent thiophenol using the method described previously.[1] The monolithium reagent derived from 1,2,3,5-tetrafluorobenzene gave the known 2,3,5,6-tetrafluorothiophenol[1] in 69% yield.

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