SYNTHESIS OF MONOFLUORINATED PCBs, FOR THE USE AS INTERNAL STANDARDS FOR PCB ANALYSIS

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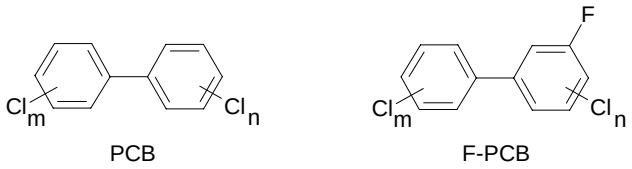
Introduction

Polychlorinated biphenyls (PCBs) are a major class of persistent environmental contaminants, despite a ban on production since the 1970s. PCB is any biphenyl that is chlorinated to varying degrees, and mixtures of PCB isomers were produced for a wide array of applications, such as capacitors and transformers, hydraulic fluids, paints, plastics and fire retardants. Their chemical stability, low flammability and electrical insulating properties lead to a worldwide use, however the chemical stability has also resulted in an accumulation of PCBs in higher organisms of the food chain.

PCBs are toxic pollutants and their toxicity depends largely on the number of *ortho*-substituents in the biphenyl molecule. The most toxic congeners are those which can adopt a partially co-planar conformation, which is found among PCBs with only one or none chlorine atoms in the *ortho* position. These congeners show similar toxic properties as dioxins and DDT and are referred to as dioxin-like PCBs.

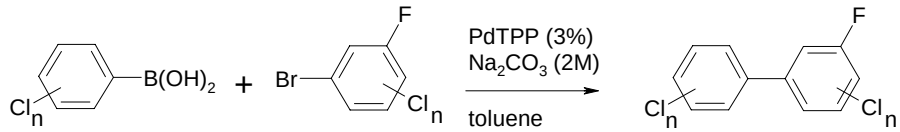
There are 209 possible PCB congeners, in which 1 to 10 chlorine atoms are attached to biphenyl. The analysis of a PCB mixture is complicated since there may be many different congeners that must be both identified and quantified. There have been reports on the elution order of all 209 congeners on high temperature gas chromatography,[1,2] so with a proper internal standard it should be possible to measure specific congeners at low concentrations. Fluorinated polyaromatic hydrocarbons (PAHs) have previously proved useful as internal standards for PAH analysis, a strategy likely to also hold for PCBs.[3]



In this work monofluorinated PCBs are prepared, which will be used as internal standards for PCB analysis. The fluorine atom does not drastically alter the properties of the PCB molecule, and the fluoro-PCB is expected to elute close to that of the corresponding PCB. Our major aim is to produce fluoro-PCB analogues to the dioxin-like PCBs, or fluorinated congeners with GC retention times close to those of the dioxin-like PCBs.

Materials and methods

The fluoro-PCBs were synthesised by Suzuki-coupling of an arylboronic acid and an aryl bromide or iodide, catalyzed by palladium triphenylphosphine (Scheme 1).[4] The Suzuki-coupling is the reaction of choice since other methods such as the Ullman, Sandmeyer and Cadogan reactions either result in low yields or can only be used for symmetrical PCBs.[5]



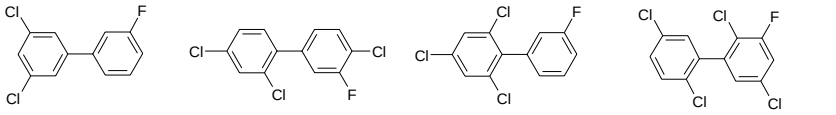
Scheme 1. Suzuki-coupling of arylboronic acid and aryl bromide, yielding the fluoro-PCB.

The Suzuki-coupling is performed in toluene under argon, using 3% (mol) $Pd(PPh_3)_4$ as catalyst and Na_2CO_3 (2M) as base. The general procedure is addition of the arylboronic acid in ethanol over 2 hours to a degassed mixture of aryl halide, $Pd(PPh_3)_4$, and Na_2CO_3 (2M). Reaction times vary with the numbers of chlorine substituents, but the mixture is stirred from 16 up to 72 hours.

Results and discussion

Ten different fluoro-PCBs have been prepared using the Suzuki-coupling. Three of these are analogues to the dioxin-like PCBs, listed by WHO as the most toxic congeners. The number of chlorine substitutents, and especially the number of *ortho*-substituents, affects both yields and reaction times. While the di- tri- and tetrachloro fluoro-PCBs are synthesised in moderate to good yields (30-60%), the yields of the penta- and

hexachloro fluoro-PCBs are quite poor (10-40%). The purities of the fluoro-PCBs are 97-98% according to GC analysis and NMR spectroscopy.

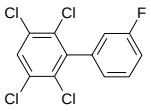


F-PCB 14 (3,5,dichloro-3'-fluorobiphenyl)

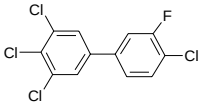
F-PCB 28 (2,4,4'-trichloro-3'-fluorobiphenyl)

F-PCB 30 (2,4,6-trichloro-3'-fluorobiphenyl)

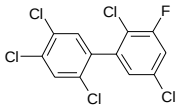
F-PCB 52 (2,2',5,5'-tetrachloro-3'-fluorobiphenyl)



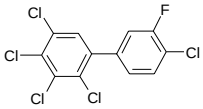
F-PCB 65 (2,3,5,6-tetrachloro-3'-fluorobiphenyl)



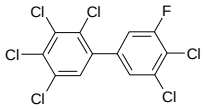
F-PCB 81 (3,4,4',5-tetrachloro-3'-fluorobiphenyl)



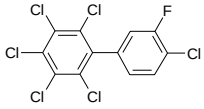
F-PCB 101 (2,2',4,5,5'-pentachloro-3'-fluorobiphenyl)



F-PCB 114 (2,3,4,4',5-pentachloro-3'-fluorobiphenyl)

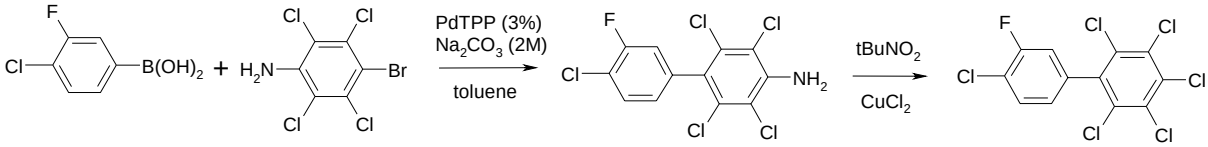


F-PCB 156 (2,3,3',4,4',5-hexachloro-5'-fluorobiphenyl)



F-PCB 166 (2,3,4,4',5,6-hexachloro-3'-fluorobiphenyl)

In the cases of congeners 65 and 166 the fluoro PCB products were too contaminated to purify. This was solved by using bromoanilines for the Suzuki-coupling, followed by deamination or conversion of the amine group into chlorine (Scheme 2). The conversions of the fluoro-PCB amines were higher than those of the fluoro PCBs, and the fluoro-PCB amines were much more easily purified.



Scheme 2. Suzuki-coupling the arylboronic acid and bromoaniline, followed by conversion of the amine, yields fluoro-PCB 166.

The fluoro-PCBs have fluorine in the *meta*-position since this is expected to result in a proper retention time in the LC or GC chromatogram. That is, baseline resolved but close to the corresponding PCB signal. The *para*-substituted fluoro-PCBs overlap the corresponging PCBs while *ortho*-substituted congeners generally show much shorter retention times.

In conclusion, fluorinated di- tri- tetra- penta- and hexa-chlorosubstituted biphenyls have been synthesised, using the Suzuki-coupling. Their qualities as internal standards for PCB monitoring are under study, and hopefully they will be useful both for analysis and as markers and tracers in toxicological studies.

Acknowledgements
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References

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