Synthesis of Hydroxychrysenes

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Chrysene and alkylchrysenes count for between 5 and 150 mg/kg of crude oil. As a four-ring PAH it is relatively resistant to microbial degradation but still fairly bio available both in water and in sediments. Due to these properties chrysene and the chrysene metabolites have attracted interest as potential biomarkers for environmental monitoring. Together with other metabolites the hydroxychrysenes are concentrated in the bile of organisms like fish. To analyse this kind of compositions there is need for pure compounds as analytical standards and reference compounds. In a technical cooperation between the University of Stavanger and RF-Akvamiljø[1)] my students and I have been making the 1-, 2-, 3- and 4-hydroxychrysenes for use as references.

The key reaction was the commonly used photochemical cyclisation of stilbenes to make the chrysene skeleton. The Wittig salts of *orto*-, *meta*- and *para*-methoxy-α-chlorotoluene, made quantitatively with triphenylphosphine, were reacted with 1-naphtaldehyde to give the corresponding stilbenes (*cis/trans* about 1:1) in close to quantitative yields. The photocyclisation were made with 1 eq. iodide in degassed toluene under inert atmosphere with a medium pressure mercury lamp. Addition of 1,2-epoxybutane to quench the formed HI helped to prevent side reactions and the methoxychrysenes could be obtained in 80-90 % yield by flash chromatography or recrystallised form the reaction mixture in 40-60% yield. The *orto*-substituted starting material gave 1-methoxychrysene and *para*-substitution gave 3-methoxychrysene. The *meta*-substituted compound gave a 1:1 mixture of 2- and 4-methoxychrysene. Recrystallisation from acetone gave 2-methoxychrysene, while the remains had to be purified by flash chromatography to obtain pure 4-methoxychrysene.

Deprotection of the methoxychrysenes to obtain pure hydroxychrysenes turned out to be more difficult. We were unable to get full reaction with BBr_3. Thus the hydroxychrysenes has to be purified from the starting material. This is possible with careful flash chromatography, but the products get discoloured by oxidation during the workup. An alternative reaction with potassium in THF reacts quantitatively, but produce chrysene as a byproduct, with similar workup-problems. Currently we are exploring other ways of doing workup, including a derivatisation step, to obtain the pure noncoloured hydroxychrysenes in an easier way.

1) G. Jonsson, I.C. Taban, K.B. Jørgensen, R.C. Sundt, *Chemosphere* **54**(2004) 1085-1097