Synthesis and Characterization of Polychlorinated Dibenzothiophenes

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Polychlorinated dibenzothiophenes (PCDBTs), sulfur analogs of PCDFs, have been found in environmental samples from waste combustion processes[1] and pulp bleaching[2]. Several congeners have been identified using standard compounds, isolated from Friedel-Crafts type reaction of various PCBs with sulfur in presence of $AlCl_3$[3]. This synthetic way always produces mixtures of chloroaromatic compounds (not only PCDBTs) with different number of chlorine atoms in molecule, which are difficult to separate. No other general synthetic methods were found in available chemical literature.

Since it is necessary to have a variety of isomerically pure congeners for any environmental or toxicological studies, we started a research program in this direction.

The objective of the first phase was to explore different synthetic methods, presumably leading to PCDBTs and to isolate 5-10 congeners in sufficient amounts and pure enough to be used as analytical standards immediately.

Four methods have been investigated :

1. Reaction of corresponding PCB with $SOCL_2$, followed by reduction of PCBDT Oxide (sulfoxide) with HBr.
2. Reaction of corresponding PCB with HSO_3Cl, followed by reduction of resulting PCDBT Dioxide (sulfone) with $LiAlH_4$.
3. Selective derivatization (chlorosulfonation) of lower chlorinated PCDBTs or their oxides or dioxides, followed by chlorosubstitution of SO_2Cl-groups and reduction of oxoderivatives as in methods 1. and 2.
4. Selective reduction of chlorine atoms in higher chlorinated PCDBTs.

Method 1.

This method seemed the most attractive, because conversion of dibenzothiopheneoxides to corresponding dibenzothiophenes goes easily (from experimental point of view) and the yields are almost quantitative[4]. Formation of sulfoxide itself was also reported (Diphenylsulfoxide, yield 70%)[5].

Unfortunately, all our numerous attempts to synthesize PCDBT oxides by this reaction resulted either in no reaction at all or in vigorous reaction with evolution of strange gases and formation of undissolvable black solids, which showed no target compounds on GC/MS.

Similar results were achieved when we have attempted to repeat the work of Sinkkonen et al.[3], with one important exception - unsubstituted dibenzothiophene can be prepared easily in good yield.

Method 2.

While reduction of sulfones seemed less reliable than that of sulfoxides, corresponding sulfones, unlike sulfoxides, have been prepared easily from several PCBs (reactions 1,3,5) by heating with an excess of chlorosulfonic acid.

2,3',4,4'-TCB, however, gives no sulfone, presumably due to predominant formation of 5-chlorosulfonyl derivative (reaction 7). One should note, that PCBs with the most reactive position other than 2, 2', 5 or 5' may show the same behavior as 2,3',4,4'-TCB.

Reduction of 3,7-Di- and 2,3,7,8-Tetra- CBDTdioxides with $LiAlH_4$ gave good (40-70%) yields of pure 3,7-DCDBT and 2,3,7,8-TCDBT respectively (reactions 2 and 4).

Reduction of 2,3,4,6,7,8-HxCDBTdioxide resulted in formation of a mixture of lower chlorinated compounds, no intermediate formation of target HxCDBT or its oxide was detected (reaction 6). One of possible explanations is that chlorines in positions 4 and 6 undergo rapid elimination. Further research is underway to determine whether this rule is common.

Method 3.

The main product of chlorosulfonation of DBT at ambient temperature is 2,8-disulfochloride (reaction 8), which was converted into corresponding 2,8-DCDBT (reaction 9). Chlorosulfonation at elevated temperature gives mainly 2,4,6,8-tetrasulfochloride (reaction 10), which, similarly, was converted into 2,4,6,8-TCDBT (reaction 12). Similar treatment of 2,8-DCDBT (reactions 11 and 13) resulted in a mixture of at least 3 main products, one of which - 2,3,6,8-TCDBT was isolated in poor yield by several successive crystallizations from chloroform and methanol.

Method 4.

Octachlorodibenzothiophene, obtained by exhaustive chlorination of dibenzothiophene (reaction 14), under Zn/AcOH reduction gave only one compound, HpCDBT (reaction 15). Elucidation of its structure presents some difficulties, because no sufficient NMR-data has been accumulated. However, it is well known, that the most active chlorine in this reaction is the most sterically hindered one (1- and 9-). Furthermore, formation of HpCDBT, rather than HxCDBT, assumes that chlorine atom, eliminated first, has a great influence on the equivalent chlorine atom in another ring - this also suggests formation of 1,2,3,4,6,7,8-HpCDBT.

Conclusions :

1. Existing synthetic methods allow to prepare a broad range of PCDBTs in pure form and significant amounts.
2. 8 congeners have been obtained. They can be used as analytical standards or for toxicology studies.

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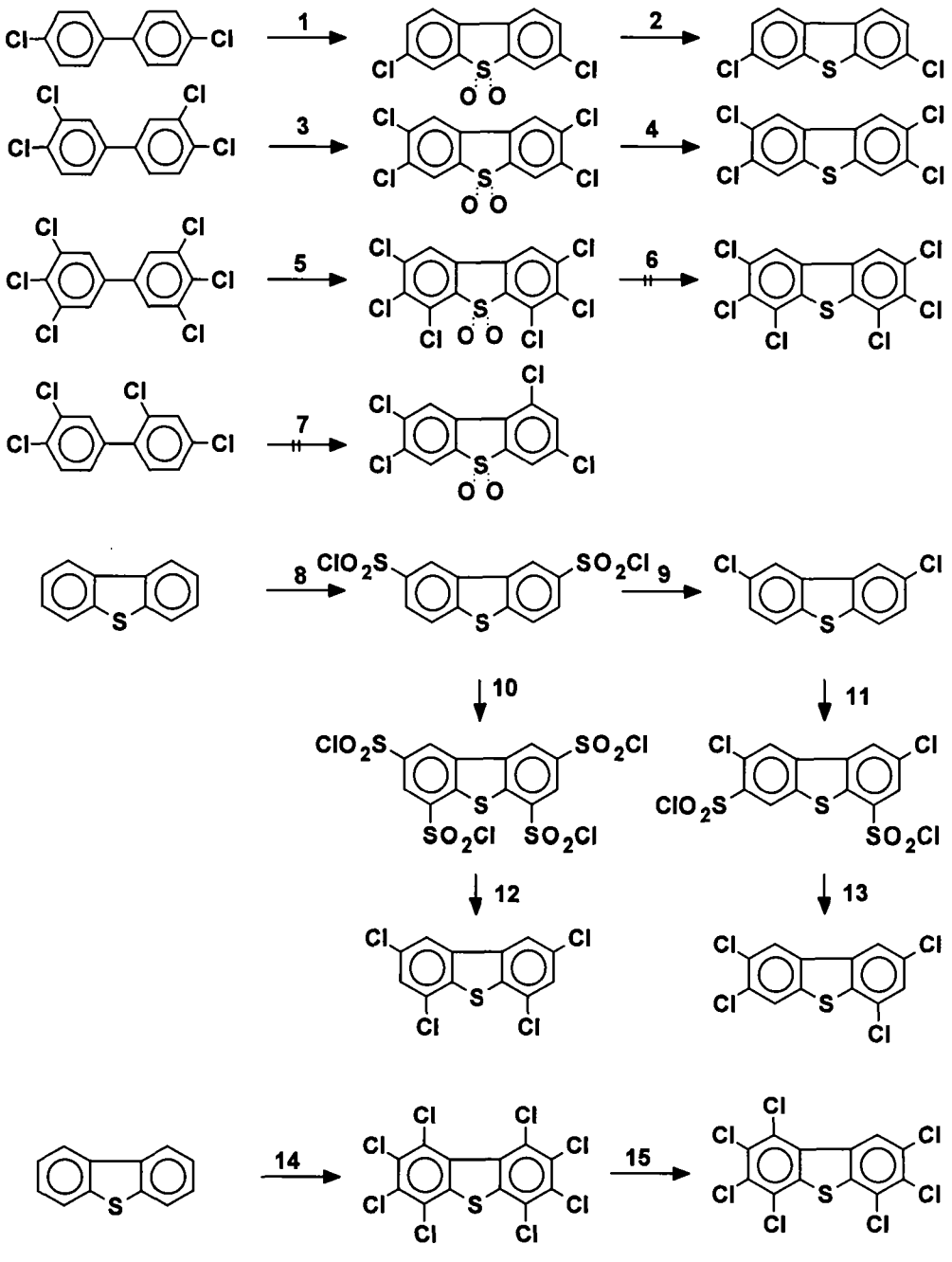

Scheme 1. Synthesis of Polychlorinated Dibenzothiophenes (PCDBT).