

## A one step synthesis of all three nona-brominated diphenyl ethers

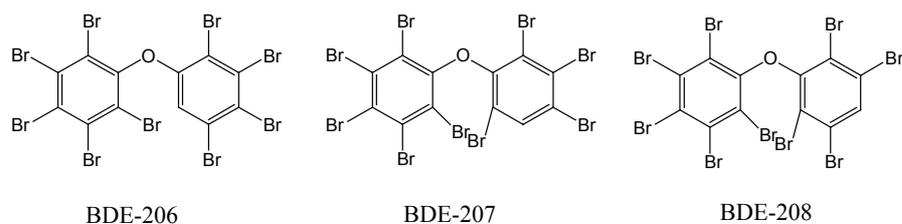
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### Introduction

Polybrominated diphenyl ethers (PBDEs) are well known and ubiquitous environmental contaminants <sup>1</sup> that theoretically can form of 209 congeners. Still it is only a limited number of these PBDE congeners that are formed when PBDE products are technically produced. PentaBDE and OctaBDE products consist of 10-20 congeners while DecaBDE almost exclusively contain the perbrominated diphenyl ether, BDE-209 <sup>2</sup>. The higher brominated diphenyl ethers are only present in OctaBDE and DecaBDE products. So far it is also only a limited number of PBDE congeners that have been reported in the environment, preferentially PBDE congeners with up to seven bromine atoms <sup>1</sup>.

Approximately 50 PBDE congeners have hitherto been synthesized and described in the scientific literature while several more are offered as analytical standards on the market. The methodologies available for PBDE congeners were recently summarized in detail by Marsh <sup>3</sup>. The major pathway for their synthesis goes via their formation from a polybromodiphenyl iodonium salt and a brominated phenolate or direct bromination of diphenyl ether <sup>3</sup>. The focus on PBDE congener synthesis has so far been on low to intermediately brominated diphenyl ethers while there has been a lack of PBDE standards substituted with eight and nine bromine atoms. The present work describes a one-step procedure to prepare all three nona-BDEs, BDE-206, BDE-207 and BDE-208 (Figure 1).



**Figure 1.** Structures of the three nona-BDE isomes that may be formed.

### Materials and Methods

*Chemicals:* Decabromodiphenyl ether from Fluka Chemie AG (Buchs, Switzerland) was used in the reaction. Sodium borohydride was obtained from Aldrich Chemical Company, Inc. (Gillingham, U.K.) and tetrahydrofuran (THF) from Acros Organics (New Jersey, USA), ethanol from Kemetyl (Haninge, Sweden), aceto nitrile and methanol from Merck (Darmstadt)

*Instruments:* High-performance liquid chromatography (HPLC) was performed on a Shimadzu LC-9A (Kyoto, Japan) equipped with an UV detector UV100 from Spectra-Physics (Fremont, USA) and a C<sub>18</sub> reversed-phase column (Ace 5 C18, 250 x 4,6 mm, 5 µm particles) from Advanced Chromatography Technologies (Aberdeen, Scotland). The detection wavelength was set at 240 nm and the mobile phase was acetonitril:methanol (8:2). The flow rate was 2 mL min<sup>-1</sup>. In the clean up procedure the column was a preparative C<sub>18</sub> reversed-phase column (Ace 5 C18, 250 x 21 mm, 5 µm particles) from Advanced Chromatography Technologies (Aberdeen, Scotland) and the flow rate was 20 mL min<sup>-1</sup> and the wavelength was 310 nm.

Gas chromatography-mass spectrometry (GC-MS) was performed on an ion trap GCQ instrument from Finnigan Mat. The gas chromatograph was equipped with a fused silica capillary column (DB-5, 15 m x 0.25 mm, 0.025 mm film thickness, J&W Scientific, Folsom, USA). The temperature program was 80°C for 5 min, raised at 10°C min<sup>-1</sup> to 280°C which was held for 15 min. The injections were made in the splitless mode using an injection temperature of 260°C. Helium was used as carrier gas. Mass spectra were recorded in electron ionization mode at an ion source temperature of 140°C and an electron energy of 70 eV.

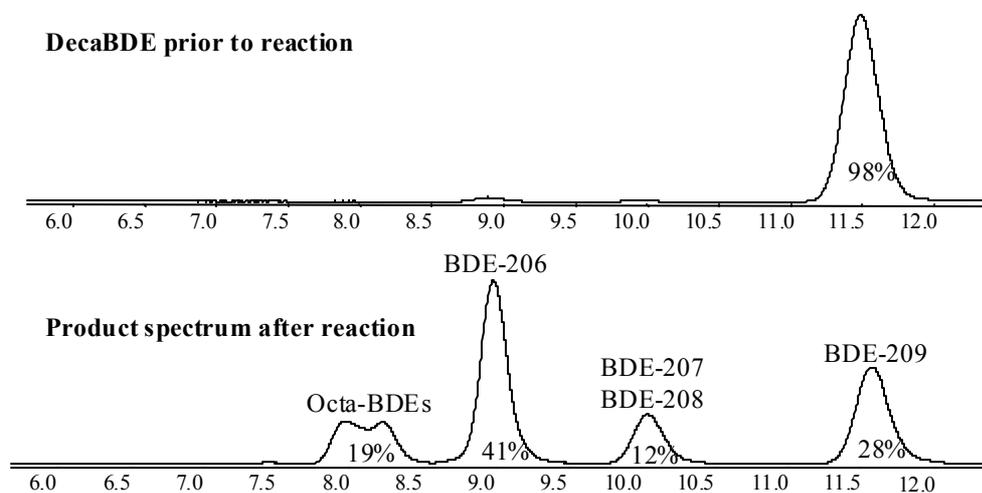
*Synthesis of nona-BDEs:* Decabromodifenyl eter (1 gram, 1 mmol) was dissolved in THF (250 ml). A saturated solution of sodium borohydride in ethanol (25 ml) was added drop-wise to the THF solution via a dropping funnel. The reaction was followed by HPLC until approximately 75% of the starting material (BDE-209) had disappeared. Water (2 ml) was added and the THF phase was isolated. The solvent was evaporated and the residue was dissolved in fresh THF. Three nona-BDE products were formed as determined by GC/MS. The three products were isolated by HPLC (Figure 2).

*Structure identifications:* The component indicated as BDE-206 in figure 2 was isolated from the preparative HPLC system. This compound was recrystallised from acetonitril/THF and its structure was determined by X-ray crystallography. The other two nona-BDE congener structures were determined by comparison to an authentic reference standard. The structure identifications are further described below.

### Results and Discussion

Since perhalogenated aromatics are rather labile to nucleophilic attack, as described for hexachlorobenzene<sup>4</sup> and more recently also for BDE-209<sup>5</sup> it is a clear possibility that bromine may be substituted with a hydrogen by using a hydride reagent. When lithium aluminum hydride first was tested it was found to be too reactive. Instead sodium borohydride was applied in the reaction described above. In this case it is possible to control the reaction and to obtain in good yield the mono-debrominated products of decaBDE (Figure 2). In this case the first eluting nona-BDE was fully separated from the other two congeners. This compound was isolated by preparative HPLC and the structure of the product was determined by X-ray crystallography. This was performed in a similar way as previously done for BDE-209<sup>6</sup>. The structure of this compound was unambiguously determined as BDE-206.

The separation of the other two nona-BDEs did not show any apparent separation but in fact it is possible to separate the two compounds by taking out a first and a second fraction when



**Figure 2.** HPLC separation of products formed by sodium borohydride reaction with decabrominated diphenyl ether.

these compounds elute. The structures of these two compounds were determined by comparison to BDE-207, synthesized in house via another route (unpublished). Hence the structures of the first eluting compound in the second peak representing nona-BDEs is BDE-207 and the second compound is BDE-208.

All three nona-BDE congeners may thus be made available as analytical standards and as test compounds in toxicological experimental work. The reactivity of BDE-209 is in fact higher than often referred to.

#### Acknowledgements

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