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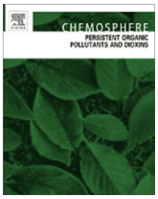

Synthesis of polybrominated diphenyl ethers via symmetrical tetra- and hexabrominated diphenyliodonium salts

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Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants (BFRs) which have become widespread environmental pollutants due to their persistence and bioaccumulativeness. Pure authentic PBDE congeners are required for chemical analysis, assessments of their chemical/physical properties and toxicological studies. We here report an improved method for synthesis of authentic PBDE congeners applying bromophenols and symmetrical brominated diphenyliodonium salts as building blocks. Altogether, 13 PBDEs were synthesized of which seven are new. The improved coupling reaction between the bromophenol and the brominated diphenyliodonium salts resulted in enhanced yields for PBDEs substituted with more than six bromine atoms. Also, improvements in iodonium salt synthesis made it possible to synthesize symmetrical hexabromodiphenyliodonium salts for the first time, i.e. 2,2′,3,3′,4,4′-, 2,2′,4,4′,5,5′- and 2,2′,4,4′,6,6′-hexabromodiphenyliodonium salts and they made it possible to prepare octabrominated PBDEs via the actual coupling method. All synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR spectra and by their melting points. Also, all products except for the diphenyliodonium salts were characterized by mass spectra in electron ionization mode.

1. Introduction

Commercial mixtures of polybrominated diphenyl ethers (PBDEs), i.e. technical PentaBDE, OctaBDE and DecaBDE, have been used as flame retardants since the 1970s. The PBDEs are additives in a variety of products, e.g. in plastics, textiles, coatings, and electrical components found in consumer goods including computers, televisions, carpets and electrical appliances (WHO, 1994). PBDEs are ubiquitous environmental contaminants present in all abiotic compartments and in humans and wildlife, as reviewed elsewhere (Hites, 2004; de Wit et al., 2006; Tanabe et al., 2008). Concerns about the PentaBDE and OctaBDE mixtures resulted in a ban within the European Union in 2004 (Cox and Efthymiou, 2003) and their withdrawal from the North America market (Great Lakes Flame Retardants, 2005). Because of their persistence, bioaccumulativeness and toxicity, PBDEs need to be assessed from an exposure perspective and to be tested for their biological potency. Individual PBDE congeners have been needed ever since they were first discovered in the environment (DeCarlo, 1979; Andersson and Blomkvist, 1981) in order to make them available as standards for analytical, toxicological and stability studies, as well as studies concerning physical-chemical properties.

Previously reported methods for the synthesis of PBDE congeners include bromination of diphenyl ether (Norström et al., 1976; Golounin et al., 1994) or a PBDE (Örn et al., 1996; Marsh et al., 1999; Teclechiel et al., 2007); coupling of bromophenols with symmetrical bromodiphenyliodonium salts (Nilsson et al., 1977; Hu et al., 1994; Marsh et al., 1999; Chen et al., 2001; Liu et al., 2006) or unsymmetrical bromodiphenyliodonium salts (Chen et al., 2001; Liu et al., 2006); S_NAr reactions of bromophenols with bromofluornitrobenzenes followed by reduction of the nitro group, diazotization and a Sandmeyer reaction (Chen et al., 2001); Suzuki coupling of bromophenol with bromoarylboronic acids (Chen et al., 2001); Ullmann diphenyl ether coupling of bromophenol with bromobenzene (Örn et al., 1996); perbromination/bromination of mono- and diaminodiphenyl ethers followed by diazotization of the amino group(s) and reduction of the diazonium ion(s) (Christiansson et al., 2006; Teclechiel et al., 2007); selective bromination of diaminodiphenyl ethers followed by diazotization of the amino groups and insertion of bromine (Teclechiel et al., 2007). Most of the synthesized PBDE congeners reported have been prepared via symmetrical diphenyliodonium salts and this is also true for the chlorinated analogues, i.e. polychlorinated diphenyl ethers (PCDEs) (Nilsson et al., 1977; Garå et al., 1981; Hu et al., 1994; Nevalainen and Koistinen, 1994). However, a limitation of PBDE synthesis via this method is the restricted number (3) of described symmetrical diphenyliodonium salts, i.e. 4,4′-dibromo-, 2,2′,4,4′-tetrabromo- and 3,3′,4,4′-tetrabromo-diphenyliodonium salts. Also, poor yields

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of hexaBDEs and heptaBDEs have been reported when prepared from tetrabromodiphenyliodonium salts (Marsh et al., 1999). The aim of the present work is to further develop a method for synthesis of symmetrical hexabrominated diphenyliodonium salts and to modify the coupling reaction between brominated diphenyliodonium salts and bromophenols, in order to synthesize new PBDE congeners, improve PBDE product yields, and avoid side-reactions with the intention of simplifying product purification.

2. Results and discussion

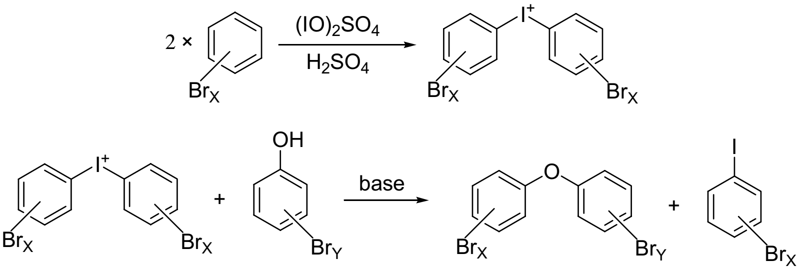
The general pathway for synthesis of diphenyliodonium salts and their coupling with phenols to produce PBDEs and the iodobromobenzene by-products is shown in Scheme 1. Thirteen PBDE congeners, substituted with 4–8 bromine atoms were synthesized via an improved diphenyl ether coupling reaction, reacting a brominated phenol with a polybromodiphenyliodonium salt as shown in Scheme 2. The purities of all PBDE products were above 98% according to GC–MS in EI mode and HPLC–UV.

Three of the staring materials, 1,2,3-tribromobenzene, 2,3,4,5-tetrabromophenol and 2,3,4,6-tetrabromophenol, were not commercially available and therefore were synthesized. 1,2,3-Tribromobenzene was prepared from 2,6-dibromoaniline following the diazotization method described by Hodgson and Walker (1933), followed by a Sandmeyer reaction according to Hodgson and Hathway (1944). 2,3,4,5-Tetrabromophenol was prepared from 4-acetamido-3-nitroanisole via 2,3,4,5-tetrabromoanisole as reported by Harrison and McOmie, 1966. 2,3,4,6-Tetrabromophenol was prepared from 3-bromophenol using an excess of bromine in acetic acid. Removal of hydrobromic acid formed during the bromination (using a stream of nitrogen) was necessary to preserve the bromophenol product intact. Without hydrobromic acid removal, a considerable amount (25–40%) of the product decomposed leading to a tedious purification process. This reaction gave a similarly high yield (97%) as previously reported when reacting 3-bromophenol with polymer bond benzyltrimethylammonium tribromide in the presence of calcium carbonate (Kakinami et al., 1989).

Three new symmetrical hexabrominated diphenyliodonium salts with hydrogen sulfate as counterion were prepared, i.e. 2,2′,3,3′,4,4′-hexabromodiphenyliodonium hydrogen sulfate, 2,2′,4,4′,5,5′-hexabromodiphenyliodonium hydrogen sulfate and 2,2′,4,4′,6,6′-hexabromodiphenyliodonium hydrogen sulfate. The new 2,2′,4,4′,5,5′-hexabromodiphenyliodonium salt was prepared with chloride as counterion as well. This allowed the synthesis of PBDE congeners with a 2,3,4-, 2,4,5- or a 2,4,6-tribromo substitution in the phenyl rings originating from each of the diphenyliodonium salts, respectively. Also, these hexabrominated diphenyliodonium salts made it possible to synthesize octaBDEs when pentabromophenol was reacted with the iodonium salt. The synthesis of hexabrominated diphenyl iodonium salts had previously failed (Garå et al., 1981; Chen et al., 2001; Nikiforov et al., 2003).

The hexabromodiphenyl iodonium salts were initially prepared by oxidizing iodine to iodyl sulfate with nitric acid in sulfuric acid (Beringer et al., 1959; Marsh et al., 1999). However, before the addition of the selected tribromobenzene, the reaction mixture was diluted with sulfuric acid to increase the solubility of the tribromobenzenes as well as the diphenyliodonium salt being formed. Also, due to the reduced reactivity of the tribromobenzenes compared to monobromobenzenes and dibromobenzenes, the reaction time for all tribromobenzenes had to be extended. With these two changes, the preparation of the three new hexabromodiphenyl iodonium salts was possible. The hexabromodiphenyliodonium salts were isolated with hydrogen sulfate as the anion. However, 2,2′,4,4′,5,5′-hexabromodiphenyl iodonium salt was also prepared with chloride as the anion. The latter iodonium salt gives a 2,4,5-tribromophenyl pattern in one of the PBDE phenyl rings after coupling with a phenol. This has previously been carried out by use of an unsymmetrical iodonium salt (4-methoxy-2′,4′,5′-tribromophenyliodonium bromide) or by S_NAr reactions by coupling bromophenols with 2,5-dibromo-4-fluoro nitrobenzene followed by reduction of the nitro group, diazotization and a Sandmeyer reaction (Chen et al., 2001; Liu et al., 2006). However, the latter two methods require additional steps to produce the desired products (Chen et al., 2001; Liu et al., 2006) resulting in lower overall yields compared to the method presented herein which applies the use of symmetrical iodonium salts.

The coupling reaction of bromophenol and symmetrical tribromodiphenyliodonium salt was modified, compared to reported methods for synthesis of PBDEs (Nilsson et al., 1977; Hu et al., 1994; Marsh et al., 1999; Chen et al., 2001; Liu et al., 2006) and chlorinated diphenyl ethers (Nilsson et al., 1977; Garå et al., 1981; Hu et al., 1994; Nevalainen and Koistinen, 1994) as follows. Previously, equivalent amounts of the phenol and the diphenyliodonium salt were reacted in water using sodium hydroxide (1–1.1 equivalents) as base. During the present work, we noticed that the solubility of the reactants, i.e. bromophenol and bromodiphenyliodonium salt, as well as the PBDE and iodobromobenzene products was poor or extremely poor in water when the total number of bromine atoms in the PBDE product was six or more and if the bromodiphenyliodonium salt was substituted with four or six bromine atoms. Consequently the reactants and products were added together as semi-solid or solid in the reaction vessel during the reaction, which resulted in limited amounts of the desired product and unwanted side-reactions. To solve this solubility problem, we introduced a co-solvent to water, i.e. 1,4-dioxane and different mixtures of these solvents were tested (data not shown). It was found that water/1,4-dioxane in the volume ratio of 1:2 gave the highest yields of PBDEs. The reaction temperature was lowered to 80 °C instead of reflux, to prevent side-reactions. This decrease in temperature had no influence on the rate of formation of the PBDE products. Also, the molar equivalent of bromodiphenyliodonium salt (compared to the phenol) was increased from 1 to 1.25, since we noticed that polybrominated diphenyliodonium salts may to



Scheme 1. The general pathway for synthesis of diphenyliodonium salts and their coupling with phenols to produce PBDEs.