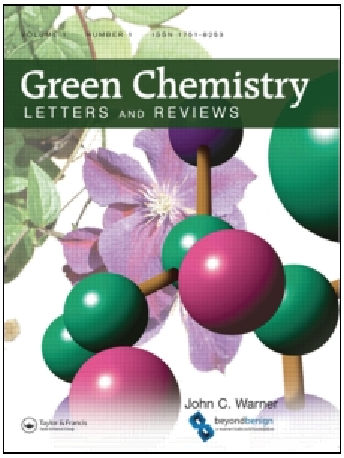


Green Chemistry Letters and Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t748292817

# Zinc dust-mediated reductive degradation of decabromodiphenyl ether

Guo-Bin Liu[a]; Hong-Yun Zhao[a]; Bin Yang[a]; Thies Thiemann[b]
[a] Department of Chemistry, Fudan University, Shanghai, P.R. China [b] Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, Japan

First published on: 22 February 2010

**To cite this Article** Liu, Guo-Bin , Zhao, Hong-Yun , Yang, Bin and Thiemann, Thies(2010) 'Zinc dust-mediated reductive degradation of decabromodiphenyl ether', Green Chemistry Letters and Reviews, 3: 1, 1 — 6, First published on: 22 February 2010 (iFirst)

**To link to this Article: DOI:** 10.1080/17518250903393882

**URL:** http://dx.doi.org/10.1080/17518250903393882

*Green Chemistry Letters and Reviews*
Vol. 3, No. 1, March 2010, 1–6

## RESEARCH LETTER

# Zinc dust-mediated reductive degradation of decabromodiphenyl ether

Guo-Bin Liu[a]*, Hong-Yun Zhao[a], Bin Yang[a] and Thies Thiemann[b]

[a]*Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, P.R. China;* [b]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1, Kasuga-koh-en, Kasuga, Fukuoka 816-8580, Japan*

*(Received 25 February 2009; final version received 7 October 2009)*

Zinc dust serves as a reducing agent in the presence of ammonium formate and NaOH, and is highly effective for the hydrodebromination of decabromodiphenyl ether to give diphenyl ether and the less brominated diphenyl ethers.

**Keywords:** decabromodiphenyl ether; debromination; zinc; degradation; detoxification

## Introduction

Over many years, polybromodiphenyl ethers (PBDEs) have been extensively utilized as flame retardants in various industrial products in order to improve their flame resistance. The amount of brominated flame retardants is increasing rapidly and also strongly linked to their presence in appliances that are being produced in increasing levels for use in homes and offices such as TVs, computers, textiles, coatings, and other pieces of electronic equipments. Flame retardants are also utilized in diverse materials such as fabrics, paints, and furnishings for car interiors. The annual world production of PBDEs is more than 70,000 metric tons per year and has dramatically increased over the year (*1,2*). As a consequence of their global use, they have become persistent organic pollutants (POPs) worldwide. Since PBDEs are lipophilic compounds, they bioaccumulate rapidly in animal and human biota through the food chains (*3–5*). It has been reported that the levels of PBDEs in breast milk of North American women appear to be doubling every two to five years (*6,7*). Although the toxicity of PBDEs is currently under investigation, recent results show that PBDEs can act as endocrine disruptors (*8*) through alterations of the thyroid hormone homeostasis (*9*), causing neurodevelopmental toxic effects (*10*). In addition, PBDEs might effect the liver (*11*) and developing reproductive organs (*12*). In vitro studies have indicated that hydroxylated PBDEs (HO-PBDEs) and methoxylated PBDEs (MeO-PBDEs) have the potential to interfer with CYP17 activity (*13,14*), and low-dose treatment with PBDEs has found to induce altered characteristics in MCF-7 cell (*13*). The US CDC has classified decabromodiphenyl ether (deca-BDE) as a possible carcinogen (*15*). The impact of PBDEs on the environment is not clear at present, but its potential toxicity has led to some calls for an urgent substitution of PBDEs, and related halogenated compounds in commercial products.

Obviously, even a rapid and comprehensive substitution of PBDEs results in the serious problem of waste elimination of existing materials in which PBDEs have been widely utilized. A number of processes for the degradation of PBDEs have been forwarded. Incineration is not always the best solution as incineration of municipal waste containing brominated phenols or diphenyl ethers can give rise to highly toxic polybrominated dibenzodioxins and dibenzofurans (*16,17*).

In recent times, the reductive dehalogenation of halogenated wastes has become of interest due to the eventual possibility of utilizing the dehalogenated products as new feedstocks (*18*). Photodegradation of PBDEs has been reported, though the debrominating efficiency has yet to be increased (*19*). Photodegradation in solution is faster than photodegradation of PBDEs adsorbed on solids such as on sand or silica gel. In addition, it has been shown that the photolytic decomposition of deca-BDE in toluene upon irradiation with UV light can lead up to 27 mono to hexasubstituted polybrominated dibenzofurans (PBDFs) (*20*). The electrochemical reductive behavior of deca-BDE has also been studied using platinum black electrodes. Here, deca-BDE debrominates easily to tetrabromo and tribromo substituted diphenyl ethers, which are more resistant to further

---

*Corresponding author. Email: liuguobin@fudan.edu.cn

ISSN 1751-8253 print/ISSN 1751-7192 online

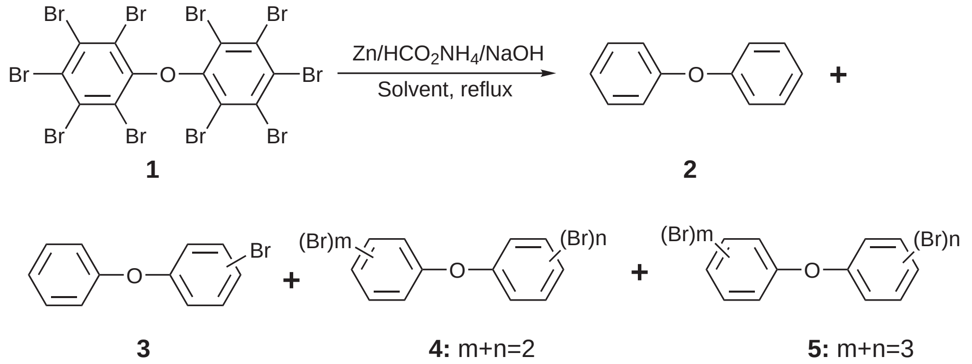
DOI: 10.1080/17518250903393882
http://www.informaworld.com

electrochemical debromination (*21*). It must be noted that the experiments on the electrochemical and some on the photochemical degradation were directed in part to establish the relationship between deca-BDE and tetrabromodiphenyl ethers, which themselves accumulate in the environment at a very rapid rate. It has been shown that deca-BDE can debrominate in vivo (*22*) and this has led to worry about the physiological effects and the toxicity of these partially brominated diphenyl ethers (vide infra). In addition, microbial reductive debromination of PBDEs with a number of anaerobic bacteria strains has been found to give a wealth of lesser brominated diphenyl ethers (*23*).

For an efficient degradation of deca-DBE it is important for the debromination to be as complete as possible. The tetrabromo and especially the more toxic pentabromodiphenyl ethers (*24*) should be held to a minimum. When reviewing debromination of aryl bromides, low-valent metals come to mind such as Li, Na, K, Mg, Fe, Zn, Cr in form of Cr(II) salts, and Sm in form of $SmI_2$ (*25*). Li has reported on the reductive debromination of PBDPEs with zero-valent iron to give partially debrominated diphenyl ethers (*26*). However, initially, reaction times were very long (5–40 days). Later, Li has forwarded the use of nano-sized iron particles bound on cation-exchange resin (*27*). The reaction rate of the debromination was reported to be far superior to those using micrometer-sized Fe particles (*26*). The reactions were carried out at room temperature and after 10 days significant amounts of deca-BDE had debrominated to the hexa and pentabrominated diphenyl ethers (*27*). Among traditional metal-based reducing agents other than Fe (vide supra), the safest and/or least toxic candidates are Mg and Zn, in which Zn as a reductant has been used both under acidic (Zn–HOAc) (*28*) and basic (Zn–NaOH) (*29*) reaction conditions for dehalogenation reactions. Zn has also been used as dehalogenating reductant in the presence of catalytic amounts of the more toxic Ni(II) in form of $NiCl_2$ (*30,31*). As a part of our program to develop new ways of degrading hazardous wastes (*32–35*), and in order to look for new reaction conditions for potential remediation technologies for PBDEs, we have developed a convenient and practical method for the degradation of PBDEs. Herein, we report our first finding on the hydrodebromination of deca-BDE by using zinc dust as reducing agent in the presence of ammonium formate and NaOH in ethanol.

## Results and discussion

The hydrodebromination was carried out by heating a mixture of deca-BDE (**1**), zinc dust, NaOH, and ammonium formate in ethanol under reflux conditions. The debromination was monitored by GC-MS. As shown in Scheme 1 and Tables 1 and 2, compound **1** was easily hydrodebrominated to afford a mixture of diphenyl ether (**2**), monobromodiphenyl ethers (**3**), dibromodiphenyl ethers (**4**), and tribromodiphenyl ethers (**5**) in the ratio of 11.0:18.4:46.1:24.5 (compounds **3**–**5** were obtained as a mixture of isomers, vide infra), when 5 eq. zinc dust, 5 eq. NaOH and 5 eq. ammonium formate were used for 1 eq. substrate and when the reaction was performed at reflux temperature (78°C) (Table 1, Run 1). Compounds **2**, **3**, **4**, and **5** were isolated by flash column chromatography [silica gel, ethyl acetate/hexane = 1/2(*v*/*v*)] in yields of 6.8%, 13.5%, 39.5%, and 20.5%, respectively, where compounds **2**–**5** were isolated as a mixture of isomers. From GC-MS data, all possible three isomers of the monobromodiphenyl ether **3** were detected, namely 2-bromodiphenyl ether (**3a**), 3-bromodiphenyl ether (**3b**), and 4-bromodiphenyl ether (**3c**). Here, 3-bromodiphenyl ether (**3b**) was formed as the minor product. Four isomers of dibromodiphenyl ethers **4** were formed, in which 4,4′-dibromodiphenyl ether (**4a**)



Scheme 1. Reductive debromination of decabromodiphenyl ether with zinc and ammonium formate.

Table 1. Debromination of decabromodiphenyl ether (**1**).[a]

| Run | Zn (eq.) | $HCO_2NH_4$ (eq.) | Solvent[b] | Temperature (°C) | Time (h) | Ratio (%)[c,d] **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 5 | 5 | EtOH | 78 | 10 | 11.0 (6.8[20]) | 18.4 (13.5[20]) | 46.1 (39.5[20]) | 24.5 (20.5[20]) |
| 2 | 5 | 10 | EtOH | 78 | 10 | 28.6 | 39.8 | 35.7 | 5.9 |
| 3 | 5 | 10 | EtOH | 78 | 16 | 31.1 (23.6) | 36.9 (30.2) | 32.0 (23.8) | 0 |
| 4 | 7 | 10 | EtOH | 78 | 16 | 32.0 | 35.4 | 32.6 | 0 |
| 5 | 5 | 15 | EtOH | 78 | 16 | 32.6 | 36.1 | 31.3 | 0 |
| 6 | 5 | 10 | MeOH | 65 | 16 | 23.2 | 26.1 | 45.5 | 5.3 |
| 7 | 5 | 10 | *i*-PrOH | 82 | 16 | 19.2 | 25.3 | 43.9 | 11.6 |
| 8 | 5 | 10 | *n*-BuOH | 116 | 16 | 20.5 | 22.2 | 47.6 | 9.7 |
| 9 | 5 | 10 | THF | 65 | 16 | 12.9 | 20.6 | 42.6 | 33.9 |
| 10 | 5 | 10 | 1,4-dioxane | 110 | 16 | 14.3 | 23.7 | 39.2 | 22.7 |

[a] **1** (4.0 mmol, 3.84 g), NaOH (20 mmol, 5 eq.).
[b] Solvent (50 ml).
[c] GC ratio.
[d] Isolated yields in parentheses.

was the main product (compared with an authentic sample from Aldrich). Five isomers of tribromodiphenyl ethers **5** were formed (five peaks were observed in GC chart), in which 2,4,6-tribromodiphenyl ether (**5a**) was identified with an authentic sample. No Wurtz–Fittig type C–C coupling products were detected as have been reported for reactions under similar conditions (aryl halide, Zn, NaOH, ammonium formate, MeOH, reflux). Most likely, the different outcome of the two reactions lies in the larger quantity of both zinc and ammonium formate used in the present case. Nevertheless, the formation of Wurtz–Fittig products under similar conditions point to an appreciable contribution of a phenyl anion intermediate (*36,37*). In addition, the reduction of dihalocyclopropanes with zinc under alkaline conditions to monohalocyclopropanes has been found to take place via the protonation of a corresponding anion intermediate (*38*). Nevertheless, it must be noted that the electron transfer from the metal to the aryl halide proceeds via a single electron transfer (SET) mechanism, and in research on the reduction of dihalocyclopropanes with zinc in MeOH a radical contribution could not be ruled out (*39*). Also, in the reductive

Table 2. Debrominaion of decabromodiphenyl ether (**1**) under different conditions.[a]

| Run | Metal | $NH_4X$ | Base | Time (h) | Ratio (%)[b,c] **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|---|---|---|
| 1 | Zn | $HCO_2NH_4$ | NaOH | 16 | 31.1 (26.6) | 36.9 (30.2) | 32.0 (27.8) | 0 |
| 2 | Zn | $HCO_2NH_4$ | – | 24 | 0 | 6.5 | 18.2 | 75.3 |
| 3 | Zn | $HCO_2NH_4$ | KOH | 16 | 31.9 | 37.0 | 31.1 | 0 |
| 4 | Zn | $HCO_2NH_4$ | CsOH | 16 | 32.8 | 35.2 | 33.0 | 0 |
| 5 | Zn | $HCO_2NH_4$ | LiOH | 16 | 1.5 | 16.3 | 51.6 | 30.6 |
| 6 | Zn | $NH_4OAc$ | NaOH | 16 | 11.2 | 29.0 | 47.9 | 11.9 |
| 7 | Zn | $NH_4Cl$ | NaOH | 16 | 9.8 | 22.3 | 54.7 | 13.2 |
| 8 | Zn | $(NH_4)_2SO_4$ | NaOH | 16 | 10.0 | 21.1 | 56.6 | 12.3 |
| 9 | Zn | $(NH_4)_3PO_4$ | NaOH | 16 | 11.8 | 28.1 | 51.2 | 8.9 |
| 10 | Zn | $NH_4NO_3$ | NaOH | 16 | 10.5 | 20.3 | 59.6 | 9.6 |
| 11 | Mg | $HCO_2NH_4$ | NaOH | 24 | 0 | 6.7 | 24.5 | 68.8 |
| 12 | Al | $HCO_2NH_4$ | NaOH | 24 | 0 | 4.2 | 21.6 | 74.4 |
| 13 | Fe | $HCO_2NH_4$ | NaOH | 24 | 0 | 5.6 | 23.6 | 70.8 |

[a] **1** (4.0 mmol, 3.84 g), base (20 mmol, 5 eq.), metal (20 mmol, 5 eq.), ammonium salt (40 mmol, 10 eq.) and EtOH (50 ml).
[b] GC ratio.
[c] Isolated yields in parentheses.

dehalogenation of polyfluoroarenes with zinc in aqueous ammonia, a reduction to radical aryl anion and subsequent fragmentation of the latter has been suggested (*40*). Thus, a likely mechanism would involve a SET from the metal, either directly or indirectly via electron carrier, to produce a radical anion, subsequent dissociation into an aryl radical and a halide anion, followed by a second SET to the anion (*41*), which is protonated in the final step.

It is known that ammonium formate plays the role of an effective proton transfer agent (*42*). When the quantity of ammonium formate was increased (to 10 eq.) in our experiments, the debromination went further and the yield of compounds **2** and **3** increased dramatically at the cost of compounds **4** and **5** (GC ratio, Table 1, Run 2 vs. Run 1). When the reaction time was prolonged to 16 h, a mixture of compounds **2**, **3**, and **4** was obtained in a GC ratio of 31.1:36.9:32.0 and with isolated yields of 23.6%, 30.2%, and 23.8%, respectively (Table 1, Run 2 vs. Run 3). An increase in the amount of zinc dust used (from 5.0 to 7 eq.), did not change the outcome of the reaction significantly, even after a reaction time of 16 h (Table 1, Run 4 vs. Run 3). In addition, a further change in the quantity of ammonium formate (from 10 to 15 eq.) did not influence the outcome of the reaction significantly, where the ratios of compounds **2**–**4** remained almost unchanged (Table 1, Run 5 vs. Run 4).

Methanol, *i*-propanol, *n*-butanol, tetrahydrofuran (THF) and 1,4-dioxane were investigated as solvents for the debromination. In MeOH, the debromination occured easily at 65°C, and after 16 h, a mixture of **2**, **3**, **4**, and **5** was obtained (Table 1, Run 6). In *i*-PrOH (82°C) and *n*-BuOH (116°C), the reduction was found to be slightly slower (16 h, reflux temperature) as compared to the reactions run in MeOH or EtOH. Also in these higher alcohols, mixtures of compounds **2**–**5** (Table 1, Runs 7 and 8) were produced. In the non-protic solvents THF (at 65°C) and in 1,4-dioxane (at 100°C), the debromination proceeded poorly, and even after 16 h at reflux temperature, only small amounts of **2** were observed (12–14%) (Table 1, Runs 9 and 10).

In the dehalogenation with Zn/ammonium formate, bases other than NaOH, such as KOH, CsOH, and LiOH were tested (Table 2). In the absence of base, the debromination proceeded very slowly. Tribromides (**5**) (75.3%, GC ratio) were detected as the main product after 16 h (Table 2, Run 2) and no diphenyl ether (**2**) was formed. In the case of using KOH or CsOH as base, the debromination proceeded well and a mixture of compounds **2**–**4** was afforded (Table 2, Runs 3 and 4). When employing LiOH as base, the debromination was slow and compound **4** was formed as the main product, albeit as a mixture with **2**, **3**, and **5** (Table 2, Run 5).

Moreover, other ammonium salts than ammonium formate ($NH_4HCO_2$) such as ammonium acetate ($NH_4OAc$), ammonium chloride ($NH_4Cl$), ammonium nitrate ($NH_4NO_3$), ammonium sulfate [$(NH_4)_2SO_4$], and ammonium phosphate [$(NH_4)_3PO_4$] were screened. In all cases, a mixture of reduced products **2**, **3**, **4**, and **5** was obtained, with **4** as the main product (Table 2, Runs 7–11). Nevertheless, ammonium formate was found to be the most effective in the reductive dehalogenation. This is in accord with the activity gradation of ammonium salts found for the reduction of different functional groups such as nitro (*42*) and oxime (*43*) to amine and hydroxylamine, where, among the ammonium salts, again ammonium formate has been found to best promote the reduction, when Zn is used as reductant.

Metals other than Zn such as Mg, Al, and Fe were also tested. When using Mg, Al, and Fe as reductant, **1** was reduced successfully to give **5** as the major product, together with some amounts of **3** and **4** (Table 2, Runs 11–13), indicating that Zn is the most successful reductant under the conditions, while among Fe, Al, and Mg a similar distribution of products is found.

## Experimental

$^1$H NMR spectra were recorded with a JEOL EX-270 spectrometer ($^1$H at 270 MHz). The chemical shifts are relative to tetramethylsilane (TMS) (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer [electron impact mode (EI), 70 eV or fast atom bombardment (FAB)] and with a GC-MS 6890[GC]/HP MS5973 combination. The GC-data given in Table 1 and 2 are GC ratios of compounds **2**–**5** and do not encompass minor side products that may have formed (renormated to 100%). To validate the GC-data given in Table 1 and 2 are GC ratios of compounds **2**–**5** and do not encompass minor side products that may have formed (renormated to 100%). To validate the GC-data of the reaction mixture in the actual organic solvent extract as matrix, actual substance isolations of compounds **2**–**5** have been performed.

Diphenyl ether (**2**), 4-bromodiphenyl ether (**3c**), and 4,4′-dibromodiphenyl ether (**4a**) were purchased from Aldrich. 2-Bromodiphenyl ether (**3a**), 3-bromodiphenyl ether (**3b**), and 2,4,6-tribromodiphenyl ether (**5a**) were prepared as reported in the literature (*35*). Deca-BDE (**1**, white powder, total bromine content = 82.5 wt%, free-bromine content = 20 ppm, particle size: 5 μm) was purchased from Haihua Risheng Chemical Co., Ltd., Suzhou, China. Zinc dust (300–400 mesh, Zn content > 98%, Pb < 0.1%, Fe < 0.05%, and Cd < 0.1%) was bought from Shijiazhuang Zongli Zinc Co., Ltd., China.

### *Typical procedure*

To a solution of deca-BDE (**1**, 4.00 mmol, 3.84 g), zinc dust (20 mmol, 1.3 g, and 300–400 mesh), and ammonium formate (40 mmol, 2.5 g) in methanol (50 ml) was added NaOH (20 mmol, 0.80 g). After the mixture had been heated at reflux for 16 h (monitored by GC-MS), it was cooled to room temperature and filtered over Celite. The residue was washed with ethyl acetate. After removal of the organic solvent, water (50 ml) was added, and the mixture was neutralized with hydrochloric acid. The solution was extracted with ethyl acetate (3 × 15 ml) and the organic layer was dried over anhydrous magnesium sulfate. After evaporation of the solvent, a mixture of diphenyl ether (**2**), monobromodiphenyl ether (**3**), dibromodiphenyl ether (**4**), and tribromodiphenyl ether (**5**) was obtained in a GC ratio of 11.0:18.4:46.1:24.5 (Table 1, Run 1). After separation by column chromatography on silica gel by using ethyl acetate and hexane ($1/2 = v/v$) as eluent, compounds **2**, **3**, **4**, and **5** were isolated in the yields of 6.8%, 13.5%, 39.5%, and 20.5%, respectively.

In general, compounds **2**–**5** were separated by column chromatography on silica gel by using ethyl acetate and hexane ($1/2 = v/v$) as eluent, when mixtures of structures were obtained from the reactions. Compounds **3**–**5** were a mixture of its isomers and compared with authentic samples by GC-analytical methods. Compounds **3**–**5** were also assigned on the basis of their GC-MS spectroscopic data.

2-Bromodiphenyl ether (**3a**) [35]: $\delta_H$ (270 MHz, $CDCl_3$) 6.92–7.00 (4H, m), 7.10 (1H, t, $J = 7.2$ Hz), 7.22 (1H, dd, $J = 7.2$ and 8.6 Hz), 7.32 (2H, dd, $J = 7.2$ and 8.6 Hz), 7.60 (1H, dd, $J = 1.6$ and 7.2 Hz); MS: 250 ([$^{81}$Br]M$^+$), 248 ([$^{79}$Br]M$^+$), 169 (M$^+$-Br), 141, 115, 84, 77, 63, 51.

3-Bromodiphenyl ether (**3b**) [35]: $\delta_H$ (270 MHz, $CDCl_3$) 6.94–7.02 (3H, m), 7.10 (1H, t, $J = 2.0$ Hz), 7.12 (1H, t, $J = 7.6$ Hz), 7.18 (1H, t, $J = 7.8$ Hz), 7.22 (1H, dd, $J = 2.0$, and 7.8 Hz), 7.32 (2H, dd, $J = 7.4$, and 7.8 Hz); MS: 250 ([$^{81}$Br]M$^+$), 248 ([$^{79}$Br]M$^+$), 169 (M$^+$-Br), 141, 115, 84, 77, 63, 51.

2,4,6-Tribromodiphenyl ether (**5a**) [35]: $\delta_H$ (270 MHz, $CDCl_3$) 6.82 (2H, d, $J = 8.6$ Hz), 7.02 (1H, t, $J = 7.2$ Hz, Ar-H), 7.32 (2H, dd, $J = 7.2$ and 8.6 Hz), 7.72 (2H, s); MS: 410 ([$^{81}$Br$_3$]M$^+$), 408 ([$^{81}$Br$_2$$^{79}$Br]M$^+$), 406 ([$^{81}$Br$^{79}$Br$_2$]M$^+$), 404 ([$^{79}$Br$_3$]M$^+$), 329 ([$^{81}$Br$_2$]DBE$^+$), 327 ([$^{81}$Br$^{79}$Br]DBE$^+$), 325 ([$^{79}$Br$_2$]DBE$^+$), 248 ([$^{81}$Br]MBE), 246 ([$^{81}$Br]MBE$^+$), 169 (M$^+$-3Br), 139, 124, 75, 50.

## Conclusion

We have developed a new and efficient method for the reductive debromination of deca-BDE using commercially available zinc powder, NaOH, and ammonium formate in methanol or in ethanol. Under these conditions, deca-BDE is debrominated easily to afford diphenyl ether (**2**), mono, di, and tribromodiphenyl ethers (**2**, **3**, and **4**). No tetra, penta, or higher brominated diphenyl ethers were detected. The use of 5 eq. Zn dust, 10 eq. ammonium formate, and 5 eq. NaOH in MeOH was found to give the best result under the conditions reported here. In comparison to Mg, Al, Fe, and Zn were found to be the best reductant under the conditions used. The most recalicitrant bromo substituents are those in the 4-position as can be evidenced in the major contribution of the 4,4′-dibromodiphenyl ether to the isomeric mixture of dibromophenyl ethers **4** formed. This is in accord with the observation of Keum and Li that reduction of tribrominated and pentabrominated diphenyl ethers with iron leads to preferential debromination at the 2 and 3-positions with a resistance of a debromination at the 4-position (*26*), but it is in juxtaposition to the photodegradation (*19*), where the bromo substituents in the 2, 3, and 4-positions are with equal ease, and to the electrochemical (*21*) and the metabolic degradation (*22*) of deca-BDE, in which preferential loss of 3 and 4-bromo substituents have been noted.

The advantages of the present approach lie in terms of the ease of manipulation of the reaction, the rapid rate of debromination and the mildness of the reaction conditions. The different conditions used for the degradation of deca-BDE as compared to existing methods, especially in regard to temperature and reaction medium, should make this protocol a valuable alternative. Further investigations in this direction on the debromination of deca-BDE and related brominated flame retardants are currently underway in our laboratory.

## References

(1) Rahm, S.; Green, N.; Norrgran, J.; Bergman, A. *Environ. Sci. Technol.* **2005,** *39*, 3128–3133.

(2) de Wit, C.A. *Chemosphere*. **2002,** *46*, 583–624.

(3) Voorspoels, S.; Covaci, A.; Jaspers, V.; Neels, H.; Schepens, P. *Environ. Sci. Technol.* **2007,** *41*, 411–416.

(4) Kierkegaard, A.; Asplund, L.; de Wit, C.A.; McLachlan, M.S.; Thomas, G.O.; Sweetman, A.J.; Jones, K.C. *Environ. Sci. Technol.* **2007,** *41*, 417–423.

(5) Soermo, E.G.; Salmer, M.P.; Jenssen, B.M.; Hop, H.; Baek, K.; Kovacs, M.; Lydersen, C.; Falk-Petersen, S.;

Gabrielsen, G.W.; Lie, E.; Skaare, J.U. *Environ. Toxicol. Chem.* **2006,** *25*, 2502–2511.

(6) She, J.; Holden, A.; Sharp, M.; Tanner, M.; Williams-Derry, C.; Hooper, K. *Organohalogen Compd.* **2004,** *66*, 3895–3900.

(7) Schecter, A.; Pavuk, M.; Papke, O.; Ryan, J.J.; Birnbaum, L.; Rosen, R. *Environ. Health Perspect.* **2003,** *111*, 1723–1729.

(8) Crump, D.; Jagla, M.; Kennedy, S. *Society of Environmental Toxicology and Chemistry 2005*, CRU-1117-814694, Baltimore, **2005**.

(9) Costa, L.G.; Giordano, G. *NeuroToxicology*. **2007,** *28*, 1047–1067.

(10) Talsness, C.E. *Environ. Res.* **2008,** *108*, 158–167.

(11) Darnerud, P.O.; Eriksen, G.S.; Johannesson, T.; Larsen, P.B.; Viluksela, M. *Environ. Health Perspect.* **2001,** *109*, S49–S68.

(12) Kuriyama, S.; Chahoud, I. *Organohalogen Compd.* **2003,** *61*, 92–95.

(13) Lundgren, M.; Darnerud, P.O.; Molin, Y.; Lilienthal, H.; Blomberg, J.; Illbaeck, N.G. *Toxicol.* **2007,** *242*, 100–108.

(14) Canton, R.F.; Sanderson, J.T.; Nijmeijer, S.; Bergman, A.; Letcher, R.J.; van den Berg, M. *Toxicol. Appl. Pharmacol.* **2006,** *216*, 274–281.

(15) CDC. Public health statement for polybrominated diphenyl ethers (PBDEs), September **2004**.

(16) Ebert, J.; Bahadir, M. *Environ. Inter.* **2003,** *29*, 711–716.

(17) Weber, R.; Kuch, B. *Environ. Inter.* **2003,** *29*, 699–710.

(18) Zanaveskin, L.N.; Aver'yanov, V.A.; Treger, Y.A. *Russ. Chem. Rev.* **1996,** *65*, 617–624.

(19) Bezares-Cruz, J.; Jafvert, C.T.; Hua, I. *Environ. Sci. Technol.* **2004,** *38*, 4149–4156.

(20) Hagberg, J.; Olsman, H.; van Bavel, B.; Engwall, M.; Lindstroem, G. Environ. Inter. *2006, 32*, 851–857 and ref. cited.

(21) Konstantinov, A.; Bejan, D.; Bunce, N.J.; Chittim, B.; McCrindle, R.; Potter, D.; Tashiro, C. *Chemosphere*. **2008,** *72*, 1159–1162.

(22) Stapelton, H.M.; Brazil, B.; Holbrook, R.D.; Mitchelmore, C.L.; Benedict, R.; Konstantinov, A.; Potter, D. *Environ. Sci. Technol.* **2006,** *40*, 4653–4658.

(23) He, J-Z.; Robrock, K.; Alvarez-Cohen, L. *Environ. Sci. Technol.* **2006,** *40*, 4429–4434.

(24) Eriksson, P.; Jakobsson, E.; Fredriksson, A. *Environ. Health Perspect.* **2001,** *109*, 903–908.

(25) Pinder, A. *Synthesis* **1980**, 425–452.

(26) Keum, Y-S.; Li, Q.X. *Environ. Sci. Technol.* **2005,** *39*, 2280–2286.

(27) Li, A.; Tai, C.; Zhao, Z.; Wang, Y.; Zhang, Q.; Jiang, G.; Hu, J. *Environ. Sci. Technol.* **2007,** *41*, 6841–6846.

(28) Shue, Y-K.; Carrera, Jr., J.M.; Nadzan, A.M. *Tetrahedron Lett.* **1987,** *28*, 3225–3228.

(29) O'Reilly, N.J.; Derwin, W.S.; Lin, H.C. *Synlett* **1990**, 339–340.

(30) Colon, I. *J. Org. Chem.* **1982,** *47*, 2622–2625.

(31) Qiu, Z.M.; Burton, D.J. *J. Org. Chem.* **1995,** *60*, 5570–5578.

(32) Liu, G-B.; Tashiro, M.; Thiemann, T. *Tetrahedron.* **2009,** *65*, 2497–2505.

(33) Liu, G-B.; Dai, L.; Gao, X.; Li, M-K.; Thiemann, T. *Green Chem.* **2006,** *8*, 781–783.

(34) Liu, G-B.; Tsukinoki, T.; Kanda, T.; Mitoma, Y.; Tashiro, M. *Tetrahedron Lett.* **1998,** *39*, 5991–5994.

(35) Marsh, G.; Hu, J.; Jakobsson, E.; Rahma, S.; Bergman, A. *Environ. Sci. Technol.* **1999,** *33,* 3033–3037.

(36) Abiraj, K.; Srinivasa, G.R.; Channe Gowda, D. *Tetrahedron Lett.* **2004,** *45,* 2081–2084.

(37) Abiraj, K.; Srinavasa, G.R.; Channe Gowda, D. *Synlett* **2004**, 877–879.

(38) Yamanaka, H.; Oshima, R.; Teramura, K.; Ando, T. *J. Org. Chem.* **1972**, *37,* 1734–1737.

(39) D'yachenko, A.I.; Korneva, O.S.; Nefedov, O.M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984,** *11*, 2653–2654.

(40) Laev, S.S.; Shteingarts, V.D. *J. Fluorine Chem.* **1999,** *96*, 175–185.

(41) Hekmatshoar, R.; Sajadi, S.; Heravi, M.M. *J. Chin. Chem. Soc.* **2008,** *55*, 616–618.

(42) Ram, S.; Ehrenkaufer, R.E. *Tetrahedron Lett.* **1984,** *25*, 3415–3418.

(43) Abiraj, K.; Channe Gowda, D. *J. Chem. Res.* **2003**, 332–334.