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# Synthesis of Mixed halogenated Dibenzodioxins (X=Br, Cl)

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#### Abstract

The conversion of dibenzodioxin with  $CuCl_2x2H_2O$  and  $CuBr_2$  results in polyhalogenated dibenzodioxins. Besides the chlorinated compounds, bromination stages 1 to 5 are obtained at chlorination levels of 0 to 7 for monobromo-, 0 to 7 for dibromo-, 0 to 4 for tribromo-, 0 to 3 for tetrabromo-, and 0 to 1 for pentabromodibenzodioxin. The 2,3,7,8 position is halogenated preferentially. © 1997 Elsevier Science Ltd

## Keywords

Copper(II)chloride, copper(II)bromide, PCDD/PCDF, analysis of mixed halogenated dibenzodioxins.

## 1. Introduction

It has been known from laboratory experiments [1] for a long time that brominated and mixed halogenated dioxins and furans are produced when materials are burned which contain brominated flame resistant agents. The same substances were detected in fly ashes of waste incineration plants [2,3]. For want of commercially available standards, this analysis is described by only a few authors who produced the reference compounds themselves [4,5]. It is for this reason that we looked for a simple, easy method of preparing reference compounds for this category of substances and, in this way, make them accessible to qualitative and quantitative analyses.

The conversion of dibenzofuran [6] and diphenylether [7] with solid copper bromide and copper chloride, alone or in a mixture, results in high yields of the desired halides at temperatures between 260 and 300°C in an inert gas flow. In an obvious step, this reaction was extended to dibenzodioxin. Because of the high toxic activity of the products, the synthesis should be conducted on a milligram scale. If a mixture of  $CuBr_2$  and  $CuCl_2x2H_2O$  is used for halogenation, contact with the dioxins generated is impossible, provided the work is done carefully, as the products exist on the solid phase and require no further purification steps. This is the chief advantage of this solidphase reaction compared to the wet chemical syntheses on the bromochlorophenol pathway, unless special position isomers must be prepared [8].

## 2. Experimental

## 2.1 Preparation of Dibenzodioxin

The synthesis of the parent substance was conducted on half the original batch by the modified method according to Gilman and Dietrich [9] with an 8% yield after two recrystallization steps from ethanol.

In this connection, the large number of byproducts of this reaction are of mechanistic interest; dibenzodioxin is only a byproduct in this preparation relative to total conversion (Fig.1).

The following substances are detected: (1) 2-hydroxydiphenylether, (2) dibenzodioxin, (3) 2-hydroxy-2' chlorodiphenylether, (4) monochlorodibenzodioxin, (5) phenol, 2-(2-phenoxyphenoxy)-, (6) phenol, 2-(2-phenoxy-chlorophenoxy)-, (7 and 9) four- and five-ring hydroxypolyphenylethers, (8 and 10) four- and five-ring chloro-hydroxypolyphenylethers.



Fig. 1: Products in dibenzodioxin synthesis according to [8].

## 2.2 Halogenation of Dibenzodioxin

For preparing the halogenated dibenzodioxins, the bromination and chlorination steps were conducted in one single synthesis step. The product composition was controlled through the quantity of copper bromide relative to copper chloride: 5 mg of  $CuBr_2$  and 5 mg of  $CuCl_2x2H_2O$  were homogenized with 300 of mg of Florisil (magnesium silicate) in a mortar, added 2 mg of dibenzodioxin, and thoroughly mixed (Fig. 2). Further conversions were performed with 15 and 30 mg each of copper halide in order to produce the even more highly halogenated compounds. One other possibility is covering the salts: 2 mg of dibenzodioxin was ground with 40 mg of  $CuBr_2$  and 150 mg of Florisil and covered with 20 mg of  $CuCl_2x2H_2O$  in 150 mg of Florisil (Fig. 3). The residence time in the first layer is controlled by the initial reaction temperature and the nitrogen flow. The mixture was transferred into a glass tube (11.5 cm long, 4 mm I.D., 6 mm O.D.), and secured with glass wool. An adsorber tube of the same dimension, filled with XAD 16, is flanged to the reaction tube. The halogenation reaction was carried out at 260-300°C in a nitrogen flow (1-20 ml/min), and the final reaction temperature was maintained for 5-10 min. The products were extracted with dichloromethane. For this purpose, an empty tube is flanged to both the reaction tube and, for a second time, the XAD filter, and the solvent is forced through under a slight overpressure. The extract is

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mixed with toluene and analyzed by GC/MS coupling without further purification. Conversion is quantitative in the presence of excess halide.



#### 3. Results and Discussion

Fig. 2: TIC of the conversion of 2 mg of dibenzodioxin with 5 mg each of copper halide.

These are the compounds detected (Fig. 2): (1) dibenzodioxin (educt), (2) chlorodibenzodioxin, (3) bromodibenzodioxin, (4) dichlorodibenzodioxin, (5) bromochlorodibenzodioxin, (6) trichlorodibenzodioxin, (7) dibromodibenzodioxin, (8) bromodichlorodibenzodioxin, (9) tetrachlorodibenzodioxin, (10) dibromochlorodibenzodibenzodioxin, (11) bromotrichlorodibenzodioxin.

Figure 3 shows the total ion current chromatogram of the products obtained after superposing the two copper salt layers.



Fig. 3: TIC of the conversion of 2 mg of dibenzodioxin in 40 mg of  $CuBr_2$  with 20 mg of  $CuCl_2$  in the second layer.

(9) tetrachlorodibenzodixin, (11) bromotrichlorodibenzodioxin, (12) tribromodibenzodioxin, (13) pentachlorodibenzodioxin, (14) dibromodichlorodibenzodioxin, (15) bromotetrachlorodibenzodioxin, (16) tribromochlorodibenzodioxin, (17,18) hexachlorodibenzodioxin, (19) dibromotrichlorodibenzodioxin, (20) tetrabromodibenzodioxin, (21+22) bromopentachlorodibenzodioxin, (23) tribromodichlorodibenzodioxin, (24) heptachlorodibenzodioxin, (25) bromohexachlorodibenzodioxin, (26) octachlorodibenzodioxin, (27) pentabromodibenzodioxin, (28) bromoheptachlorodibenzodioxin.

A striking finding, compared to the conversion reactions with diphenylethers and dibenzofurans, is the selectivity of halogenation. Almost no isomer clusters are obtained. The directing influence of the symmetrical oxygen bridges is very pronounced: In the tetrahalogenated compounds there is a clear domination of the 2,3,7,8 position. In fourfold chlorination almost only this cogenerated product (9) can be detected. In the dichloro- and dibromodibenzodioxin 5 respectively 6 congeners can be detected with high resolution mass spectroscopie, the formation of the 2,3,7,8 tetrabromodibenzodioxin on irradiation in tetrachloromethane [10]: here a 1:1 mixture of 2,7 and 2,8 dibromodioxin is obtained. Only at a halogenation level above five, more isomers are obtained.



Fig. 4: Mass spectrum of tribromodichlorodibenzodioxin.

#### Figure 4 shows the mass spectrum of tribromodichlorodibenzodioxin by way of example.

On the whole, bromination levels of 1 to 5 were obtained at chlorination levels of 0 to 7 for monobromo-, 0 to 6 for dibromo-, 0 to 3 for tribromo-, 0 to 3 for tetrabromo-, and 0 to 1 for pentabromodibenzodioxin.

The spectra of the  $Br_2Cl_{4/5}$ ,  $Br_3Cl_{3/4}$ ,  $Br_4Cl_{1/2/3}$ , and  $Br_5Cl_1$  isomers, which are eluated even later, can be detected in the total ion current method only by way of the molecular cluster (Fig. 5).

Although this synthesis does not supply the whole variety of possible cogenerated products, the mixture of substances lends itself well to the development of analytical methods. By means of the method described in the literature [11,12], the time windows for a SIM measurement can be estimated for GC-MS analysis, because halogenation preferably attacks position 2 of the dioxin and causes the 2,3,7,8 positions to be occupied. By

measuring the bromine trace, GC-AED coupling allows the quantification, independent of any substance, of selected isomers, which are then also measured by GC-MS coupling. In this way, a useful measuring technique can be developed by establishing calibration factors against known standards.



Fig. 5: Molecular cluster of tetrabromodichlorodibenzodioxin (MG 564).

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