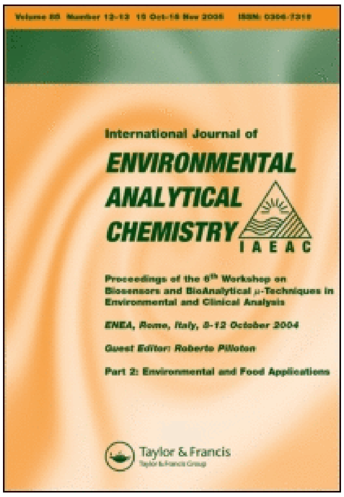

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RAPID SYNTHESIS OF SOME LOWER BROMINATED ^{13}C-LABELLED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS AND MIXED BROMINATED/CHLORINATED DIBENZO-*p*-DIOXINS

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A rapid synthesis of $^{13}C_{12}$-labelled mono- and dibromodibenzo-*p*-dioxin and mono-, di- and tribromodibenzofuran isomers is described. Commercially available $^{13}C_{12}$- 2,3,7-tribromodibenzo-*p*-dioxin and 2,3,7,8-tetrabromodibenzofuran dissolved in *n*-alkanes were irradiated for several minutes using UV light. This resulted in one or two predominant isomers for each of the above mentioned homologue groups. For theoretical reasons all congeners should be substituted only at lateral positions. When $^{13}C_{12}$-2,3,7,8-tetrabromodibenzo-*p*-dioxin was irradiated in carbon tetrachloride, Br/Cl exchange took place to yield all three 2,3,7,8-substituted mixed halogenated dibenzo-*p*-dioxins (Br_3ClDD, Br_2Cl_2DD, $BrCl_3DD$) as well as 2,3,7,8-Cl_4DD. A clean-up of the resulting mixtures was not necessary. The yield was better than 50% in each case. The procedure is simple and the handling of toxic substances is reduced to a minimum. The prepared substances can be used as internal standards for the analysis of brominated and mixed halogenated dibenzo-*p*-dioxins and dibenzofurans.

KEY WORDS: Lower brominated and mixed halogenated dioxins; $^{13}C_{12}$-labelled internal standards; synthesis.

INTRODUCTION

In recent years brominated as well as mixed chlorinated/brominated dibenzo-*p*-dioxins (DDs) and dibenzofurans (DFs) have gained attention due to their formation during the combustion of brominated flame retardants[1-3] and their presence in automotive exhaust[4-6]. While the combustion of brominated flame retardants leads primarily to higher brominated and mixed halogenated DDs and DFs, combustion of leaded gasoline containing halogenated scavengers in vehicles results in Br_xCl_yDDs and DFs with $x + y = 1–4$. A reliable analysis of the lower halogenated compounds has been hampered to date by the absence of commercially available ^{13}C-labelled internal standards. The presence of at least one chlorinated and one brominated internal standard per halogenation level would bring a significant improvement: the chlorinated and brominated compounds could then be quantified directly using the internal standards, while for the mixed halogenated compounds one could assume that the analytical recoveries lie between that of the pure chlorinated and pure brominated standards.

The only synthesis of $^{13}C_{12}$ mono- to tribrominated DDs that we are aware of is the one described by Nestrick *et al.*[7]. These authors used a high-temperature (240°C)

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bromination of $^{13}C_{12}$-dibenzo-*p*-dioxin with iron(III) bromide. This procedure is not isomer specific and results in mixtures of about three halogenation levels. On the other hand, syntheses leading to distinct isomers like condensation reactions of phenols[8] and catechols[9] or cyclizations of halogenated diphenyl ethers[10] are laborious and cumbersome. In addition, these methods are often only applicable to quantities greater than 100 mg which produces large amounts of hazardous waste and creates laboratory security problems.

It was the aim of the present study to synthesize at least one isomer of $^{13}C_{12}$-mono- to tribrominated DD and DF in µg quantities by means of photochemically induced bromine/hydrogen exchange. This reaction has been postulated for the photodegradation of brominated DDs and DFs in the environment and has been observed in the laboratory[11,12]. The mechanism is trivial. Homolytic cleavage of the Ar-Br bond is followed by the abstraction of a hydrogen atom from the solvent. In mixed brominated/chlorinated aromatics the bromine atom is exclusively replaced[11,12]. For details, one should consult Lenoir *et al.*[12] and the literature cited therein. It is important that the radical which is formed by cleavage of the Ar-Br bond is a δ-radical. This means that no delocalization of the radical character into the aromatic ring system occurs and hence no isomerization is possible. The incoming substituent always enters the molecule at the same position where the leaving group was situated[13]. According to the literature[11,12] reductive debromination occurs primarily from the higher brominated carbon ring, so the number of expected isomers should therefore be reduced to the ones with both rings substituted equally. On the basis of previously measured quantum yields and half lives[12] the reaction should be very fast. Since there was also an immediate need for the three ^{13}C-labelled mixed brominated/chlorinated 2,3,7,8-X_4DDs and no reports of the synthesis of these compounds were found in the literature, the well-known photochemically induced halogen/halogen exchange[14] in aromatics in the presence of CCl_4 was also tested.

EXPERIMENTAL

Chemicals

NaBr, $Hg(NO_3)_2 \cdot H_2O$ and $Pb(NO_3)_2$ were reagent grade (Merck, Darmstadt, FRG). Solvents (*n*-hexane, toluene, carbon tetrachloride) were nanograde (Promochem, Wesel, FRG). $^{12}C_{12}$-2,3,7,8-Br_4DD/F, $^{12}C_{12}$-2,3,7,8-Cl_4DD, $^{12}C_{12}$-2-Br-3,7,8-Cl_3DD, $^{12}C_{12}$-2,3-Br_2-7,8-Cl_2DD, $^{12}C_{12}$-2,3,7-Br_3DD, $^{13}C_{12}$-2,3,7,8-Br_4DD/F and $^{13}C_{12}$-2,3,7-Br_3DD (special manufacture) were obtained from Cambridge Isotope Laboratories, (Woburn, MA, USA). The following $^{12}C_{12}$ native standards had been synthesized previously in our laboratory[15], the correct substitution pattern not being known in one case: Br_1DF, 2,8-Br_2DF, 2-BrDD, 2,3-Br_2DD, 2,7/2,8-Br_2DD (ca. 1:1 mix) and 2,3,7-Br_3-8-ClDD. A Br_3DF standard was not available. The gas chromatograms of these compounds showed no detectable impurities using a mass selective detector in full-scan mode (100–600 amu).

Apparatus and materials

A Rayonett Photochemical Reactor RPR-100 (Southern New England Ultraviolet Co.) equipped with two (180° geometry) low-pressure mercury lamps coated with white phosphorus RPR 3000 A was used for irradiation. The emission spectrum of these lamps resembles a Gaussian bell curve (λ_{max} = 300 nm, 10% intensity at 340 nm) showing no distinct lines. A special irradiation vessel (Figure 1) made from pyrex glass (ca. 1 mm wall thickness) was allowed to rotate axially in a merry-go-round without chemical filter solution when irradiating the Br_3DD. When irradiating the Br_4DD and the Br_4DF the same vessel was placed exactly in the middle of the reactor, i.e. exactly between the two lamps. No rotation was applied. The three chemical filter solutions used are listed in Table 1 together with the transmission data. Unfortunately, it was not possible to measure the spectrum of the filtered light inside the reaction vessel. According to the transmission data of the filters, the low-energy tail of the lamp spectrum should have passed through the reaction vessel.

Gas chromatography-mass spectrometry

Product identifications were conducted on a Hewlett Packard Model 5989A MS-Engine equipped with electronic pressure control operating at unit resolution with electron impact ionization; source temperature: 250°C; carrier gas: He; first column type: XTI-5

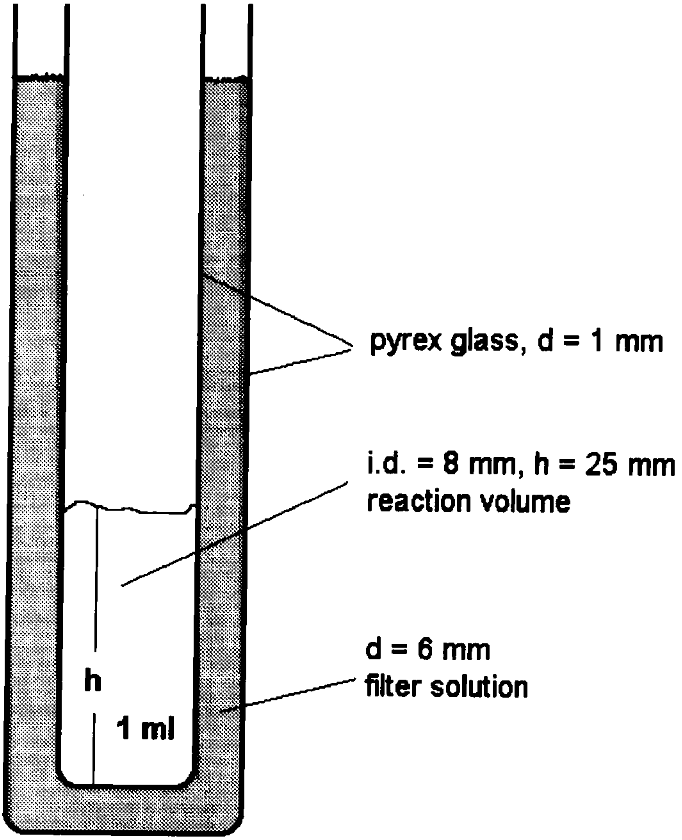

Figure 1 Irradiation vessel.

Table 1 Composition and spectral properties of aqueous filter solutions (cut-off filters).

*Solutions**	*Transmission (%), d = 1 cm (quartz cell)*		
	10	*50*	*90*
Pyrex glass alone (d = 1 mm)	300 nm	315 nm	330 nm
Solution A	310 nm	321 nm	333 nm
Solution B	320 nm	331 nm	343 nm
Solution C	335 nm	345 nm	355 nm

*Solution A: 200 g/l NaBr + 1 g/l $Hg(NO_3)_2 \cdot H_2O$;
Solution B: 200 g/l NaBr + 0.3 g/l $Pb(NO_3)_2$;
Solution C: 200 g/l NaBr + 3 g/l $Pb(NO_3)_2$.

(Restek), 30 m and 60 m × 0.25 mm i.d., 0.25 μm film; second column type: Sp-2331 (Supelco), 60 m × 0.25 mm i.d., 0.20 μm film.

Programme A: splitless injector 300°C; interface: 300°C; 170°C, 1 min hold, 2°C/min to 320°C, constant pressure: 25 psi.

Programme B: splitless injector 270°C; interface: 250°C; 130°C, 1 min hold, 1°C/min to 270°C, pressure programme: 28 psi, 1 min hold, 0.08 psi/min to 39 psi, 20 min hold (= 30 cm/s He over total temperature range).

Procedure

Four experiments, indicated as Reactions 1–4 (cf. Table 2 below) were carried out.

1. Br_3DD. A solution of 13 μg of $^{13}C_{12}$-2,3,7-Br_3DD in toluene was transferred to the irradiation vessel and evaporated to dryness by applying a gentle stream of nitrogen. 0.2 ml of *n*-hexane was added and again evaporated to dryness to remove any residues of toluene. Then 1.0 ml of *n*-hexane was added, the solution was sonified in an ultrasonic bath for 10 min and then irradiated at room temperature without chemical filter in the merry-go-round for 6.5 min. Sub-samples of 30 μl were isolated and after reduction in

Table 2 Product yields of reaction 1–4.

Reaction	*Yield (mol%)*					
	DD	Br_1DD	Br_2DD	Br_3DD		*Total*
Reaction 1	$\sim$5	33	34	0		72
	DF	Br_1DF	Br_2DF	Br_3DF	Br_4DF	
Reaction 2	0	0	$\sim$5	31	44	80
Reaction 3	$\sim$5	23	44	0	0	72
	Cl_4DD	$BrCl_3DD$	Br_2Cl_2DD	Br_3ClDD	Br_4DD	
Reaction 4	7	8	12	14	9	50

volume to 10 µl, directly injected into the GC (full scan) to monitor the progress of the reaction. When the reaction was complete, the contents of the irradiation vessel were transferred to a 5 ml volumetric flask and made up to volume with toluene.

2. *Br_3DF.* A solution of 11.2 µg of $^{13}C_{12}$-2,3,7,8-Br_4DF in *n*-nonane was transferred to the irradiation vessel and concentrated to 1.0 ml with the help of nitrogen. After sonification (10 min) the solution was irradiated for 18 min at room temperature in the middle of the photoreactor without the merry-go-round while protected by filter B (Table 1). The work-up was as described above.

3. *Br_4DF.* A solution of 11.2 µg of $^{13}C_{12}$-2,3,7,8-Br_4DF was treated as described in (2) and irradiated for 50 min at room temperature. Filter A was applied.

4. *Br_4DD.* A solution of 22.5 µg of $^{13}C_{12}$-2,3,7,8-Br_4DD in *n*-nonane was evaporated to dryness. The residue was redissolved in about 1 ml of CCl_4 and again evaporated to dryness to remove any residues of nonane. The residue was again redissolved in 1.0 ml of CCl_4, sonified and irradiated in the middle of the photoreactor at room temperature for 25 min. Filter A was applied. Then the CCl_4 was again evaporated, the residue redissolved in toluene and transferred to a 5 ml volumetric flask.

The yield of the reactions was calculated from co-injection with stock solutions of the corresponding $^{12}C_{12}$ standards assuming an equal response factor within one homologue group. The non-polar column and the fast temperature programme were employed. If more than one isomer per bromination level had formed the peaks were integrated together. $^{13}C_{12}$-Br_3DF was quantified with $^{12}C_{12}$-Br_3DD assuming an equal response.

RESULTS AND DISCUSSION

The major products of each experiment are listed in Table 2. One predominant and, in the case of the dibenzofurans, a number of minor isomers were synthesized for each of the desired homologue groups with yields better than 50%. No irregularities in the mass spectra (100–600 amu) were observed and no $^{12}C_{12}$ contamination was detected (< 0.2 %). The reactions were very easy to conduct.

It was not necessary to remove reagents from the products as no reagent but light was used. No byproducts were detectable in the products of Reactions 1–3 using gas chromatography and a mass selective detector in full-scan mode (100–600 amu) except contaminants that were present in the starting material. Higher hydrocarbons that were found in the nonane solution of the purchased Br_4DD liquid standard are probably the reason for the small amounts (< 5%) of reduction products observed following irradiation of Br_4DD in CCl_4. Br_3DD, Br_2ClDD, $BrCl_2DD$ and Cl_3DD arising from Br/H exchange were identified from their mass spectra (see Figure 2). If desired, this finding could be used to prepare these reduction products by irradiating Br_4DD in a suitable mixture of *n*-hexane and CCl_4. However, the yield per single compound would probably be low.

On the other hand, there must have been some polar byproducts as the yield of dibenzofuran from Br_4DF or Cl_4DD from Br_4DD following prolonged irradiation was low. When the exposure times in reactions 3 and 4 were extended until all of the Br_1DF or the $BrCl_3DD$ had disappeared, the yields of dibenzofuran and Cl_4DD, respectively, did not exceed 20%. Cooling the reaction mixture might be one approach to reducing the production of byproducts.

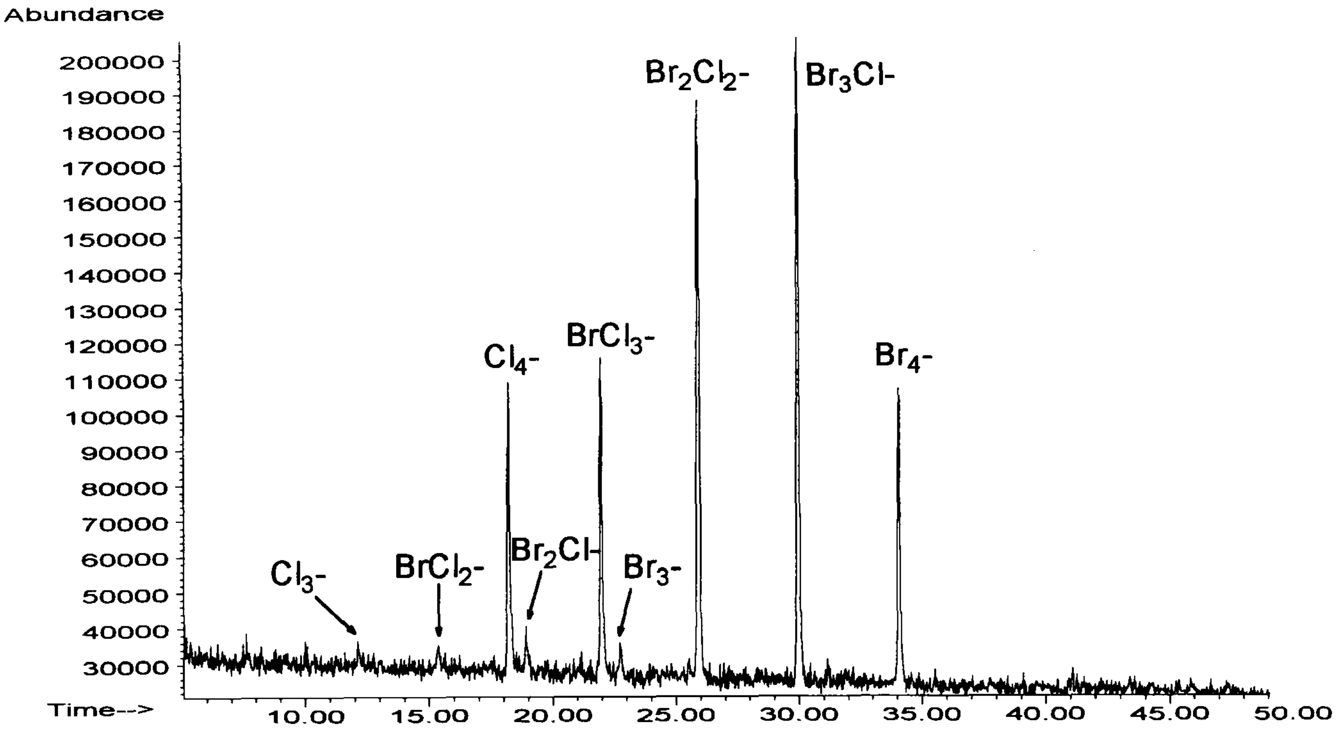

Figure 2 TIC (100–600 amu) of reaction products (reaction 4; $^{13}C_{12}$-X_4DDs). GC conditions: 30 m XTI-5, 170°C/1 min // 2°C/min to 320°C; 25 psi.

While there are likely polar byproducts arising from, e.g., ring fission and subsequent degradation, they could at most account for 20–50% since the total yield of identified products was 50–80%. Furthermore, due to their polar character these byproducts would be removed during the working up of real samples. The possibility of several isomers coeluting was not considered a significant problem as the current analytical methods for brominated and mixed halogenated DD/F are limited to the quantification of homologue sums due to the paucity of unlabelled isomer standards to verify the chromatographic separation. The same response factor is generally assumed for the same reason. Hence it was felt that a clean-up step—the most laborious step in many synthetic procedures—was not necessary and that the resulting mixtures could be used directly as internal standards.

It was found that light of about 320 nm is necessary for the reactions. A repetition of reaction 2 with a filter solution with a cut-off point at about 340 nm (solution C) resulted in no measurable conversion of Br_4DF within one hour.

The Br/H exchange could not be stopped at one level of bromination. However, since the rate constant for the debromination of Br_4DF is higher than the rate constant for the debromination of Br_3DF, and this one is higher than the one for Br_2DF, and so on[12], only two products could be detected at the same time in reasonable amounts. Br_4DF for instance had completely disappeared when Br_1DF began to form. Therefore, the reaction was optimized in such a way that two levels of bromination each were formed in about equal amounts: Reaction 1 giving Br_2DD and Br_1DD; Reaction 2 giving Br_4DF and Br_3DF; and Reaction 3 giving Br_2DF and Br_1DF. These solutions could now be mixed as desired. Because the Br/H exchange induced by UV light was even faster in the dibenzofuran series than in the dibenzodioxin series, chemical filters were used to shift the spectrum in the reaction vessel to even longer wavelengths. The resulting irradiation times were more convenient and made the reaction more reproducible. If $^{13}C_{12}$-2,3,7-Br_3DD is not available the degradation can of course be started from $^{13}C_{12}$-2,3,7,8-Br_4DD, the overall yield being likely somewhat lower. In this case chemical filters could also be useful.

The Br/Cl exchange in CCl_4 differs somewhat from the Br/H exchange described above. Since there is no stabilizing effect during the reaction by the loss of bromine atoms the reaction could not be optimized in the same way. Substitution of bromine by chlorine even seemed to accelerate the further debromination rather than to hinder it (see below). The product distribution was broader, which meant that it was not possible to prepare e.g. only Br_2Cl_2DD and Br_3ClDD in equal amounts with no $BrCl_3DD$ and Br_4DD. Considerable amounts of Cl_4DD formed before Br_4DD had disappeared (see Figure 2 and Table 2). Since side-reactions are taking place it is easiest to prepare Br_3ClDD and most difficult to prepare $BrCl_3DD$ with good yields. The conditions given for Reaction 4 are a compromise between overall yield and equal distribution of the three mixed halogenated X_4DDs.

Product identification

$Br_{1/2}DD$: The chromatograms obtained using the non-polar XTI-5 column (60 m, temperature programme A or B) showed only a single peak per level of bromination. The chromatograms obtained using the polar column SP-2331 (programme B) again showed a single peak for Br_1DD but two quite well resolved peaks for Br_2DD. Only one Br_1DD isomer is possible from debromination of 2,3,7-Br_3DD, namely 2-BrDD. For the Br_2DDs a mixture (ca. 1:1) of 2,7- and 2,8-Br_2DD was formed but no detectable amount (< 1%)

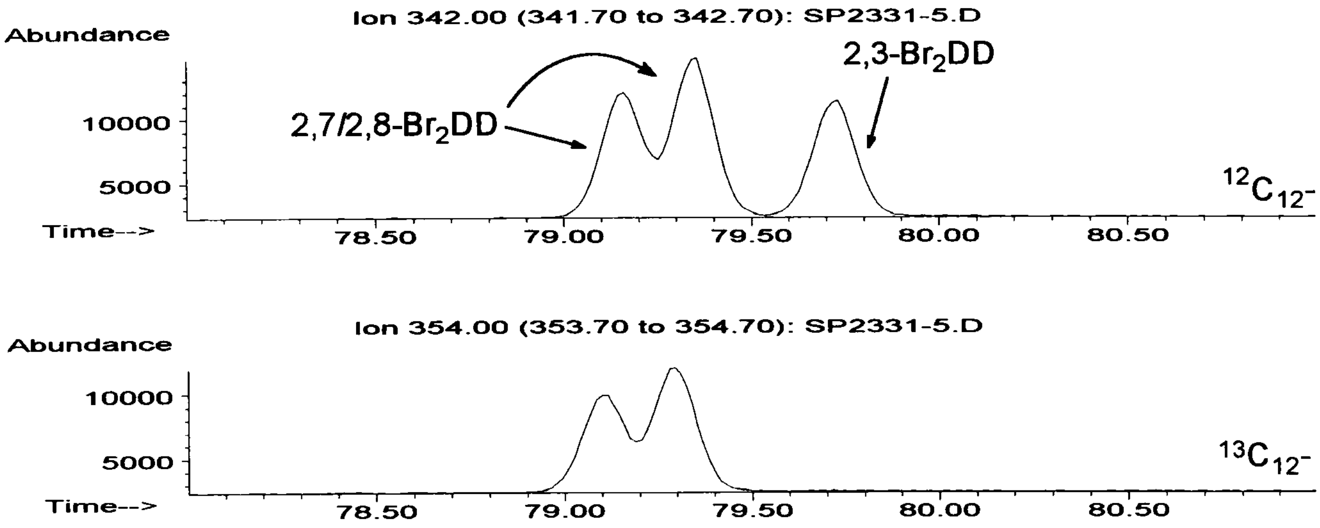

Figure 3 Mass traces of reaction products (reaction 1; $^{13}C_{12}$-Br_2DDs). GC conditions: 60 m Sp-2331; 130°C/1 min // 1°C/min to 270°C; 28 psi/1 min // 0.08 psi/min to 39 psi.

of the 2,3 isomer, as was seen by a comparison with the native $^{12}C_{12}$ standards (Figure 3). This is in good agreement with the findings of Buser[11] and Lenoir *et al.*[12].

Br$_1$DF: The chromatograms from the XTI-5 column (60 m, programme B) showed two poorly resolved Br$_1$DF peaks, a large one and a very small one. According to Donnelly *et al.*[16] the minor (first eluting) isomer must be 3-BrDF and the major (later eluting) one must be 2-BrDF. Chromatograms from the polar column (programme B) again showed the two peaks (ca. 19:1), but now more than baseline-resolved (the minor one again eluting earlier). There is further evidence that the major isomer was 2-BrDF: Since the main Br$_2$DF is the 2,8 isomer (see below), only 2-BrDF can be formed by splitting off bromine.

Br$_2$DF: The chromatograms from the XTI-5 column (60 m, programme B) showed two or three poorly resolved peaks (Figure 4). According to Donnelly *et al.*[16] the 2,7 and the 3,7 isomers elute together under the given conditions while the 2,3 and the 2,8 isomers elute very close to but more than baseline-resolved from the first pair. Assuming that the 2,3 isomer was not formed in significant quantities (see the results for the dioxins and refs. 11 and 12), the large peak should be the 2,8 isomer and the small peak the 2,7 and/or the 3,7 isomer. Chromatograms from the polar column (programme B) showed three well resolved peaks (ca. 25:10:1; Figure 5). The 2,8 isomer was identified as the main product using a native $^{12}C_{12}$ standard. Based on mechanistic considerations (see below), the intermediate peak was assigned to the 2,7 isomer and the small one to the 3,7 isomer.

Br$_3$DF: Chromatograms from the XTI-5 column (60 m, programme B) showed only one sharp peak as has been reported elsewhere[16]. Chromatograms from the polar column (programme B) showed two well resolved peaks (ca. 5:1), the minor one eluting earlier. Since the main Br$_2$DF was the 2,8 isomer, the main Br$_3$DF must have been 2,3,8-Br$_3$DF.

X$_4$DD: Chromatograms from the polar as well as the non-polar column (programme B) showed only a single peak per homologue group. Apart from a slight isotopic shift the retention times of the products coincided with the retention times of the native $^{12}C_{12}$ standards. Retention index calculations[17] predict a retention index difference of 19 units between 2,3-Br$_2$-7,8-Cl$_2$DD and the 2,7/2,8-Br$_2$-3,8/3,7-Cl$_2$DDs, which coelute. Even 10 RI units would have been easily measurable for the chromatographic conditions used (30 m XTI-5, programme A). Thus the $^{13}C_{12}$-Br$_2$Cl$_2$DD formed was very likely 2,3-Br$_2$-7,8-Cl$_2$DD. This indicates that the debromination of Br$_3$ClDD was favoured more by a neighbouring chlorine than by a neighbouring bromine.

Mechanism

Figure 6 shows a proposed mechanism for the debromination of 2,3,7,8-Br$_4$DF. The only way to explain the occurrence of 2,8-Br$_2$DF as the main dibromofuran product is through preferential removal of the bromines at the 3 and 7 positions. This means that the adjacent oxygen must be activating the C-Br bond. Since 3,7-Br$_2$DF can only be formed through two unfavourable bond fissions, this isomer should correspond to the smallest peak (Figure 5). Since there are favourable as well as unfavourable debrominations to yield 2,7-Br$_2$DF, it should correspond to the medium peak. 3-BrDF can only be generated by two unfavourable debrominations and one favourable compared to two

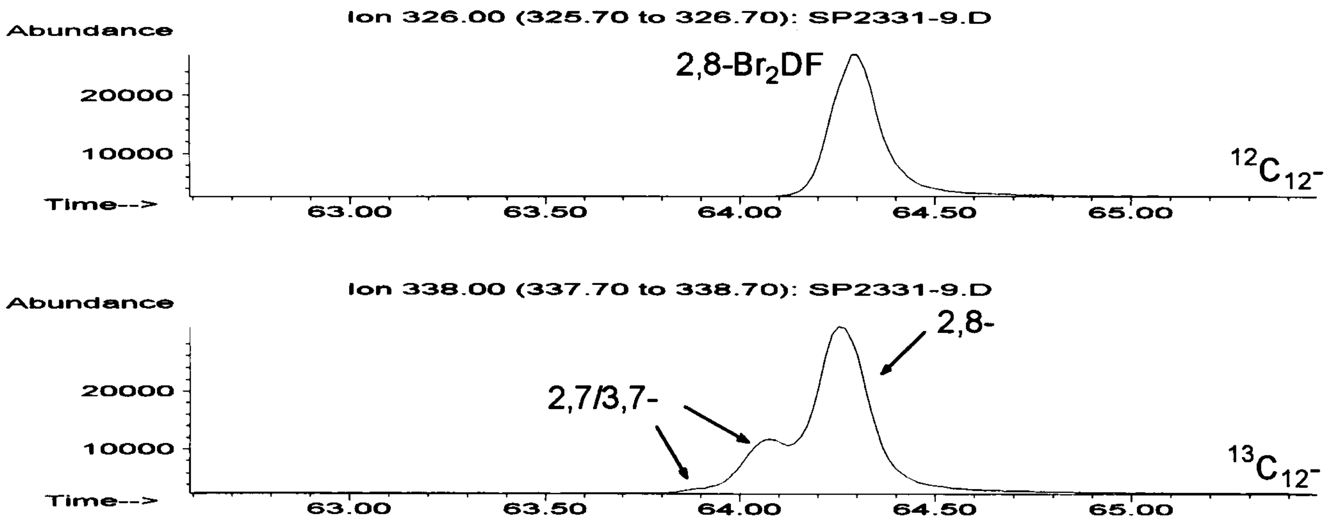

Figure 4 Mass traces of reaction products (reaction 3; $^{13}C_{12}$-Br_2DFs). GC conditions: 60 m XTI-5; 130°C/1 min // 1°C/min to 270°C; 28 psi/1 min // 0.08 psi/min to 39 psi.

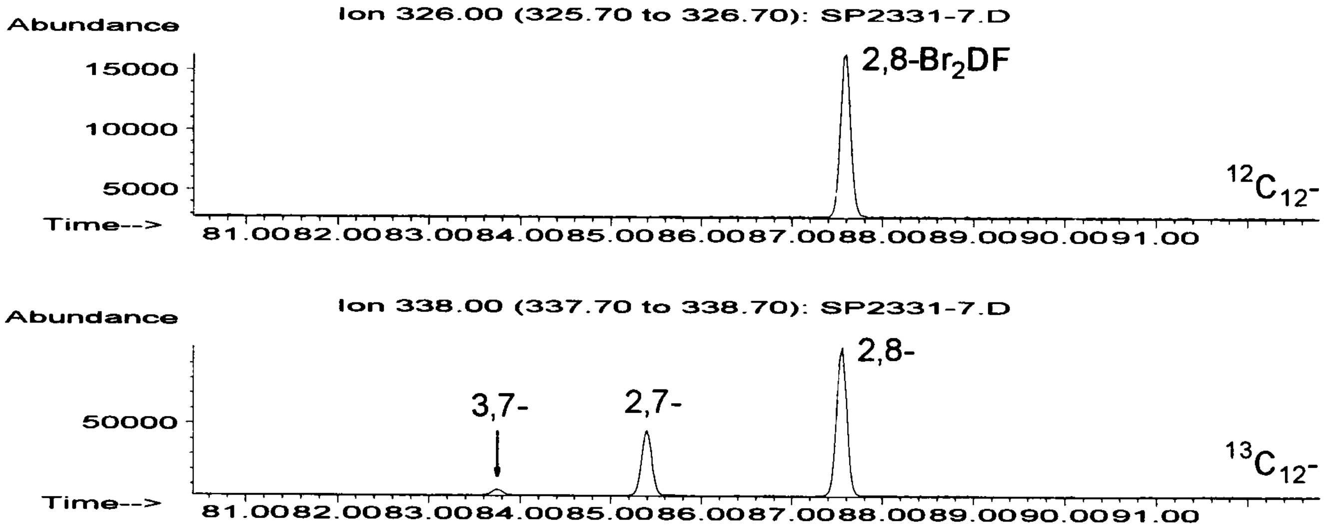

Figure 5 Mass traces of reaction products (reaction 3; $^{13}C_{12}$-Br_2DFs). GC conditions: 60 m Sp-2331; 130°C/1 min // 1°C/min to 270°C; 28 psi/1 min // 0.08 psi/min to 39 psi.

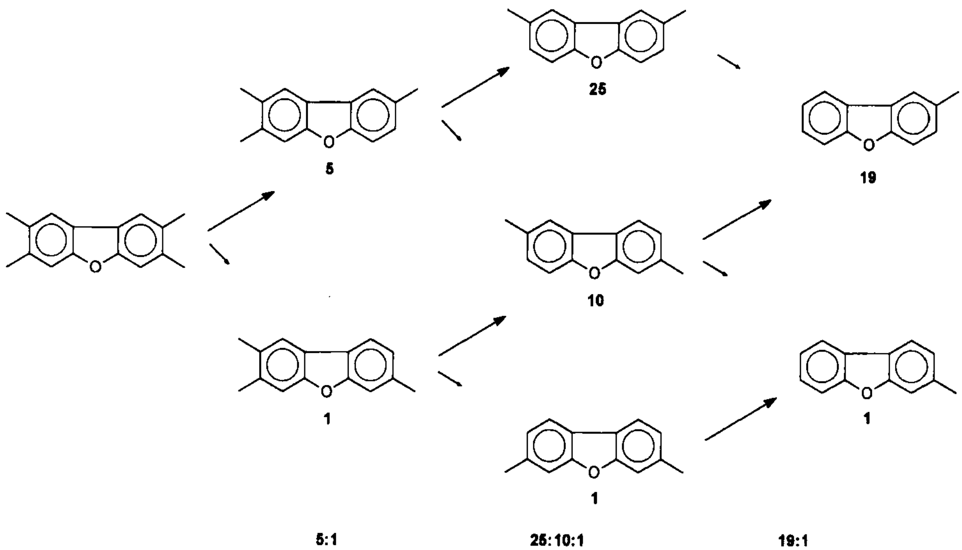

Figure 6 Proposed mechanism of debromination of 2,3,7,8-Br_4DF. Long arrow means high rate constant, short arrow means low rate constant.

favourable debrominations and only one unfavourable with 2-BrDF. This explains the extraordinary low occurrence of 3-BrDF.

Application

In order to verify the suitability of the prepared compounds as internal standards, a ca. 1:1 mixture was made of all $^{13}C_{12}$ compounds together with the corresponding native $^{12}C_{12}$ compounds. This mixture was subjected to a typical dioxin sample work-up consisting of an acidic/basic silica column followed by an alumina column (B, Super I). The ratio of external/internal standard was measured before work-up as well as after work-up for every pair of external/internal standards. In the case of the 'perfect internal standard' the pre-work-up and post-work-up ratios have to be identical. The difference in the ratios did not exceed 10% for any of the standard pairs in the three parallel runs that were conducted. A 10% deviation lies within the reproducibility of the GC-MS apparatus. This confirmed that no clean-up of the reaction products was necessary and that the solutions were suitable for use as internal standards.

Since the preparation of the first lot of the above described internal standards about 100 soil samples have been analysed for BrDD/F. The appearance of the $^{13}C_{12}$ mass traces of the gas chromatograms from different columns using the real samples was the same as for the pure standards. Up until the introduction of the standards no quantitative analysis of the lower brominated DD/F was possible due to the variability and uncertainty in the analyte recoveries. The use of the internal standards has solved this problem and facilitated the optimization of the method so that the routine recoveries now lie above 50%.

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