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SYNTHESIS OF POLYFLUORINATED DIBENZO-p-DIOXINS

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ABSTRACT

Fluorinated dibenzo-p-dioxins (PFDD) have been selectively synthesized from fluorophenols and isolated by liquid-column- and thin layer chromatography. The structures were confirmed by IR, MS, HR-MS, ^{1}H-NMR and ^{19}F-NMR-spectroscopy. Reaction times, melting points and the IR-absorption bands are presented for several PFDD's as well as ^{1}H- and ^{19}F-NMR-spectra for two PFDD's and the mass-spectrum for 2,3,7,8-T_4FDD.

KEYWORDS: PFDD, synthesis, melting points, GC/MS, ^{19}F-NMR, ^{1}H-NMR, IR

INTRODUCTION

Polyhalogenated dibenzo-p-dioxins (PXDD) and -furans (PXDF) are well known as hazardous compounds. While a lot of information is available about the occurence and toxicity of chlorinated (PCDD) and brominated (PBrDD) dioxins there is nearly no information about PFDD. It can be assumed that in certain thermal processes in which organic and fluorine compounds coincide (e.g. industrial production of aluminium) PFDD/F may be generated. Thermolytic reaction of hexafluorobenzene in the presence of air shows the formation of O_8FDD. To investigate the formation of PFDD, their occurence and behaviour in the environment, PFDD-reference compounds were synthesized. Only the synthesis of 2,3-D_2FDD (from 1,2,4,5-tetrafluorobenzene and catechol) [1], 2,7-D_2FDD (from potassium-1-bromo-4-fluoro-phenolate in methanol) [2] and O_8FDD (from pentafluorophenolate with copper powder at 300°C) [3] have been previously described.

EXPERIMENTAL

GC-MS analysis were carried out on a HP 5890 system using direct coupling (fused silica transfer-line 1.0 m x 0.25 mm), split/splitless injection, retention gap (1 m x 0.52 mm fused silica deactivated tubing) and a 30 m DB-5 (0.33 mm i.d.; 0.3 μm f. th.) fused silica capillary column with a head pressure of 77 kPa ; carrier gas

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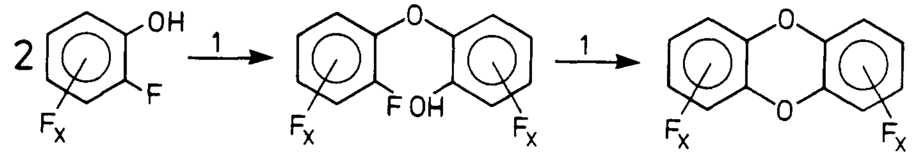
helium and the following temperature program 50 °C, 2 min, 5 °C/min, 140 °C, 30°C/min, 270 °C, 15 min. The GC-MS transferline temperature was 270 °C. The mass-spectra were obtained by an INCOS 50, Finnigan MAT in the EI- and total ion chromatogramm (TIC) mode, 70 eV. High resolution mass spectrometry was carried out on a VG AutoSpec, with direct coupling to a HP 5890 II (30 m DB-5, 0.25 mm i.d., 0.25 μm f.th.), with a resolution of 15 000. Infrared spectra were obtained by an EFS 48, Bruker, ^{1}H-NMR-spectra were determined in deutero-dichloromethane on a AM 270, Bruker and ^{19}F-NMR-spectra in deutero-chloroform on a FX 90 Q, Joel. 2,4-Di-, 2,5-Di-, 2,3,5-Tri-, 2,4,5-Tri- and 2,3,5,6-Tetrafluorophenoles were obtained from Aldrich, Steinheim, Germany; Pentafluorophenole from Fluka, Neu-Ulm, Germany; 2,3,6-Tri- and 2,3,4-Trifluorophenoles from Yarsley, Wolverhampton, England and 2,3-Di- and 2,6-Difluorophenoles from ABCR, Karlsruhe, Germany. All solvents were p.a. grade and obtained from Merck, Darmstadt, Germany.

RESULTS AND DISCUSSION

Like synthesizing PCDD's from chlorophenols [4], reaction of fluorophenols yield PFDD's.



1.: base, heat, aprotic polar solvent

Figure 1: synthesis of PFDD's from F_x-phenols

Table 1: reaction times, yields, melting points and starting compounds of some PFDD's

PFDD	FP	rt	yield	mp [°C]
1,6-D$_2$FDD	2,6-D$_2$FP	12 h	5,4 %	163
2,7-D$_2$FDD	2,5-D$_2$FP	3 d	2,9 %	174-176
2,7-D$_2$FDD	2,4-D$_2$FP	2 d	43,5 %	174-176
1,2,6,7-T$_4$FDD	2,3,4-T$_3$FP	6 d	13,3 %	167
1,3,6,8-T$_4$FDD	2,3,5-T$_3$FP	8 d	12,0 %	-
2,3,7,8-T$_4$FDD	2,4,5-T$_3$FP	2 d	17,5 %	183
1,2,4,6,7,9-H$_6$FDD	2,3,5,6-T$_4$FP	6 d	10,6 %	133-134
O$_8$FDD	P$_5$FP	4 d	2,5.%	161

FP: fluorophenol; rt: reaction time; mp: melting point

This reaction of fluorophenols involves an intermolecular nucleophilic aromatic substitution, followed by an intramolecular one, to give the corresponding PFDD's (**Fig. 2**).

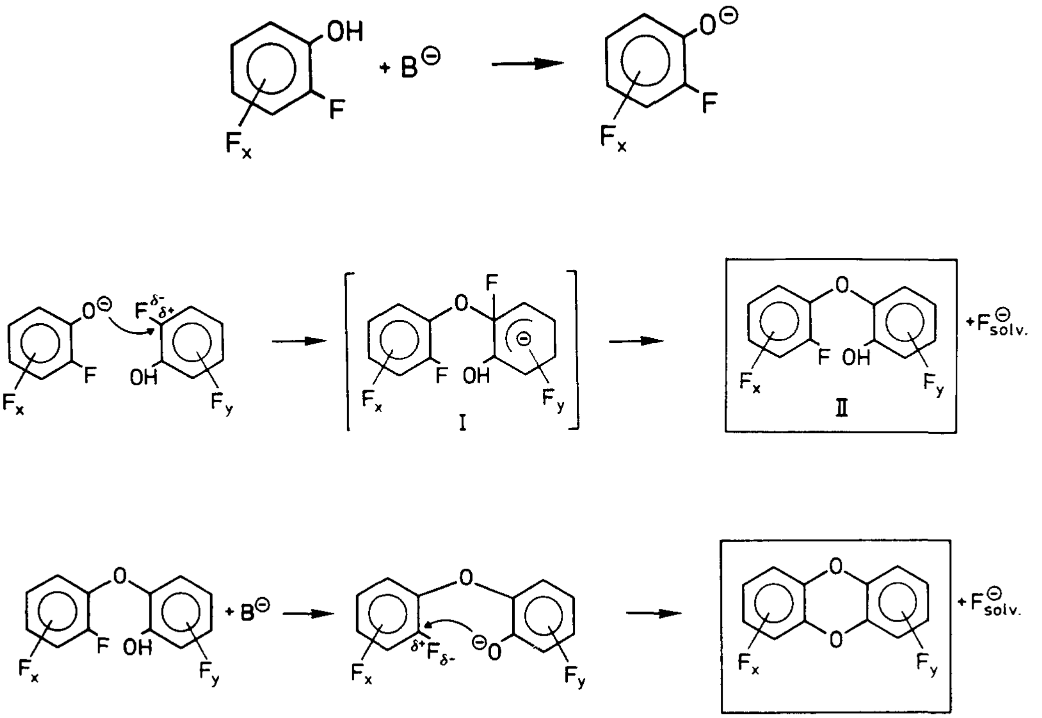
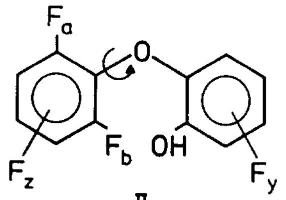


Figure 2: Synthesis of PFDD's via nucleophilic aromatic substitution of polyfluorinated phenols

If there are two fluorine atoms in the ortho-position to the oxygene (biphenylether II, **Fig. 2** and **Fig. 3**), rotation around the C-O-bond allows the formation of different products depending on which fluorine (F_a or F_b) will be removed by nucleophilic substitution in the next step.



II

Figure 3: Polyfluorinated biphenylether

This simple reaction has the advantage, that all starting compounds (except 2,3,4,5- and 2,3,4,6-tetrafluorophenol) are commercially available.

The reactions were carried out in a polar, aprotic solvent (to stabilize the ionic intermediate I, **Fig. 2**) in the presence of a base at elevated temperatures. Reaction time may vary up to 8 days (**Tab. 1**).

The resulting PFDD's were isolated from the reaction mixture by liquid-column- and, when necessary, thin layer chromatography with silicagel and n-hexane as eluent.

Fig. 4 - 7 show the ^{1}H-NMR and ^{19}F-NMR-spectra of the symmetric 2,3,7,8-T_4FDD and the non-symmetric 2,7-D_2FDD.

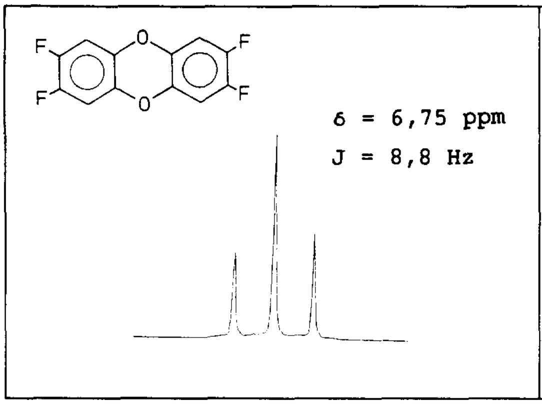


Figure 4: ^{1}H-NMR-spectrum of 2,3,7,8-T_4FDD

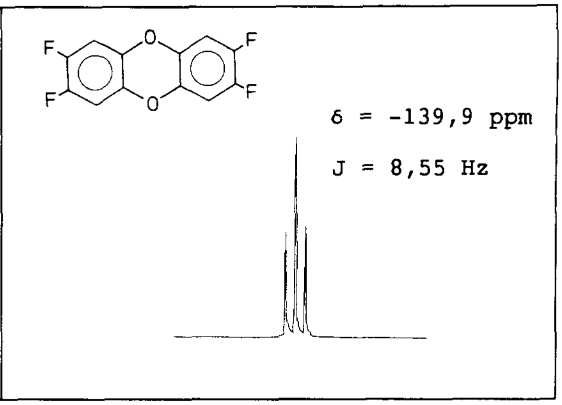


Figure 5: ^{19}F-NMR-spectrum of 2,3,7,8-T_4FDD

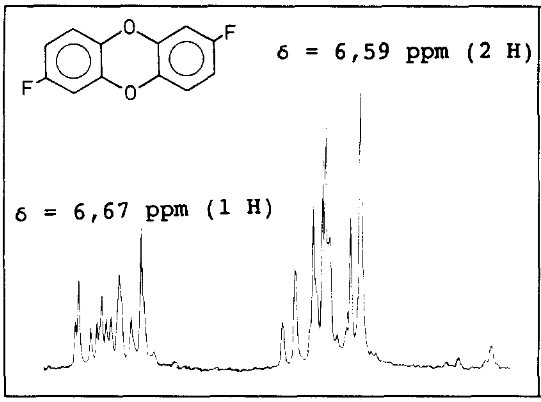


Figure 6: ^{1}H-NMR-spectrum of 2,7-D_2FDD

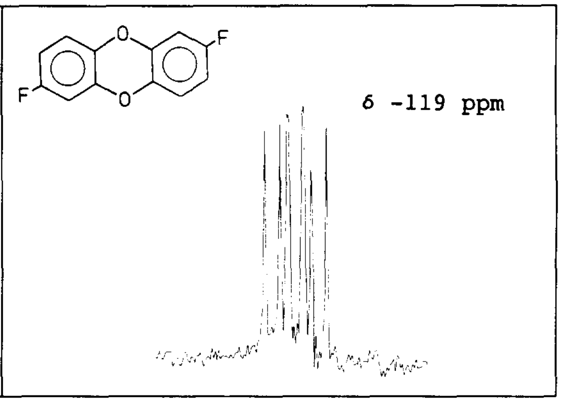


Figure 7: ^{19}F-NMR-spectrum of 2,7-D_2FDD

2,3,7,8-T_4FDD can be described as an AA'XX'-system, 2,7-D_2FDD as an A,B,C,X-system, where H_A and H_B have nearly the same chemical shift (**Fig. 8**).

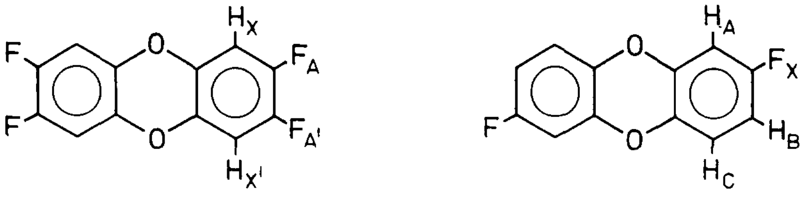


Figure 8: NMR-system of 2,3,7,8-T_4FDD and 2,7-D_2FDD

Fig. 9 shows the mass-spectrum of 2,3,7,8-T_4FDD. The fragmentation is analogous to that of the corresponding TCDD [5,6] but the intensities of the fragments are different.

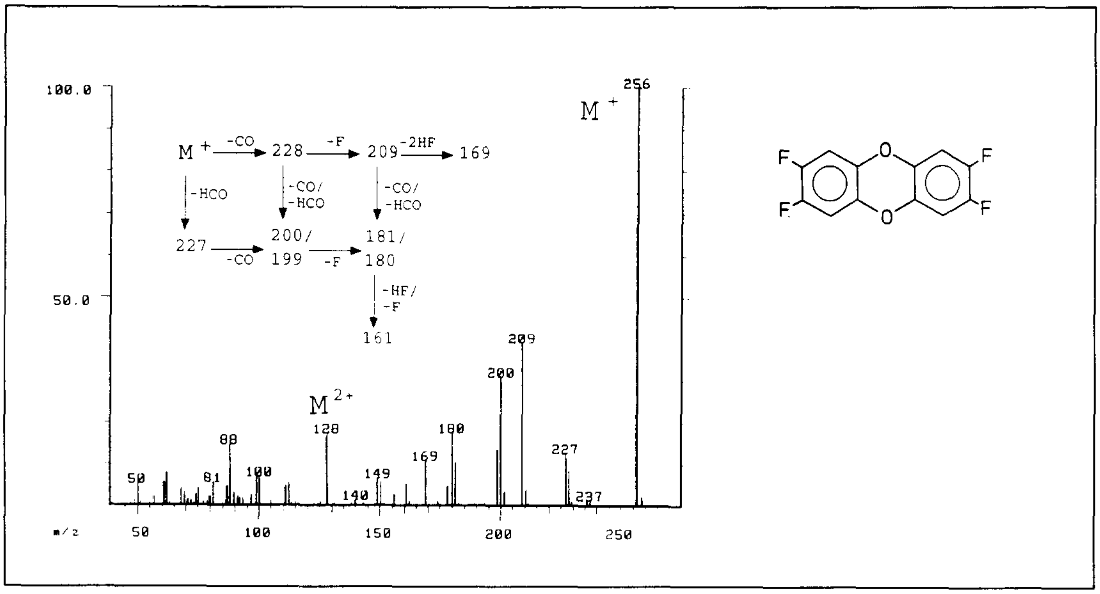


Figure 9: EI-mass-spectrum of 2,3,7,8-T_4FDD

Fig. 10 shows the IR-spectrum of 2,3,7,8-T_4FDD and **Tab. 2** presents the IR-absorption bands of 7 different PFDD's compared to 2,3,7,8-TCDD [6].

2,3,7,8-T_4FDD and O_8FDD show a lack of the aromatic ring breathing absorption band. All investigated PFDD's show no aromatic C-H-stretch absorption band and no aromatic C-F-absorption in the detected area. 2,7-D_2FDD shows an additional absorption band at 1137 cm^{-1}. The isomers can be distinguished by their IR-spectra.

Table 2, IR-absorption bands of PFDD's and 2,3,7,8-TCDD [6]

IR-absorption-bands [cm^{-1}]	2,3,7,8-T_4CDD	2,3,7,8-T_4FDD	2,7-D D_2FDD	1,2,6,7-T_4FDD	1,6-D_2FDD	1,2,3,4,6-P_5FDD	O_8FDD	1,3,6,8-T_4FDD
$\nu_{C-H, ar}$	3122, 3028	--	--	--	--	--	--	--
$\nu_{C=C, ar}$	1569, 1493 1473, 1464 1457, 1394	1516s -- -- --	1636w 1605w 1497s 1447s	1524m 1485s	1635w 1593m 1508s 1477s	1612w 1501s 1474s	1535 -- 1501s 1477s	1647 1605 1512s 1454s
$\nu_{as'; Ar-O-Ar'}$ $\nu_{s'; Ar-O-Ar'}$	1327s 1212s	1381w 1258s	1323 1254m	1339m 1242s	1319s 1254m	1292m 1250m	1354w 1157m	1227 1119s
$\delta_{C-H, ar, in plane}$	1173	1173	1215m	1065s	1069s	1061s	1057s	1096
$\delta_{ar ring-breathing}$	1115	--	1099m	1018s	1119w	1018m	--	999m
$\delta_{C-H, out of plane}$	876 870 --	906m 864m --	960m 849m 802w	798m -- --	845w 771m 706w	-- 771w --	-- -- --	841m -- --
$\nu_{C-Cl, ar}$ $\nu_{C-F, ar}$	798	--	--	--	--	--	--	--

measuring range: 400 - 4000 cm^{-1} --: no absorption detected

Ar: aromat ar: aromatic as': asymmetric s': symmetric δ: deformation ν: strech m:medium s: strong w: weak

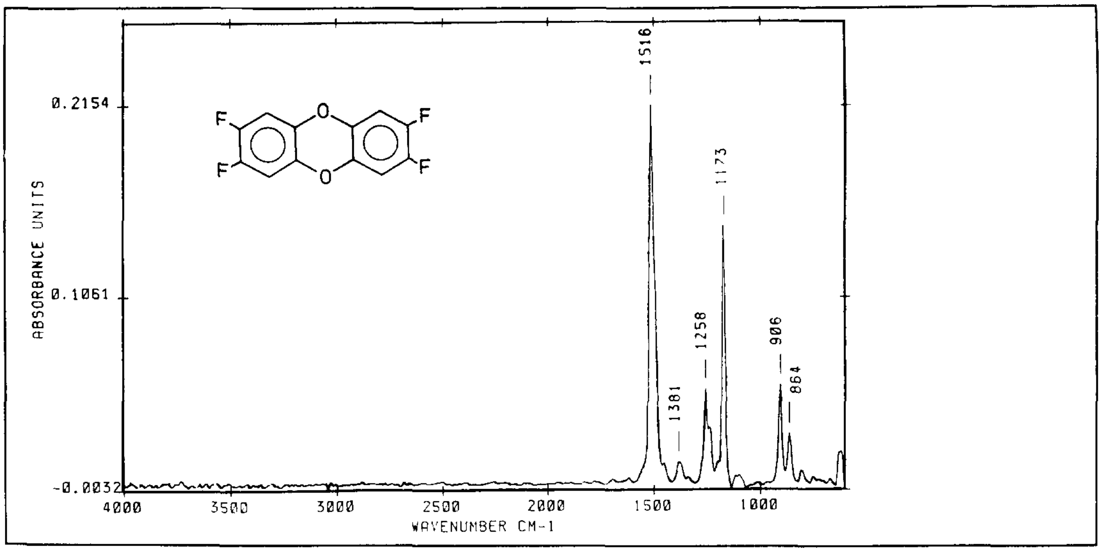


Figure 10: IR-spectrum of 2,3,7,8-T_4FDD

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