SYNTHESIS OF POLYFLUORINATED DIBENZO-p-DIOXINS

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1. Abstract

Fluorinated dibenzo-p-dioxins have been selectively synthesized from fluorophenols and isolated by column- and thin layer chromatography.

2. Introduction

During certain thermal processes in which organic and fluorine compounds coinside (e.g. industrial production of aluminium) we assume that fluorinated dibenzo-p-dioxins (PFDD) and -furans (PFDF) may be generated. Mass spectrometric analysis of the products obtained by thermolytic reaction of hexafluorobenzene in the influence of air suggests the formation of O_8FDD/F. To enable more detailed investigations, if and to which extent PFDD/F's are released in thermal processes, reference-PFDD/F-compounds are a necessity. 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.

3. Experimental and results

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

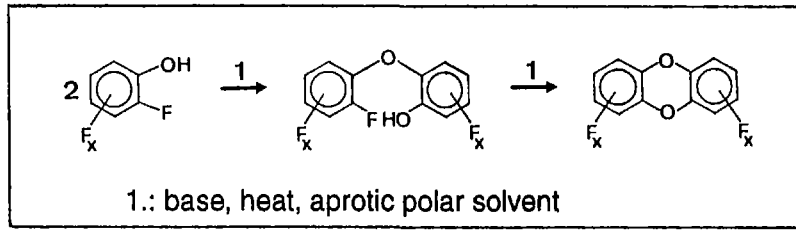

Figure 1: synthesis of PFDD's from F_x-phenols

This reaction of fluorophenols envolves an intermolecular nucleophilic aromatic substitution, followed by an intramolecular one, to give the corresponding PFDD's. The reactions were carried out in a polar, aprotic solvent in the presence of a base at higher temperatures. Reaction time may vary up to 8 days (see Tab.1).

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

PFDD	FP	reaction time	mp[°C]
1,6-D_2FDD	2,6-D_2FP	12 h	163
2,7-D_2FDD	2,5-D_2FP	3 d	174-176
2,7-D_2FDD	2,4-D_2FP	2 d	174-176
1,2,6,7-T_4FDD	2,3,4-T_3FP	6 d	167
1,3,6,9-T_4FDD	2,3,5-T_3FP	8 d	-
2,3,7,8-T_4FDD	2,4,5-T_3FP	2 d	183
1,2,4,6,7,9-H_6FDD	2,3,5,6-T_4FP	6 d	133-134
O_8FDD	P_5FP	4 d	161

FP: fluorophenol; mp:melting point

The resulting PFDD's were isolated from the reaction mixture by column- and, when necessary, thin layer chromatography with silicagel and n-hexane as eluent.
This simple synthesis has the advantage, that all starting compounds are commercially available (except 2,3,4,5- and 2,3,4,6-tetrafluorophenol).
The structures of the obtained PFDD's were confirmed by IR, MS, ^{1}H-NMR and ^{19}F-NMR. Figures 2 - 5 show the IR-, MS- and NMR-spectra in the case of the symmetric 2,3,7,8-T_4FDD, figures 6 + 7 show the NMR-spectra of the non-symmetric 2,7-D_2FDD.

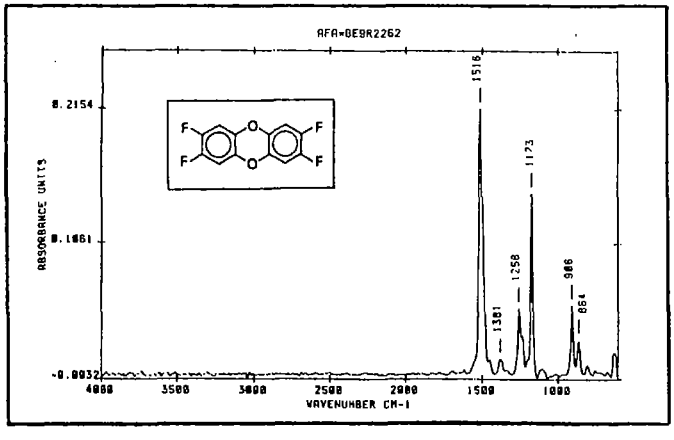

Figure 2: IR-spectrum of 2,3,7,8-T_4FDD (EFS 48, Bruker)

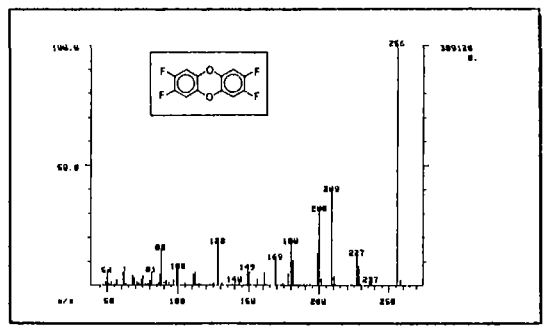

Figure 3: EI-mass-spectrum of 2,3,7,8-T_4FDD (INCOS 50, Finnigan MAT)

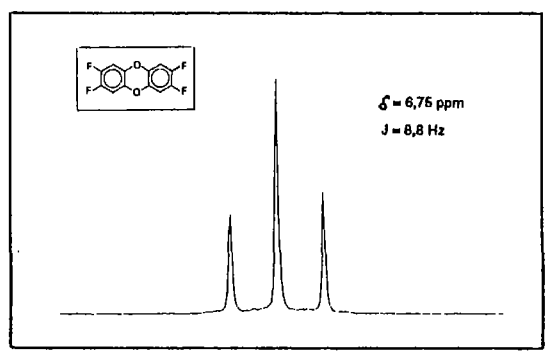

Figure 4: ^{1}H-NMR-spectrum of 2,3,7,8-T_4FDD (AM 270, Bruker)

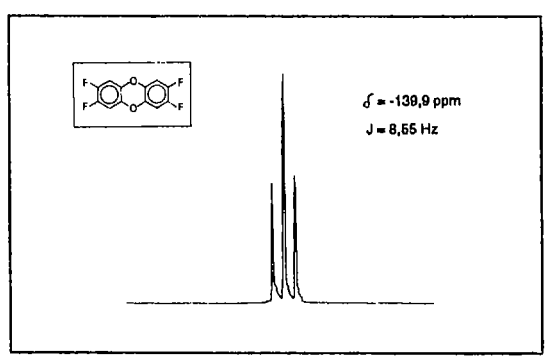

Figure 5: ^{19}F-NMR-spectrum of 2,3,7,8-T_4FDD (FX 90 Q, Joel)

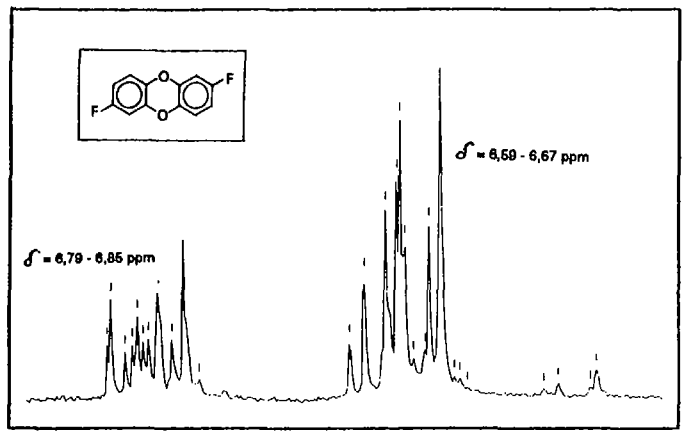

Figure 6: ^{1}H-NMR-spectrum of 2,7-D_2FDD (AM 270, Bruker)

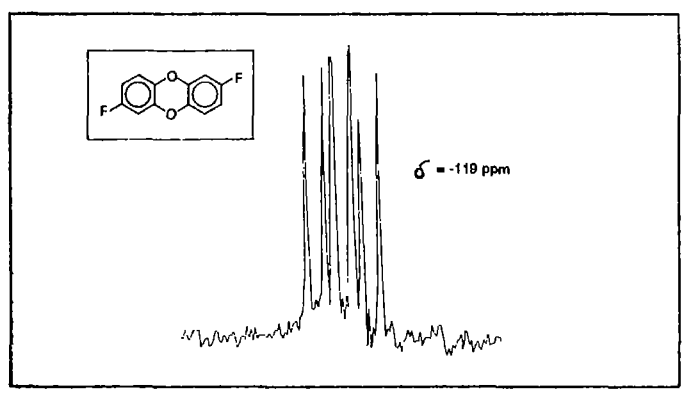

Figure 7: ^{19}F-NMR-spectrum of 2,7-D_2FDD (FX 90 Q, Joel)

4. References

1 Kende AS, Wade JJ, Ridge D, Poland A. *J.Org.Chem.*1974;7:931-7
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4 Buu-Hoi et al., *J.Heterocycl.Chem.* 1979;51:2273-2275