

**MODEL COMPOUND SYNTHESIS FOR THE STRUCTURE DETERMINATION OF NEW UNKNOWN
PLANAR AROMATIC COMPOUNDS ORIGINATING FROM PULP MILL**

Tapio Nevalainen and Jaana Koistinen
University of Jyväskylä, Department of Chemistry
Kyllikinkatu 1-3, SP-40100 Jyväskylä, Finland

ABSTRACT

Different model compounds have been synthesized and analyzed to find out the possible structure of new unknown planar aromatic compounds (UPACs) observed in HRGC/LRMS analyses of PCDD/Fs in pulp mill products, effluents, sediments and mussels. The mass spectra of synthetic alkylated polychlorodibenzofurans (C_6 -PCDFs) were different, but those of alkylated polychlorobibenzyls (C_7 -PCBBs) very similar to the spectra of UPACs.

INTRODUCTION

In determination of PCDDs and PCDFs in pulp mill effluents and coffee filter paper were found new chlorinated unknown planar aromatic compounds (UPACs)¹. At the retention window of TCDDs of a bleached kraft pulp sample were found three UPACs with LRMS ions of m/z 320 and 322. Intensity ratios of the peaks indicate a dichloro compound. In the same pulp sample were also detected one monochloro UPAC (m/z 266) and four isomers of trichloro-UPACs by selected ion monitoring at the values m/z 354 and 356.

UPACs were first suggested to be alkylated polychlorodibenzofurans (R-PCDF), that have been previously identified by Buser et al². The mass spectra of UPACs indicate the structure of chlorinated alkyl bibenzyls (1,2-diphenylethanes) rather than R-PCDFs as were previously erroneously suggested. Different synthetic mixtures of dipropyl- and diisopropyl-polychlorodibenzofurans (C_6 -PCDFs) and chlorinated methyl substituted bibenzyls (C_7 -PCBBs) have been analyzed by HRGC/LRMS to find out the structure of UPACs.

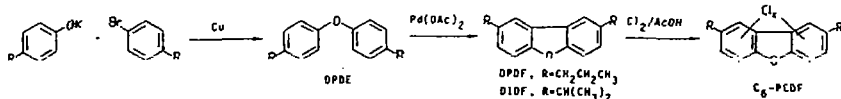
EXPERIMENTAL

Apparatus And Operating Conditions

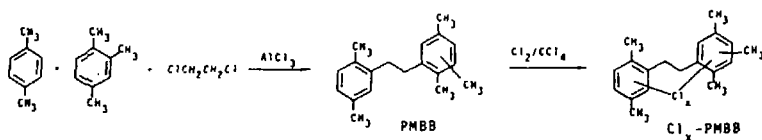
The pulp sample and synthetic mixtures were analyzed with GC/MS using HP 5970 mass selective detector with quartz capillary column SE-54 (length 25 m, i. d. 0.2 mm) with temperature program 100°C (1 min) to 180°C at 20°C/min and then to 290°C at 5°C/min. The mass spectra were recorded at 70 eV from mass number 50 up to 500 amu.

Synthesis of Model Compounds

Dipropyl- and diisopropyl-PCDFs were prepared by chlorination of 2,8-dipropyl- (DPDF) and 2,8-diisopropyldibenzofuran (DIDF) with elemental chlorine in acetic acid. DPDF and DIDF were prepared by palladium(II) acetate-promoted cyclization of 4,4'-dipropyl- and 4,4'-diisopropyl-diphenylether (DPDEs) according to the known method³. DPDEs were prepared by the classical Ullman ether synthesis -coupling of potassium salt of 4-propyl- and 4-isopropylphenol with 4-propyl- and 4-isopropylbromobenzene in the presence of copper catalyst⁴.



Methyl substituted bibenzyls were prepared by treating the corresponding methylbenzenes with 1,2-dichloroethane in the presence of AlCl₃. Mixture of p-xylene (0,05 mol) 1,2,4-trimethylbenzene (0,05 mol), 1,2-dichloroethane (0,005 mol) and AlCl₃ (0.001 mol) was stirred 1,5 h at 90°C. The reaction mixture was washed with diluted sodium hydroxide solution and water and dried with sodium sulfate. Distillation under reduced pressure for removal of unreacted alkylbenzenes gave mixture of methyl substituted bibenzyls. The product was chlorinated with elemental chlorine in CCl₄ in the presence of FeCl₃. The reaction mixture was washed with sodium bisulphide solution, water and dried with magnesium sulphate.



RESULTS AND DISCUSSION

In the pulp sample were found one mono- and three isomers of dichloro-UPACs, whose molecular formula could be $C_{19}H_{23}Cl$ (M^+ 286) and $C_{19}H_{22}Cl_2$ (M^+ 320). Basic non-chlorine compound ($C_{19}H_{24}$, M^+ 252) was not detected in the pulp sample. UPACs gives peaks at m/z 119 (base peak), 91 and 77 typical for phenylalkyl compound. Also very small fragments at m/z 167 (Cl_1 -UPAC) and 201 (Cl_2 -UPAC) of $M^+-C_7H_{11}$ were found in mass spectra of UPACs. In figure 1 are presented EI mass spectra for mono- and dichloro-UPACs found in the pulp sample.

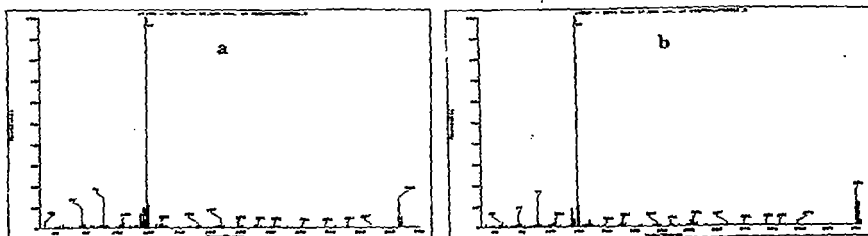


Figure 1. EI mass spectra of (a) mono- and (b) dichloro-UPAC found in the pulp sample.

The mass spectra of synthetic polychloro-DPDFs and -DIPFs were totally different from those found for UPACs. In synthetic mixtures were found 2,8-dipropyl- and 2,8-diisopropyl-PCDF isomers with M^+ of m/z 286, 320, 354, 388 and 422 for mono- to pentachloro congeners. The EI mass spectra of the 2,8-dipropyl-PCDFs show intense base peak $M^+-C_2H_5$ -ions. 2,8-diisopropyl-PCDFs have in their mass spectra a M^+-CH_3 base peak. All isomers showed very similar spectra. Typical EI mass spectra of a synthesized dichloro- DPDF and a dichloro-DIDF are presented in Figure 2.

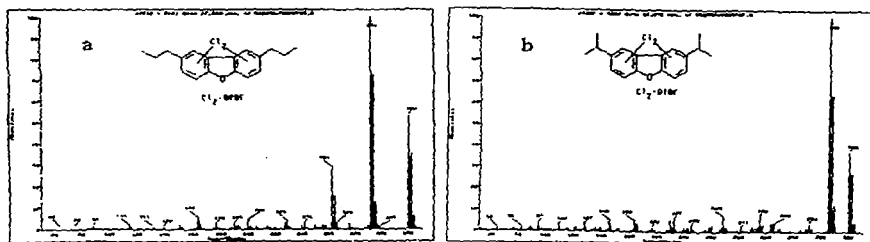


Figure 2. EI mass spectra of a synthesized (a) dichloro-DPDF and (b) a dichloro-DIDF.

To indicate the similar fragmentation between UPACs and C_5 -PCBBs a synthetic mixture of methyl substituted bibenzyls were prepared from p-xylene, 1,2,4-trimethylbenzene and dichloroethane. In the reaction mixture were found isomers of tetra- (TMBB, M^+ 238), penta- (PMBB, M^+ 252) and hexamethyl-bibenzyls (HMBB, M^+ 266). TMBBs give base peak at m/z 119, but PMBB and HMBB give base peak at m/z 133. After chlorination in the reaction mixture were found isomers of mono- and dichloro-PMBBs, those mass spectra were very similar to those of UPACs. In figure 3 is presented mass spectra of a monochloro-PMBB and a dichloro-PMBB found in the synthetic mixture after chlorination.

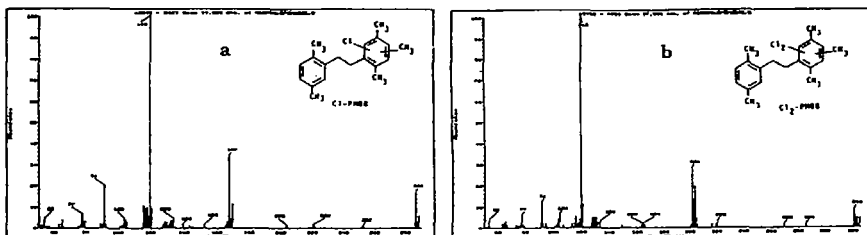
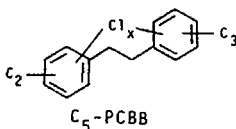


Figure 3. EI mass spectra of (a) a monochloro- and (b) a dichloro-PMBB isomer identified in chlorination reaction products.

Chlorinated methyl substituted bibenzyls behave like PCDDs and PCDFs in their analytical clean up with carbon column-reversed elution and with basic alumina chromatography. It seems very obvious, that UPACs are alkylated polychlorobibenzyls (C_5 -PCBBs), that could have the following structure:



REFERENCES

1. J. Paasivirta, K. Mäntykoski, J. Koistinen, T. Kuokkanen, E. Mannila and K. Rissanen, *Chemosphere*, 19, (1989), 149-154.
2. H.-R. Buser, L.-O. Kjeller, S.E. Swanson and C. Rappe, *Environ. Sci. Technol.*, 23, (1989), 1130-1137.
3. Å. Norström, K. Andersson and C. Rappe, *Chemosphere*, 6, (1976), 419-423.
4. K.-P. Zeller and S. Berger, *J. Chem. Soc., Perkin Trans. 2.*, (1977), 54-58.