Characterization of the Components of Technically Polychlorinated Biphenyl Mixtures—II

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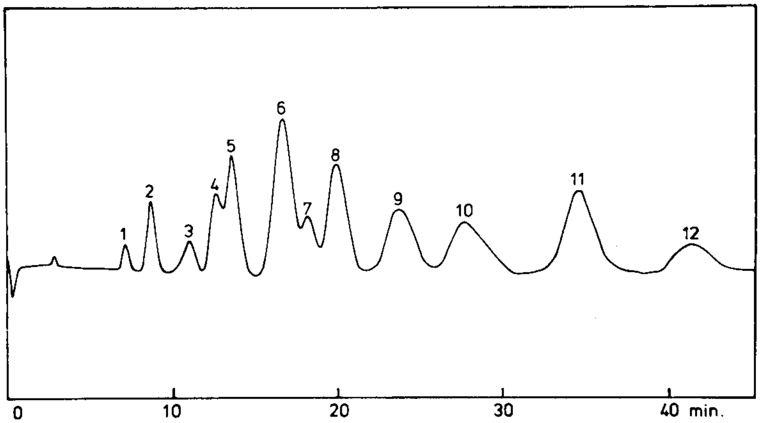
Three more components of technically polychlorinated biphenyl mixtures (PCB) have been unequivocally identified.

Introduction

The contamination of the environment by polychlorinated biphenyls (PCB) and the occurrence of these products in wildlife (1-4), and even human tissues induced us to identify the exact structure of the major components of these mixtures and to synthesize them in a pure form in order to make toxicity studies possible.

In Figure 1 the gaschromatogram of a batch of the technical product Phenochlor DP6 is shown, other batches and trade products showing only minor differences (2, 5).



Gaschromatogram of Phenochlor DP6. Column: glass, 1.9 m x 3 mm i.d., packed with 3% OV-1 on gaschrom. Q, 80-100 mesh, temp. 180°C, flow 60 ml N_2/min. Detection: electron capture

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Recently we published the structure and the synthesis of the components, indicated in the gas-chromatogram as peak numbers 6, 8, 11 and 12 (5). The products proved to be 2,2',4,4',5,5'-hexachlorobiphenyl, 2,2',3,4,4',5'-hexachlorobiphenyl, 2,2',3,4,4',5,5'-heptachlorobiphenyl and 2,2',3,3',4,4',5-heptachlorobiphenyl, respectively.

The very strong absorption at 813 cm^{-1} in the IR spectrum of the PCB suggested that still other products with an 1,2,3,4-substitution pattern in the benzene nuclei could be present among the unindentified peaks. In that case the chlorine atoms are possibly attached to the 2,3 and 6 positions.

On synthesis of some of these products we succeeded in the identification of:

2,2',3,3',6,6'-hexachlorobiphenyl (I)
2,2',3,4',5',6-heptachlorobiphenyl (II)
2,2',3,3',4,5,6'-heptachlorobiphenyl (III)

as the main components of peak numbers 3, 5 and 10 respectively. Syntheses of these compounds were performed by the Ullmann reaction, starting with the appropriate polychloroiodobenzenes (6) which were in turn synthesized from commercially available products by known methods.

Identification was established by IR spectra and by the retention times on three different GLC columns of both the components isolated from the PCB mixture, and the synthesized compounds, whereas the NMR spectra of the synthetic products gave an additional proof of their exact structure.

Experimental

IR spectra were recorded with a Hilger and Watts H-1200 apparatus. Absorptions are given in cm^{-1}.

NMR spectra were recorded with a Jeol A60 apparatus, $CHCl_3$ being the internal standard and CCl_4 being the solvent. Chemical shifts are given in ppm relative to TMS.

Control GLC was carried out by using:

1. a Carlo Erba Fractovap GV apparatus, supplied with either of the following glass columns:
   - a - 1.9 m x 3 mm i.d., packed with 3% OV-1 on gaschrom. Q, 80-100 mesh, temp. 180°C, flow 60 ml N_2/min.
   - b - 1.9 m x 3 mm i.d., packed with 1.8% OV-1 and 2.7% QF-1 on gaschrom. Q, 80-100 mesh, temp. 180°C, flow 60 ml N_2/min.

2. a Microtek MT 220 gaschromatograph supplied with Ni-63 EC detector and a glass column 6' x 1/4", packed with 3% DEGS (stabilized) on gaschrom. Q, 80-100 mesh, temp. 190°C, flow 75 ml Ar with 10% methane/min. Retention times are given, relative to aldrin.

Preparative GLC was carried out by using an Aerograph A-90-P apparatus. Column:stainless steel 2 m x 5 mm i.d., packed with 20% SE-30 on chromosorb W/AW, temp. 240°C, flow 60 ml H_2/min.

The mass spectrum was recorded with an Atlas CH5 apparatus using the direct inlet system.

Syntheses

2,5-dichloro-4-nitracetanilide and 2,5-dichloro-6-nitracetanilide.

2,5-Dichloroaniline was acetylated and nitrated according to the directions of Holleman and Van Haeften (7). A mixture of approximately 80% 2,5-dichloro-4-nitracetanilide and 20% 2,5-dichloro-6-nitracetanilide was obtained. On recrystallization of this mixture from ethanol a considerable quantity of nearly pure 2,5-dichloro-4-nitracetanilide crystallized out. Further purification was performed by a repetition of the same procedure. From the filtrate a mixture of both isomers in a ratio of approximately 1:1 (IR) was obtained.

Three extractions at room temperature with benzene, in which the 6-isomer is only sparingly soluble, and one recrystallization from the same solvent yielded 2,5-dichloro-6-nitracetanilide in a pure form.

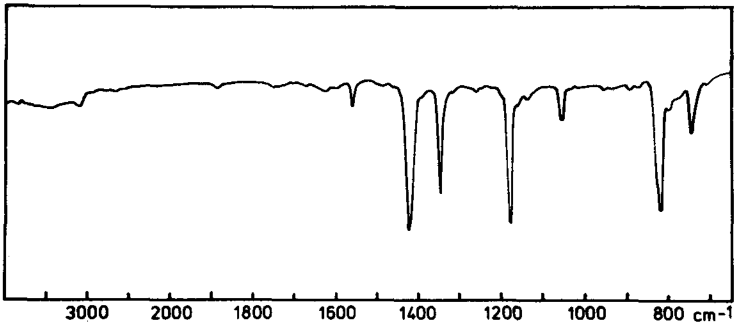
2,4,5-trichloroiodobenzene and 2,3,6-trichloroiodobenzene.

Of the appropriate 2,5-dichloronitracetanilide 3 g (0.012 moles) were heated for 45 min. in 15 g of 98% sulphuric acid at 95-100°C (7).After cooling the mixture was poured on cracked ice, while being stirred, and the 2,5-dichloronitraniline was filtered off and washed with water. The crude aniline was suspended in 35 ml of concentrated hydrochloric acid and treated dropwise with 0.85 g (0.012 moles) of sodium nitrite in 2 ml of water at 20-35°C. Under these conditions the nitro-group of both isomers was replaced by a chlorine atom, while the diazonium-group remained intact (7,8,9). After stirring for 45 min. at 25-30°C, the diazonium solution was filtered and cooled to -50°C. At this temperature 2 g (0.012 moles) of potassiumiodide in 10 ml of water was added dropwise. The reaction mixture was extracted twice with ether, washed with water and sodiumthiosulphate and finally dried over sodiumsulphate.

After removal of the solvent and recrystallization from ethanol 2,2-2,4 g (60-66%) of the product was obtained.

The IR spectrum and the physical constants of 2,4,5-trichloroiodobenzene have been described formerly (5).

2,3,6-trichloroiodobenzene.
Mw: 306; three Cl atoms (from mass spectrum)
Mp: 35-36°C
Bp: 88-91°C, 0.5 mm
IR spectrum: Figure 2.



IR spectrum of 2,3,6-trichloroiodobenzene
(liquid film)

2,3,4,5-tetrachloroiodobenzene has also been described in our first paper (5).

The appropriate polychloroiodobenzenes were heated with 10% more than the equal quantity of activated copper powder at 215-225°C with occasional stirring for 2½ hr (10). After cooling the reaction mixture was extracted five times with boiling hexane. The solvent being removed, the polychlorobiphenyls were purified by preparative GLC.

I. 2,2',3,3',6,6' hexachlorobiphenyl as the only product from 2,3,6-trichloroiodobenzene
Mp: 114-114.5°C (from ethanol)
R_t value of I on 1a 2.08; on 1b 2.07; on 2 3.33
of peak no. 3 on 1a 2.09; on 1b 2.06; on 2 3.33
IR spectrum: Figure 3A
NMR spectrum: δ= 7.49 (2,d,J=8.5 cps) and
δ=7.37 (2,d,J=8.5 cps)

II 2,2',3,4',5',6-hexachlorobiphenyl as the major product from an 1:1 mixture of 2,3,6- and 2,4,5-trichloroiodobenzenes.

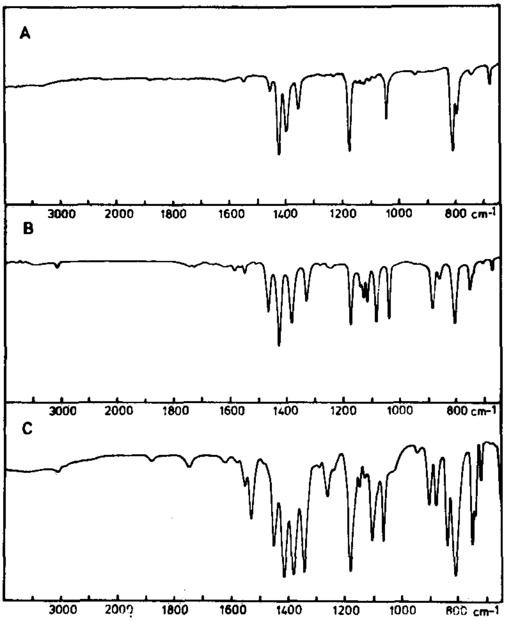
Could not be obtained in a crystalline form.

R_t value of II on 1a 2.58; on 1b 2.59; on 2 3.89
of peak no. 5 on 1a 2.57; on 1b 2.59; on 2 3.89

IR spectrum: Figure 3B

NMR spectrum δ=7.64 (1,s); δ=7.48 (1,d,J=8.5 cps)
δ=7.36 (1,d,J=8.5 cps) and δ= 7.30 (1,s)

Byproducts: I (see afore) and 2,2'4,4',5,5'-hexachlorobiphenyl, formerly described (5).



IR spectra of (A): 2,2',3,3',6,6'-hexachlorobiphenyl (I) (supercooled film); (B): 2,2',3,4',5',6-hexachlorobiphenyl (II) (liquid film); (C): 2,2',3,3',4,5,6'-heptachlorobiphenyl (III) (supercooled film)

III 2,2',3,3',4,5,6'-heptachlorobiphenyl as the major reaction product from an 1:1 mixture of 2,3,6-trichloroiodobenzene and 2,3,4,5-tetrachloroiodobenzene.

Mp: 130.5-130.7°C (from ethanol)

R_t value of III on 1a 5.25; on 1b 5.22; on 2 6.90
of peak no. 10 on 1a 5.25; on 1b 5.20; on 2 6.89

IR spectrum: Figure 3C

NMR spectrum: δ=7.50 (1,d,J=8.5 cps); δ=7.38 (1,d,J=8.5 cps) and δ=7.27 (1,s)

Byproducts: I (see afore) and 2,2',3,3',4,4',5,5'-octachlorobiphenyl, formerly described (5).

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