

SYNTHESIS OF HP-SED - A MAJOR TOXAPHENE CONTAMINANT IN TREATED LAKE SEDIMENTS

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Introduction

An examination of sediment cores from two toxaphene treated lakes in Canada showed that toxaphene peak pattern and concentration may differ depending on sediment depth¹. The peak patterns of sediments from the years of treatment were similar to that of the technical toxaphene standard, while the peak patterns of the near-surface sediments were very different due to the absence of octa- and nonachlorobornane peaks in the chromatograms. The most abundant hexachlorobornane is labeled as Hx-Sed (2-*exo*,3-*endo*,6-*exo*,8b,9c,10a-hexachlorobornane) and the most abundant heptachlorobornane as Hp-Sed (2-*endo*,3-*exo*,5-*endo*,6-*exo*, 8c,9b,10a-heptachlorobornane). Both compounds could be identified after isolation from 10 kg Chatwin lake surface sediment by Stern et al.². Hp-Sed constituted up to 99 % of total toxaphene concentration in sediment and fish samples from the treated lakes³.

To our knowledge, there is no any toxicological study with Hp-Sed due to the lack of this compound in sufficient amounts. By the same reason there is only very little information about the environmental behaviour of Hp-Sed. The aim of this study is therefore to show a synthesis pathway for Hp-Sed from P 32 (2,2,5-*endo*,6-*exo*,8,9,10-heptachlorobornane) that can be isolated in gram amounts from the technical mixture⁴. Our results indicate furthermore that other environmentally relevant toxaphene congeners can be obtained in this way.

Materials and Methods

(+)-Camphene and silica gel were purchased from Merck (Darmstadt, FRG). The Parlar 22 standard and technical toxaphene standard were obtained from Dr.Ehrenstorfer (Augsburg, FRG).

The GC/MS measurements were performed with HP 5970 MSD equipment. The column used was a DB-5, 30 m, i.d. 0.25 mm, film thickness 0.25 μm . The GC temperature program was: 100 °C for 3 min, then at 10 °C /min to 260 °C and held for 15 min. Injector temperature was 250 °C. Helium was employed as carrier gas with 1.5 ml/min. A Dani GC 86.10 gas chromatography equipped with an electron capture detector (ECD) was used too. The operating conditions were as follows: 60 m HR DB-5 column (Phenomenex, i.d. 0.32 mm, film thickness 0.25 μm), flow rate (N₂) 1.3 ml/min, the temperature program was 80 °C for 2 min then 30 °C /min to 220 °C for 120 min.

A 500 MHz Inova-500 from Varian was used for NMR spectroscopy. Structures of two new heptachlorobornanes were confirmed by MS and NMR

Photolysis of toxaphene

A solution containing 1.24 g of toxaphene in 75 ml of n-hexane was irradiated with a UV lamp ($\lambda \geq 230 \text{ nm}$, HPK 125 W, Philips inc. Netherlands) for 12 hours. The color of the solution changed to dirty yellow after irradiation.

Synthesis

Step 1: Isolation of P 32

P 32 was synthesized after modifying a procedure previously published⁴. A magnetically stirred solution of 35 g (+)-camphene in 300 ml of CCl₄ was chlorinated at 0 °C. When a maximum concentration for P 32 was reached the reaction was broken off. A 25 g portion of the product obtained, which contained P 32 ca 10 % was separated by column chromatography using 1.7 kg silica gel 60, Merck, No. 1.07734, 63-200 µm. This procedure was repeated for further 3 portions, each of 25 g. 1100 mg P 32 was isolated in a purity of 99 % after recrystallisation from n-hexane. The yield was 1.1 %.

Step 2: Dechlorination of P 32 by reduced hematin to obtain e-Hx-Sed

The reaction was performed as described by Saleh and Casida with little modifications⁴. Briefly, 1050 mg of P 32 was treated with reduced hematin. From nearly 840 mg of crude product, which was purified with n-pentane on a silica gel column (100 × 2,4 cm), 90 mg of 2-*exo*-3-*endo*,6-*endo*,8b,9c,10a-hexachlorobornane (e-Hx-Sed) could be obtained in pure form besides 440 mg of Hx-Sed, 152 mg of 2,5-*endo*,8,9,10-pentachlorotricyclene and 47 mg of 2,5-*endo*,6-*exo*,8,9,10-hexachlorobornene.

Step 3: Chlorination of e-Hx-Sed and isolation of Hp-Sed

A solution of 90 mg of e-Hx-Sed in 100 ml CCl₄ was chlorinated at 0° C under a sun lamp. To avoid over chlorination, the reaction was broken off after consumption of approximately half of e-Hx-Sed. The chlorination product was chromatographed on a silica gel column (100 x 1.4 cm) to isolate the remaining e-Hx-Sed that was chlorinated again as described above to increase Hp-Sed yield. The purification of Hp-Sed was performed by using a silica gel column (100 x 1.4 cm). n-Pentane was used as elution solvent. 27 mg of Hp-Sed could be obtained by this way, in a purity of ca. 93 %. As by-products, 14 mg of 2 (purity ca. 70 %) and 2 mg of 3 (purity ca. 65 %) were isolated .

Results and Discussion

Structures of the heptachlorobornanes Hp-Sed, 2, and 3 were confirmed by MS and NMR as 2-*endo*,3-*exo*,5-*endo*,6-*exo*,8c,9b,10a-heptachlorobornane, 2-*exo*,3-*endo*,6-*endo*,8b,9b,9c,10a-heptachlorobornane, and 2-*exo*,3,3,6-*endo*,8b,9c,10a-heptachlorobornane, respectively. Hp-Sed is one of the major peaks in the HRGC-ECD chromatogram of a toxaphene solution photolysed at wavelengths above 230 nm. The HRGC-peak pattern of irradiated solutions depends on photolysis time (Figure 1). After an irradiation time of approx. 6 hours the Hp-Sed peak is the major peak but it must be noted according to EI mass spectra that there are several compounds coeluted. The rise in Hp-Sed concentration can be due to photo stability of this compound and/or degradation of especially highly chlorinated toxaphene components. e-Hx-Sed is only a minor toxaphene component. However by photolysis of toxaphene, the concentration of this compound raised first, but with further reaction time it was negligible, indicating that e-Hx-Sed is degraded by UV light .

Hp-Sed is by far the main chlorination product among heptachlorobornanes formed from e-Hx-Sed. P 32, one of the most well-known toxaphene components, has a concentration of 8.2 %, whereas Hp-Sed's proportion is 49.5 %, and those of the compounds 2, 3, 5, and 6 are 19.4, 5.7, 2.2, and 15.3 %, respectively. An octachlorobornane is also formed amongst other by products as a result of the unavoidable further chlorination of heptachlorobornanes by the radical character of the reaction. It must be in all likelihood 2-*endo*,3-*exo*,5-*endo*,6-*exo*-8,8,9,10-octachlorobornane (B8-1412) on the basis of relative retention time⁵ and EI mass spectrum⁶. This octachlorobornane has been detected in marine organisms and is one of the most persistent chlorobornanes⁶. It seems that some other

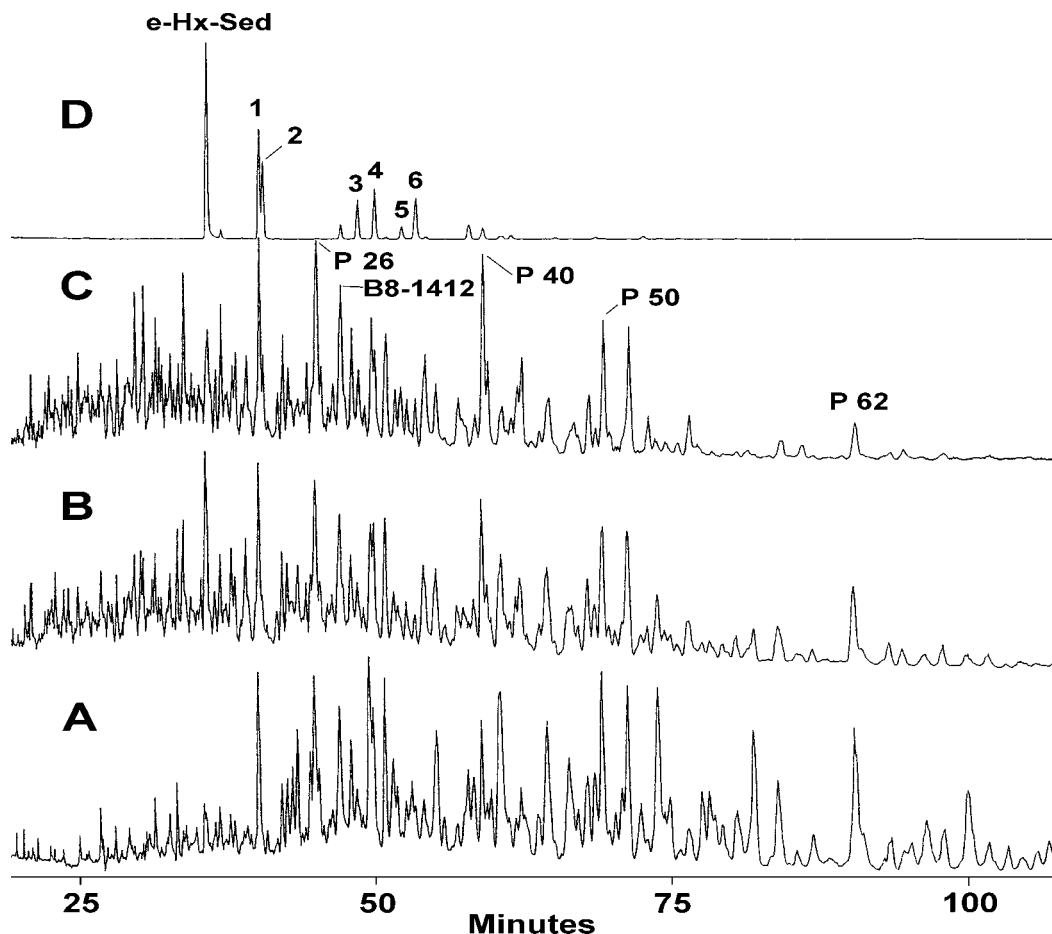


Figure 1. HRGC-ECD chromatograms of technical toxaphene (A), irradiated toxaphene for 2 h (B) and 6 h (C), and heptachlorobornanes formed by chlorination of e-Hx-Sed (D).

environmentally important toxaphene components can also be synthesized directly from precursor compounds such as Hp-Sed.

One of the compounds formed should be 2-*exo*,3-*endo*,6-*endo*,8,9,10,10-heptachlorobornane (compound 6), which has been isolated from chlorination product of camphene⁶. The relative retention time given for this compound was only 0.1 % lower in our experiments. The structure of the compound 5 was deduced as 2-*exo*,3-*endo*,6-*endo*,8,8,9,10-heptachlorobornane from its mass spectrum.

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