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Formation of Cyclohexyl-PCBs upon UV Irradiation of PCBs in Cyclohexane

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Photochemical degradation is a very important degradation pathway for polychlorinated biphenyls (PCBs) in the environment (Bunce and Kumar 1978). Numerous studies (Hutzinger *et al.* 1972, Bunce *et al.* 1978, Zabik 1983) have demonstrated that the main decomposition mechanism is reductive dechlorination. Some authors (Crosby and Moilanen 1973, Ruzo *et al.* 1974) also observed the formation of hydroxy and alkoxy-PCB derivatives when irradiation was performed in aqueous or alcoholic solvents. In a previous publication (Lépine *et al.* 1992) formation of cyclohexyl-PCBs was observed by GC-MS upon sunlight and UV irradiation of Aroclor 1254 in cyclohexane. Because of the highly hydrophobic nature of PCBs, photochemical formation of alkylated PCB derivatives might be environmentally important. The objectives of this study is to elucidate the photochemical formation of these cyclohexyl-PCBs using pure PCB congeners.

MATERIAL AND METHODS

The cyclohexane used was of "spectrograde" quality and used without further purification. Most PCB congeners were purchased from Analab (Norwalk, CT). Congeners 74 and 48 were obtained using the Cadogan coupling procedure (Cadogan 1962) with 2,4,5-trichloroaniline and chlorobenzene. All PCB congeners were over 97% pure as determined by GC-MS. The PCB solutions in cyclohexane (4 ppm) were degassed and irradiated in a Rayonet reactor equipped with a merry-go-round adaptor and three RPR 3000 lamps with maximum emission at 300 nm for a 20 min period. Samples were run in triplicate. Identification and quantification of the products were performed using a Varian 3500 gas chromatograph interfaced to a Finnigan ITD 800 as described previously (Lépine *et al.* 1991). In order to get preparative amounts of cyclohexyl-PCB adduct 600 mL of a 166-ppm solution of congener 118 were

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irradiated in glass bottles using 12 RPR lamps for 130 min until similar degradation of the starting material was obtained compared to the dilute solutions experiment described previously (Lépine *et al.* 1991). Solvent was evaporated and the cyclohexyl-PCB II was isolated using a Varian Vista 5500 HPLC equipped with a 25-cm RP-18 reversed-phase column (Supelco) with methanol-water as solvent. NMR spectra were taken using a 300 MHz Varian Gemini. Gamma irradiation of congener 77 was performed on a 62-ppm cyclohexane solution containing 5.0 mM of nitroethane. The solution was irradiated using ^{60}Co in a Gammacell 200 for a total radiation dose of 2 Mrad.

RESULTS AND DISCUSSION

Table 1. Formation of cyclohexyl-PCBs upon 300-nm UV-irradiation of PCB congeners in cyclohexane.

Congener[a]	Amounts of cyclohexyl adducts[b]	Destruction of starting material
2,2',4,5 (48)	traces	8 %
2,2',5,5' (52)	ND[c]	0 %
2,4,4',5 (74)	6%	97 %
3,3',4,4' (77)	ND	1.1%
2,2',4,5,5' (101)	ND	3.3%
2,3',4,4',5 (118)	6%	67 %
2,2',3,4',5' (138)	1%	48 %
2,2',4,4',5,5' (153)	traces	8.1%
2,2',3,4,4',5,5' (180)	ND	14 %
2,2',3,4,4',5',6 (183)	ND	69 %

[a] Numbers in parentheses are the corresponding IUPAC nomenclature.
[b] Only the major compounds are quantitated. The percentage is calculated with respect to the starting material.
[c] Not Detected.

Table 1 shows the amounts of cyclohexyl-PCBs formed upon irradiation of various PCB congeners along with the percentage destruction of the starting material. At 300 nm, a wavelenght that can reproduce the effects of sunlight on PCBs (Herring *et al.* 1972, Lépine *et al.* 1991), congeners 48, 52, 77, 101 and 153 undergo very little degradation, and no, or trace amounts, of cyclohexyl-PCBs are obtained. Congener 74, 118 and 138 are largely degraded and produce significant amounts of cyclohexyl addition products. Higher chlorinated congeners such as 180 and 183 do not produce cyclohexyl-PCBs even though congener 183 is largely degraded under these conditions.

The mass spectra of these cyclohexyl addition products display a molecular ion which corresponds to a cyclohexyl

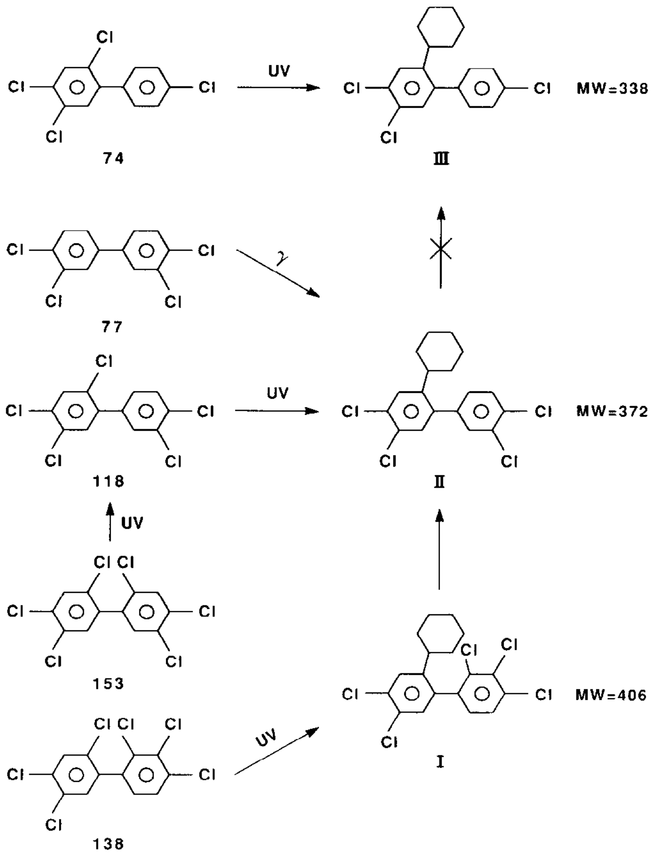

Figure 1. Formation of cyclohexyls-PCBs

adducts containing one chlorine atom less then the starting material except for congener 153 whose cyclohexyl addition product has two chlorine atoms less than the starting material. Congener 138 generates two cyclohexyl addition products of molecular weight 406 and 372, compound I and II, respectively, in Figure 1, in roughly equal amounts. Isolation of these two compounds by HPLC, followed by UV irradiation in cyclohexane, showed that I is the precursor of II. Compound II is also produced in small amounts upon irradiation of congener 153, and in considerable amounts with congener 118. Formation of II from congener 153 probably occurs throught the intermediate of congener 118 which is produced upon irradiation of congener 153 (Lépine *et al.* 1991).

In order to investigate the structure of the addition product II, congener 77 was gamma-irradiated in cyclohexane in the presence of nitroethane. Previous work in

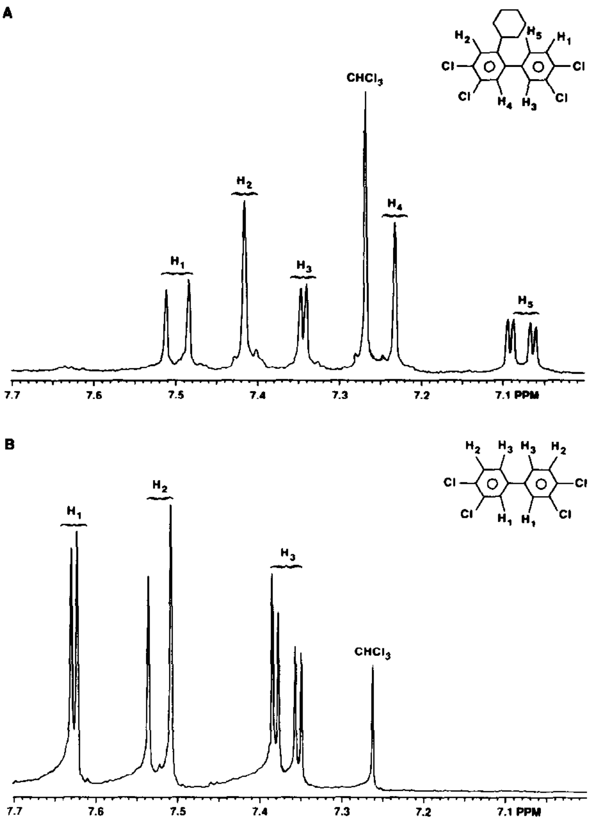

Figure 2. Aromatic portion of NMR spectra of cyclohexyl-PCB II a) and of congener 77 b) in $CDCl_3$

our laboratories (Lépine *et al.* 1990) have shown that under these conditions PCB congeners react to give cyclohexyl addition products without undergoing dechlorination. Gamma irradiation of congener 77 gave only one cyclohexyl addition product with identical retention time and mass spectrum to II. This experiment suggest that II still bears chlorines at the 3,3',4 and 4' positions and that the cyclohexyl ring is in the 2,5 or 6 position. In order to specify the exact position of the cyclohexyl ring of II, about 100 mg of congener 118 were UV irradiated and II isolated by HPLC. The aromatic portion of the NMR spectra of II and congener 77 are presented in Figure 2. The fact that the spectrum of II only shows two protons with a J_3 coupling indicates that the cyclohexyl substituent has to be located at the 5 or 6 position of one aromatic ring. The chemical shift and the lack of a J_4 coupling constant on H_2 of II indicate that the cyclohexyl ring has to be located at the 6 position as depicted in Figure 2. The J_4 coupling constant between two ortho chlorines is evident for H_5 and H_3 of II as well as for H_1 and H_3 of congener 77. The cyclohexyl ring adds at the same position than the departing chlorine of congener 118.

Photochemical substitutions at the position of the departing chlorine have been observed by Crosby and Moilanen (1973) and by Ruzo and coworkers (1974) in aqueous and methanolic solvents. In the latter study, substitution of the departing chlorine by a methoxy group is thought to proceed by nucleophilic attack of methanol on the PCB molecule in the triplet excited state. In cyclohexane the reaction must proceed through a different mechanism. In a first step, homolytic cleavage of a chlorine-carbon bond must occur. Then, the PCB or chlorine radical formed, abstracts a hydrogen from cyclohexane to produce a cyclohexane radical which either adds to the initial PCB radical in a radical-radical recombination reaction or on another PCB molecule in an electrophilic type of attack. However, the fact that only one cyclohexyl-PCB adduct is formed tends to favor the first hypothesis, especially considering that dechlorination of congener 118 proceeds over 99.9% through loss of its ortho chlorine (Lépine *et al.* 1991).

Having established the structure of II, the structure of its precursor I can be deduced. The proposed structure of I as depicted in Figure 1 is the only possibility if direct substitution of a chlorine atom by the cyclohexyl ring is the reaction mechanism, as observed for congener 118. In the case of congener 138, however, it is the ortho chlorine of the 2,3,4 substituted ring which is lost preferentially upon photolysis in cyclohexane (Lépine *et al.* 1991), but the steric hindrance at this position is likely to inhibit substitution at this position. This could also account for the relatively low yield of formation of cyclohexyl addition products even if the degradation of the starting material is considerable.

UV irradiation of congener 74 produces a cyclohexyl-PCB adduct of molecular weight 338 (compound III). Irradiation of pure II in cyclohexane showed that it is not a precursor of III. The proposed structure of III, as presented in Figure 1, is deduced by analogy with congener 118. Photodechlorination of congener 74 occurs over 99.5% through loss of the ortho chlorine to produce congener 37 (data not shown), which further supports the proposed structure of III. The fact that II is not a precursor of III can be explained by preferential loss of any of the three other chlorines present in II.

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