DESTRUCTION OF PCBS AND OTHER POLYHALOGENATED POLYAROMATIC COMPOUNDS VIA CARBONYLATION ON A MODIFIED COBALT CATALYST. III. PCB-MONO- AND POLYCARBOXYLIC ACIDS AND CARBONYLATION OF 2,4,8-TriCDF, PCNs and PBDE-99.

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Introduction

Destruction and transportation to the destruction site of PCB-containing materials and toxic wastes of similar type is restricted in many countries and therefore very expensive. Our research is directed towards development of safe and flexible carbonylation technology capable of destruction of polyhalogenated aromatic compounds on site with help of a mobile unit[1]. In a previous report we have demonstrated the applicability of our method for destruction of SOVOL and SOVTOL – commercial PCB formulations produced in the USSR[2,3]. Now we report on structure elucidation of mono- and polycarboxylic acids formed via carbonylation of specific PCB congeners. The applicability of our method for destruction of PCDDs/PCDFs, PBDEs, and PCNs was demonstrated on model compounds.

Materials and methods

PCB congeners were synthesized in gram quantities by known methods. Carbonylation method was the same for all studied compounds. In a 30 ml flask, equipped with a magnetic stirrer, 200 mg of PCB congener, 20 mg of $Co_2(CO)_8$ in 10 ml of methanolic NaOH, and 1 ml of activator were allowed to react with CO at 60°C and atmospheric pressure for 6-8 hours. Reaction mixture was allowed to cool, diluted with water, extracted with toluene to remove possible remaining PCB, and acidified with HCl. Precipitate was filtered, washed with small amount of water, dried, and analyzed without further purification.

NMR chemical shift assignments and locations of carboxylic functionalities have been deduced based on one-dimensional ^1H and proton composite pulse (waltz-16) decoupled ^{13}C NMR as well as PFG (Pulsed Field Gradient) $^1H,^{13}C$ HMQC (Heteronuclear Multiple Quantum Coherence), PFG $^1H,^{13}C$ HMBC (Heteronuclear Multiple Bond Correlation), and PFG DQF (Double Quantum Filtered) $^1H,^1H$ COSY (Correlation Spectroscopy) spectra measured with a Bruker Avance DRX 500 FT NMR spectrometer for dilute acetone-d_6 solutions at 30°C.

Results and Discussion

Mono- and polycarboxylic acids from carbonylation of PCB isomers are shown on Fig. 1.

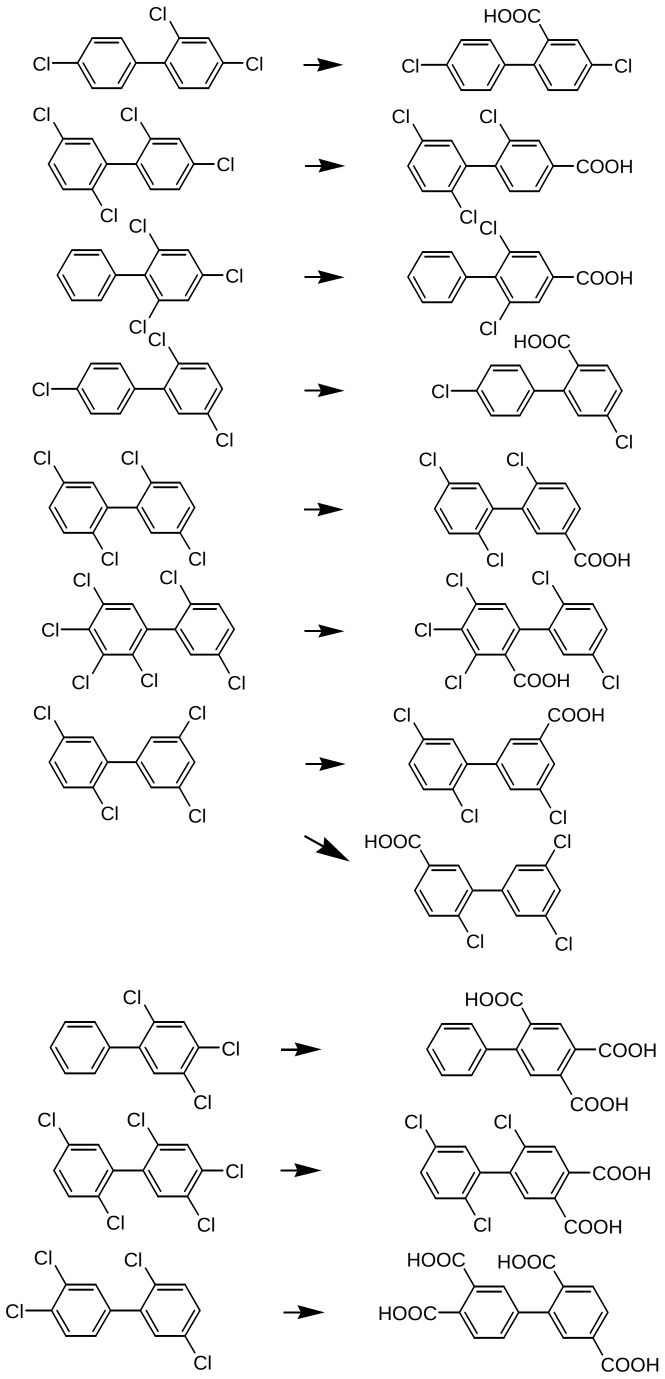

Fig. 1. Mono- and polycarboxylic acids from PCBs

In addition to the previously reported NMR data for PCB-acids, accurate mass measurements for the compounds were performed (Table 1). Electrospray mass spectrometric measurements were performed using LCT time of flight (TOF) mass spectrometer with electrospray ionization (ESI; Micromass LCT). Leucin-enkephalin (10-50 ng/µl) was used as a reference. Potentials of 30-32 V and 3 V for the sample and extraction cones were applied. RF lens was set at a potential of 400-850 V and potential in the capillary at 3000-3300 V. The desolvation temperature was set at 150°C and the source temperature at 100°C.

Table 1. Results of molecular weight determinations by ESI-TOF MS

PCB – starting material	Position of COOH group(s)	Molecular formula	$[M-H]^-$ experimental	$[M-H]^-$ calculated	Δ, ppm
2,4,4’-TriCB	2	$C_{13}H_7O_2Cl_2$	264.9823	264.9823	0.2
2,4,6-TriCB	4	$C_{13}H_7O_2Cl_2$	264.9823	264.9823	0.2
2,4’,5-TriCB	2	$C_{13}H_7O_2Cl_2$	264.9823	264.9823	0.1
2,2’,5,5’-TeCB	5	$C_{13}H_6O_2Cl_3$	298.9447	298.9433	4.7
2,3’,5,5’-TeCB	3’	$C_{13}H_6O_2Cl_3$	298.9432	298.9433	0.5
2,3’,4’,5-TeCB	2, 3’, 4’, 5	$C_{16}H_9O_8$	329.0309	329.0297	3.4
2,2’,3,4,5,5’-HxCB	2	$C_{13}H_4O_2Cl_5$	366.8663	366.8654	2.6

Model compounds: 1,2,3,4-Tetrachloronaphthalene (1,2,3,4-TePCN), 1,2,4,5,6-Pentachloronaphthalene (1,2,4,5,6-PePCN), and 2,2’,4,4’,5-Pentabromodiphenyl ether (2,2’,4,4’,5-PePBDE) (Fig. 2) yielded complex mixtures of polycarboxylic acids. We were unable to isolate individual products from those mixtures. 2,4,8-Trichlorodibenzofuran (2,4,8-TriCDF) underwent complete dechlorination; the product was extremely soluble in water, why instead of the expected 2,4,8-dibenzofurantricarboxylic acid it was suggested to be hydroxydiphenyltricarboxylic acid formed via opening of the furan ring system.

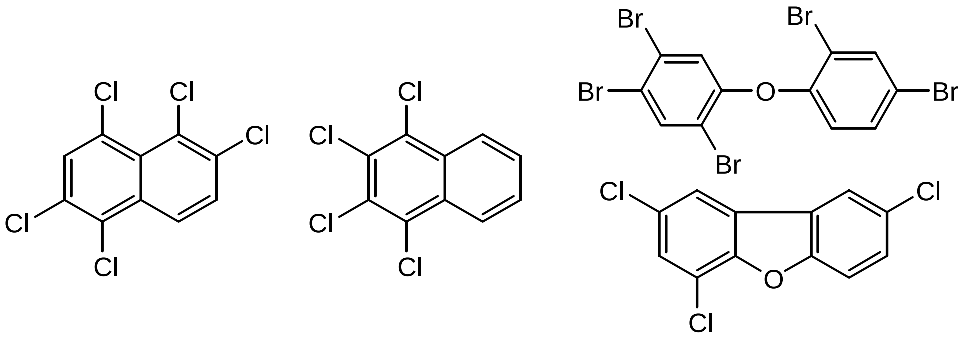

Figure 2. Other model compounds that can be destroyed by carbonylation on Cobalt catalyst

Mechanism of catalytic carbonylation involves electron transfer to a PCB molecule from a Cobalt-containing moiety followed by elimination of chloride with formation of Co-Ar bond; the complex then yields the PCB-carboxylic acid methyl ester, which can be converted into free acid (Fig. 3).

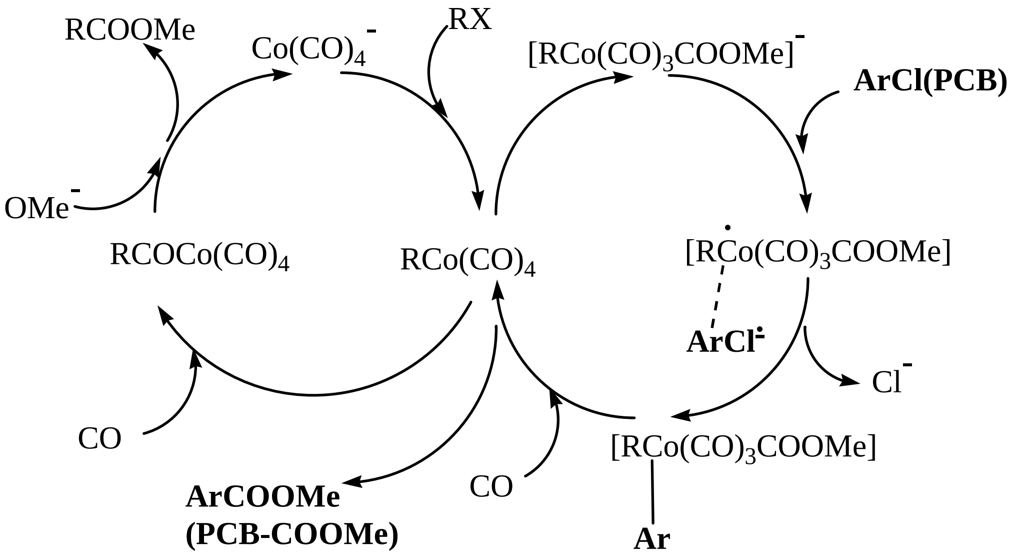

Figure 3. Catalytic cycle of PCB carbonylation

In conclusion, our findings confirm that carbonylation is a method of choice for destruction of PCBs, as well as PCNs or PBDEs. Experiment with 2,4,8-trichlorodibenzofuran demonstrates that the method can be used to produce dioxin-free PCB-polycarboxylic acids.

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