DESTRUCTION OF PCBS AND OTHER POLYHALOGENATED POLYAROMATIC COMPOUNDS VIA CARBONYLATION ON A MODIFIED COBALT CATALYST. II. STRUCTURAL STUDY OF PCB-CARBOXYLIC ACIDS AND CARBONYLATION OF SOVTOL

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Introduction

Destruction and transportation of PCB containing materials and toxic wastes of similar type to the destruction site is restricted in many countries and, therefore, very expensive. Our research is directed towards the development of a safe and flexible carbonylation technology, capable of destruction of polyhalogenaromatic compounds on the spot, with help of a mobile unit. In a previous report we have demonstrated the applicability of our method for destruction of PCBs, PCNs, PBDEs and PBBs[1]. Now we report on structure elucidation of six carboxylic acids, formed via carbonylation of specific PCB congeners.

Materials and methods

Six PCB congeners – 28, 30, 31, 49, 52 and 70 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 cobalt octacarbonyl in 10 ml of methanolic NaOH and 1ml of an activator - propylene oxide - 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.

Reaction products were first checked by ^{1}H NMR in DMSO-d_6 with a Bruker AMX 300. Detailed structural analysis was done with a Bruker Avance DRX 500 spectrometer in acetone-d_6 at 30 °C. Molecular weight was confirmed by performing an accurate mass measurement with a Micromass LCT time of flight (TOF) mass spectrometer with electrospray (ESI) ionization.

Results and Discussion

Structure of PCB-carboxylic acids

Main products of carbonylation of each PCB isomer are shown on Fig. 1.

Selectivity of carbonylation is rather high, though factors that influence on the positional selectivity are unclear. Several empirical rules can be postulated:

- Mono-*orhto*-PCBs (eq. 1 and 4) yield 2-carboxylic acids, thus Cl in *ortho*-position is the most reactive.

- Di-*ortho*-PCBs (eq. 2, 3 and 5) yield *meta*- and *para*-PCB-carboxylic acids; *ortho*-Cl atoms remain intact. No difference is observed between a PCB having both *ortho*-Cl atoms in the same ring and a PCB having the *ortho*-Cl atoms in separate rings.
- Exhaustive carbonylation with substitution of all Cl atoms can be achieved (eq. 6). It is not yet known, whether this PCB congener is much more reactive than others or is it due to difference in catalytic activity of different batches of cobalt carbonyl.
- These results demonstrate that under certain conditions each and every Cl atom can be effectively removed via carbonylation.

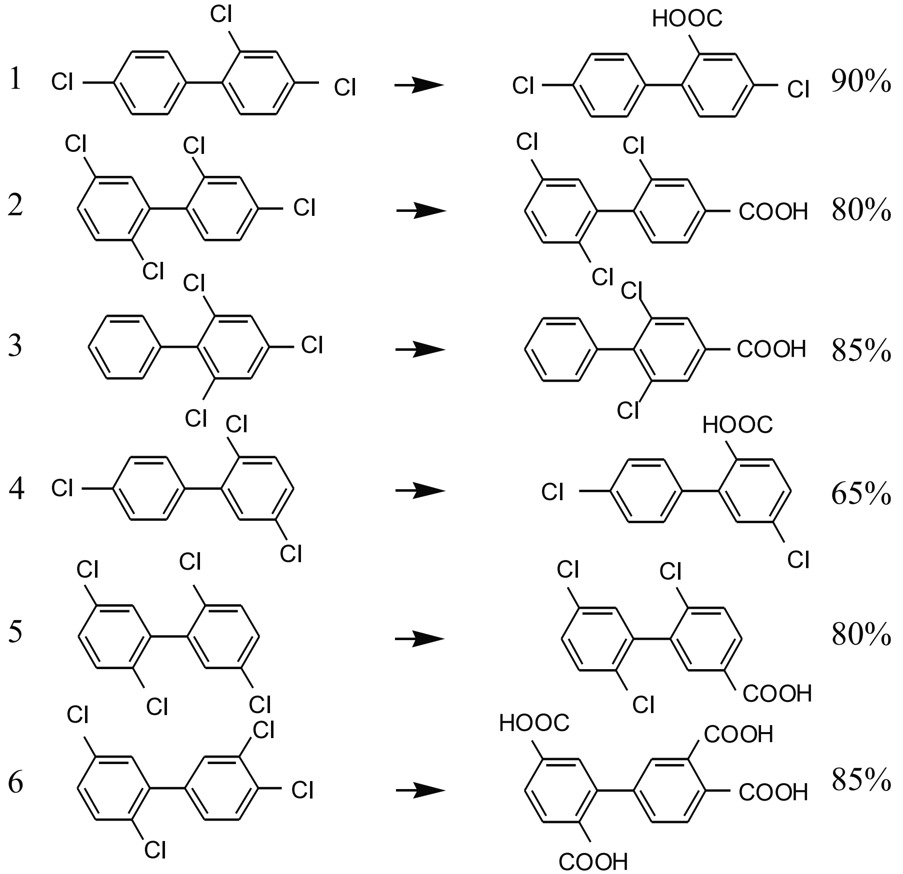

Figure 1. Carboxylic acids from PCBs.

^{1}H and ^{13}C NMR chemical shift assignments are based on Pulsed Field Gradient (PFG) ^{1}H,^{13}C Heteronuclear Multiple Quantum Coherence (HMQC), Heteronuclear Multiple Bond Correlation (HMBC) and PFG DQF ^{1}H,^{1}H COSY measurements with a Bruker Avance DRX 500 spectrometer in acetone-d_6 at 30 ^{o}C. ^{1}H and ^{13}C NMR chemical shifts in ppm from internal TMS are given in Tables 1 and 2.

Table 1. ^{1}H NMR chemical shifts of PCB-derived carboxylic acids (ppm from TMS, acetone-d_6 500 MHz)

Pos. of ^{1}H	1. 4,4’-DiCB-2-carboxylic acid	2. 2,2’,5’-TriCB-4-carboxylic acid *	3. 2,6-DiCB-4-carboxylic acid	4. 4’,5-DiCB-2-carboxylic acid	5. 2,2’5’-TriCB-5-carboxylic acid *	6. 2,3’,4’,5-biphenyltetra carboxylic acid
2	-	-	-	-	-	-
3	7.87d	8.05d	8.07s	7.93d	7.75d	8.06d
4	-	-	-	7.54dd	8.01dd	8.17dd
5	7.64dd	7.98dd	8.07s	-	-	-
6	7.43d	7.53d	-	7.43d	7.85d	8.07d
2’	7.37d	-	7.31d	7.39d	-	7.84d
3’	7.43d	7.66d	7.53t	7.44d	7.65d	-
4’	-	7.58dd	7.48t	-	7.57dd	-
5’	7.43d	-	7.53d	7.44d	-	7.89d
6’	7.37d	7.64d	7.31d	7.37d	7.56d	7.67dd

* - In DMSO-d_6 at 300 MHz

Table 2. ^{13}C NMR chemical shifts of PCB-derived carboxylic acids (ppm from TMS, acetone-d_6 126 MHz)

Position of ^{13}C	1. 4,4’-DiCB-2-carboxylic acid	3. 2,6-DiCB-4-carboxylic acid	4. 4’,5-DiCB-2-carboxylic acid	6. 2,3’,4’,5-biphenyltetra carboxylic acid
1	140.84	144.49	144.25	141.77
2	*	133.95	137.68	136.23
3	130.57	130.04	132.85	131.26
4	134.04*	133.95	128.60	130.01
5	132.12	130.04	137.68	134.15
6	133.47	133.95	131.48	132.58
1’	140.13	137.38	140.01	144.41
2’	131.17	130.04	131.15	130.13
3’	129.09	129.40	129.07	133.97
4’	134.09*	129.49	134.25	132.94
5’	129.09	129.40	129.07	130.11
6’	131.17	130.04	131.15	131.83
<u>C</u>OOH	167.98	165.67	168.30	168.56(2), 168.78(3’), 168.83(4’), 166.72(5)

* - C-2 is overlapping with another (yet unidentified) C. Difference between chemical shifts of C-4 and C-4’ is too small to make unequivocal assignment

Carbonylation of higher chlorinated PCB formulation - Sovtol

In the preceding article we reported on carbonylation of PCB technical product - Sovol-30, commercially produced in the USSR for decades[1]. Sovol-30 is a mixture of PCBs, containing 30 % of chlorine by weight. Conversion of 30 % was achieved; higher chlorinated congeners reacted faster than lower chlorinated ones. It was important to try our method for destruction of another Soviet formulation – Sovtol (or Sovol-50), containing mainly penta- and hexachlorobiphenyls. Under similar conditions more than 95 % of Sovtol was converted into acids[2] (Fig. 2).

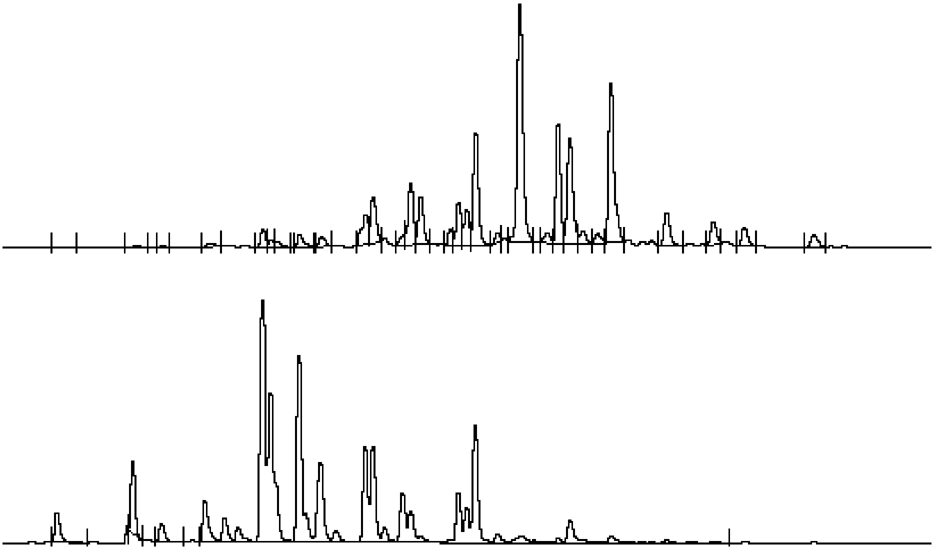

Figure 2. Sovtol before (upper chromatogram) and its remains after (lower chromatogram) carbonylation. The ratio of Y-scales is 50:1 (the upper to the lower).

Thus our findings confirm that carbonylation is a method of choice for destruction of PCBs. Chlorine atoms can be substituted from any position of the aromatic ring. Moreover, complete dechlorination yields Cl-free polycarboxylic acids, which may find some good use.

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