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Uncatalyzed Hydrodechlorination of Dichlorobiphenyls

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Abstract—Mono-, di-, and trichlorobiphenyls showed different reactivities toward alkali in 2-aminoethanol under reflux: 3-chlorobiphenyl remained unchanged, 2,4,5- and 2,4′,5-trichlorobiphenyls were completely converted to hydroxy derivatives, whereas 3,4-dichlorobiphenyl and a mixture of 2,4′-, 3,4′-, and 4,4′-dichlorobiphenyls gave rise to chlorobiphenyls in addition to hydroxybiphenyls.

Keywords: polychlorobiphenyls, congeners, nucleophilic substitution, hydrodechlorination, hydroxy derivatives.

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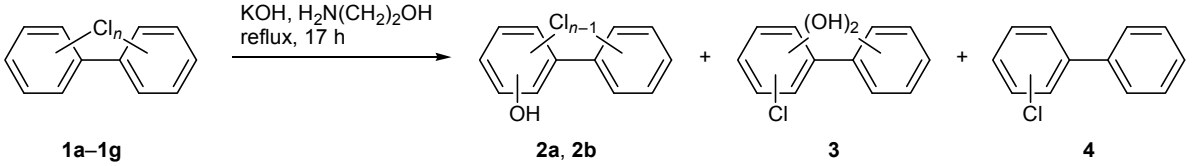
The interdisciplinary approach to the disposal of polychlorinated biphenyls (PCBs), which is developed in recent years, implies initial chemical functionalization of these compounds and subsequent complete mineralization of the new PCB derivatives by the action of bacteria [1, 2]. The microbiological stage involves a problem related to the transportation of PCB derivatives to aquatic habitat of bacteria. Taking into account that PCB congeners are hydrophobic, the first stage of the above approach should produce hydrophilic derivatives. Undoubtedly, introduction of hydroxy groups into PCB molecules should enhance their hydrophilicity. However, conventional alkaline hydrolysis of PCBs (KOH, DMSO, H_2O) does not ensure their complete conversion [3], so that the hydrophilicity of the hydrolysis products is insufficient.

The present work was aimed at studying nucleophilic substitution of chlorine in mono-, di-, and trichlorobiphenyls by the action of alkali in 2-aminoethanol.

The substrates were 3-chlorobiphenyl (PCB 2, **1a**), 3,4-dichlorobiphenyl (PCB 12, **1b**), 2,4,5-trichlorobiphenyl (PCB 29, **1c**), 2,4′,5-trichlorobiphenyl (PCB 31, **1d**), and a mixture of 2,4′-, 3,4′-, and 4,4′-dichlorobiphenyls (PCB 8, PCB 13, PCB 15; **1e**–**1g**) which were prepared by the Gomberg–Bachmann–Hey coupling from the corresponding polychlorobenzenes and polychloroanilines in the presence of isopentyl nitrite [4]. The reactions of all congeners **1a**–**1g** with potassium hydroxide in 2-aminoethanol (2AE) were carried out under similar conditions: PCB–KOH–2AE ratio 1 : 6 : 40, temperature ~170°C (reflux), reaction time 17 h (Scheme 1). The reaction mixture was then acidified with dilute aqueous HCl to pH ≤7 and extracted with toluene, and the extract was analyzed by GC/MS. The components were quantitated by the internal normalization method based on peak areas (Table 1).

It was found that compound **1a** did not react with KOH in 2AE (no any new derivative was detected in the reaction mixture). Unlike **1a**, the conversion of trichlorobiphenyls **1c** and **1d** under the same conditions was complete: compound **1c** was converted to three isomeric dichloro(hydroxy)biphenyls **2b**, and com-

Scheme 1.



1, X = 3-Cl (**a**), 3,4-Cl_2 (**b**), 2,4,5-Cl_3 (**c**), 2,5,4′-Cl_3 (**d**), 2,4′-Cl_2 (**e**), 3,4′-Cl_2 (**f**), 4,4′-Cl_2 (**g**); **2**, n = 2 (**a**); 3 (**b**).

pound **1d** gave rise to a mixture of four isomeric hydroxydichlorobiphenyls **2b** and two isomeric chloro (dihydroxy) biphenyls **3**.

The mass spectra of all dichloro(hydroxy)biphenyl isomers **2b** obtained from **1c** and **1d** were similar: the base peak was that with *m*/*z* 238 $[M]^{+\cdot}$ with an isotope peak ratio corresponding to the number of chlorine atoms in the molecule; also, fragment ion peaks with *m*/*z* 202 $[M - HCl]^{+\cdot}$, 168 $[M - 2Cl]^{+\cdot}$, and 139 $[M - 2Cl - HCO]^{+}$ (relative intensity 20–40%). The mass spectra of chloro(dihydroxy)biphenyls **3** showed a similar pattern. The molecular ion peak with *m*/*z* 220 $[M]^{+\cdot}$ had the maximum intensity, and fragment ion peaks with *m*/*z* 191 $[M - HCO]^{+}$, 184 $[M - HCl]^{+\cdot}$, 157 $[M - Cl - CO]^{+}$, and 128 $[M - HCl - 2CO]^{+}$ with intensities of 10 to 15% were present. The mass spectra of **2b** and **3** coincided with those given in NIST2014 database.

The conversion of **1d** with the chlorine atoms located in both aromatic rings was higher than the conversion of **1c** where all chlorine atoms are located in the same ring. Presumably, nucleophilic substitution of chlorine in **1d** by the action of KOH in 2AE follows two mechanisms, classical S_NAr (*ipso*-substitution) and aryne (*cine*-substitution). In the case of compound **1c**, similar conclusions cannot be regarded as reliable since only three isomers **2b** were isolated. Analogous results were obtained previously in the reactions of 2,4-dichlorobiphenyl (PCB 7) and 2,4,4′-trichlorobiphenyl (PCB 28) with sodium methoxide [5]. Due to the lack of authentic samples, we failed to unambiguously determine the position of substituents in new compounds **2** and **3**.

The results of reactions of **1b** and mixture **1e**–**1g** with KOH in 2AE were more surprising. The conversion of **1b** (both chlorine atoms are located in the same benzene ring) was complete, whereas congeners **1e**–**1g** (chlorine atoms are located in different rings) were converted by 53%. The initial ratio **1e**/**1f**/**1g** was ~62:28:10, whereas the product ratio was 79:16:5; i.e., the conversion of **1g** (PCB 15) was the highest, and the conversion of **1e** (PCB 8, nonplanar *ortho*-substituted biphenyl) was the lowest.

Both **1b** and **1e**–**1g** were converted mainly to chloro(hydroxy)biphenyls **2a**, but in both cases relatively large amounts of chlorobiphenyls **4** were detected. In the mass spectra of **2a** formed from **1b** and **1e**–**1g**, the base peaks were those with *m*/*z* 204 $[M]^{+\cdot}$, and low-intense (I_{rel} 5–10%) fragment ion peaks with *m*/*z* 168 $[M - HCl]^{+\cdot}$ and 141 $[M - Cl - CO]^{+}$ were observed. The mass spectra of **2a** were generally consistent with the mass spectra of structurally related compounds included in the NIST2014 database.

Table 1. Reactions of compounds **1b**–**1g** with potassium hydroxide in 2-aminoethanol

Initial comp. no.	Product no.	Number of isomers	Concentration, %	Conversion, %
1b	**4**	2	17.7	100
	2a	2	82.3	
1e–**1g**	**4**	2	5.0	53
	2a	4	47.9	
1c	**2b**	3	100	100
1d	**2b**	4	95.7	100
	3	2	4.3	

Obviously, monochlorobiphenyls **4** are formed as a result of uncatalyzed hydrodechlorination of **1b** and **1e**–**1g**. On the basis of analytical and chromatographic data [6], compounds **4** were identified as 3-chlorobiphenyl (**1a**, PCB 2) and 4-chlorobiphenyl (PCB 3), which confirmed the low reactivity of **1e** (PCB 8).

As a rule, high conversion in the hydrodechlorination of chloroarenes is attained in the presence of metal catalysts, palladium ones being the most efficient [7–9]. The source of hydrogen for the reductive dehalogenation may be both external (gas cylinder or generator) and internal (generated *in situ*). Organic compounds belonging to different classes, such as alkanes, alcohols, hydrazines, etc., can act as an internal hydrogen source. Uncatalyzed hydrodechlorination of chloroarenes in the presence of an internal hydrogen source requires harsh conditions, e.g., supercritical fluids [10].

Catalytic hydrodechlorination of chloroarenes by the action of alkalies in propan-2-ol has been studied in sufficient detail [11–14]. In these studies, the substrates were polychlorobenzenes, PCBs, and polychlorinated dibenzodioxins and dibenzofurans. It was found that in the hydrodechlorination of chloroarenes over Pd/C, Rh/C, or Rh–Pt/C as catalyst, the source of hydrogen (more precisely hydride ion), is the solvent (α-hydrogen atoms in *i*-PrOH). This was confirmed by using deuterium-labeled alcohols in the reductive dechlorination [12]. Initially, an alcohol molecule is coordinated on the solid catalyst surface through lone electron pairs on the hydroxy oxygen atom, which increases the lability of α-hydrogen atoms in *i*-PrOH and enhances their intermolecular bonds with chlorine

atoms of chloroarenes. Next follow cleavage of the C_{arom}–Cl bond in the chloroarene and of the C_{sp^3}–H bond in the alcohol and exchange of Cl^- for H^-.

In our case, the hydrodechlorination of **1b** and **1e**–**1g** occurred in the absence of a catalyst which could coordinate 2-aminoethanol as the only source of hydrogen. In addition, the reaction conditions do not favor formation of potassium 2-aminoethoxide. Alkali metal alkoxides derived from polyalkanolamines are usually obtained from organic lithium, sodium, or potassium compounds at low temperature in a dry inert atmosphere [15]. The nucleophilic aromatic substitution mechanism (S_NAr) implies elimination of Cl^- (*ipso*, *cine*) or H^+ (*cine*) from chloroaromatic substrate. Free chloride ions can be neutralized with KOH to form KCl or with H^+ to give HCl. Presumably, hydrogen chloride generated *in situ* protonates 2-aminoethanol, which is partially converted to ammonium salt $[HO(CH_2)_2NH_3]^+ Cl^-$ with radically different electron density distribution in comparison to neutral 2AE. The dipole moment of the latter is 2.30 D [16], and the terminal heteroatoms therein (nitrogen and oxygen) each possess lone electron pairs. The polarity of $[HO(CH_2)_2NH_3]^+$ is likely to be higher than that of 2AE since the charge density on the oxygen atom increases. Probably, just this factor makes the α-hydrogen atoms in the salt more labile, so that they are coordinated to **1b** or **1e**–**1g**, and the subsequent hydrodechlorination scheme becomes consistent with the data of [11–14].

To conclude, we have found that reactions of some dichlorobiphenyls with alkali in 2-aminoethanol, apart from those following S_NAr mechanism, lead to the formation hydrodechlorination products. The obtained results require further study.

The mass spectra (electron impact, 70 eV) were recorded in the range 20–1000 a.m.u. on an Agilent 7890A/5975C inert XL EI/CI GC/MS system using an HP-5MS quartz capillary column.

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CONFLICT OF INTERESTS

The authors declare the absence of conflict of interests.

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