

# Regularities of Pd/C-Catalyzed Reduction of Trichlorobiphenyls with 2-Propanol in Basic Medium

E. A. Kostenko<sup>a</sup>, E. V. Eliseenkov<sup>b</sup>, and A. A. Petrov<sup>b\*</sup>

<sup>a</sup> St. Petersburg State Institute of Technology (Technical University), St. Petersburg, Russia

<sup>b</sup> St. Petersburg State University, Universitetskaya nab. 7–9, St. Petersburg, 199034 Russia

\*e-mail: aap1947@yandex.ru

Received June 15, 2017

**Abstract**—Reduction of a series of trichlorobiphenyls with 2-propanol in basic medium catalyzed by Pd/C has been studied. Regioselectivity of the reduction has been determined. In the studied cases, the chlorine atom in para or meta positions of the more substituted ring has been more reactive. Using isotope labeling, it has been demonstrated that the reaction occurs via the stage of 2-propanol dehydration on palladium catalyst, followed by catalytic hydrogenation of the polychlorinated biphenyls.

**Keywords:** polychlorinated biphenyls, catalytic hydrogenation, relative reactivity, regioselectivity, isotope labeling, reduction mechanism

**DOI:** 10.1134/S1070363217080023

Polychlorinated biphenyls (substituted biphenyls containing 1 to 10 chlorine atoms,  $C_{12}H_{10-n}Cl_n$  with  $n = 1–10$ ) belong to the class of synthetic organochlorine compounds. 209 known individual polychlorinated biphenyls (congeners) are different in the number and positions of chlorine atoms in the biphenyl structure. Commercial biphenyls are complex mixtures of 50–70 congeners. They have been recognized for a set of unique physicochemical properties such as thermal stability, resistance to oxidation, poor solubility in water, and good solubility in hydrocarbons and fats, due to which polychlorinated biphenyls are widely used in many industrial fields [1–3].

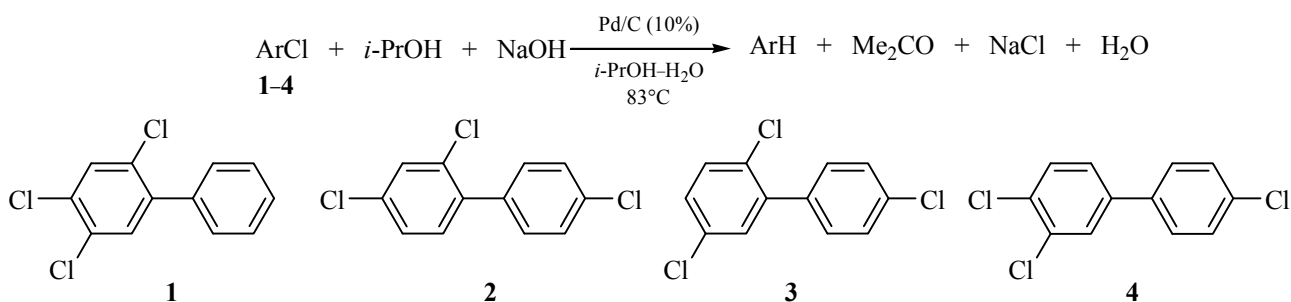
Unfortunately, these compounds are toxic. They can be transferred to a far location via air, water, or food chains and can get into an organism via contact with skin (absorption), inhalation (breathing), or ingestion, causing damage of immune, endocrine, and nervous systems and some other diseases. Since polychlorinated biphenyls are water-insoluble and resistant against chemical and biological degradation, they are accumulated in the environment for years. Production of polychlorinated biphenyls has been banned but they still pollute the environment, mainly due to leakages from old hardware and liquid industrial wastes dumping [4]. Therefore, development of efficient and cheap methods of chemical utilization of

concentrated polychlorinated biphenyls remains an open issue. Their transformation into safer chemicals has been found advantageous over combustion. The transformation methods include nucleophilic substitution of chlorine atoms with hydroxyl or alkoxy groups [5–11], carbonylation affording diphenylpolycarboxylic acids [12–14], and reduction into biphenyl [15–23]. It should be noted that mechanism and regioselectivity of carbonylation [24, 25], solvolysis [11, 26, 27], and anion-radical reduction [28–30] have been studied in detail for certain individual congeners, whereas the studies of the catalytic reduction have been limited to applied research on reduction of the technical mixtures.

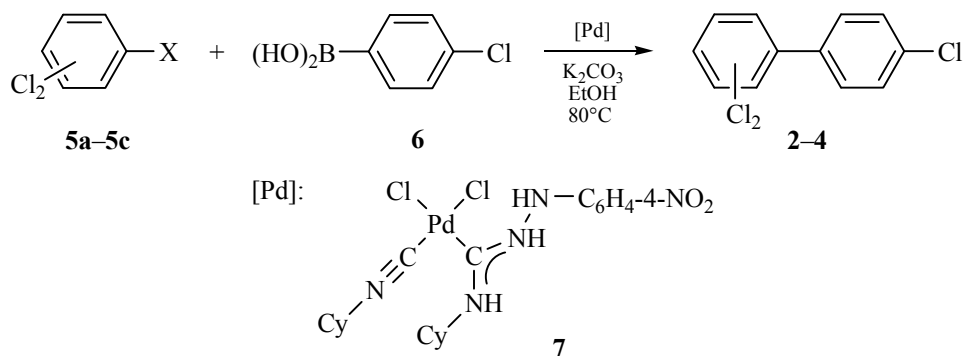
The available reference data on the mechanism of palladium-catalyzed hydrodechlorination of aryl chlorides with 2-propanol in basic medium are controversial. The anion-radical mechanism has been suggested, at least in the presence of triethylamine as the base [31]. Alternatively, dehydration of 2-propanol into acetone on Pd catalyst, followed by hydrogenation of aryl chloride with the released hydrogen has been postulated [32–36].

Determination of the reaction regioselectivity using low-chlorinated congeners as substrate is a convenient method of elucidation of the mechanism of polychlorinated biphenyls reactions. Herein, we studied

Scheme 1.



Scheme 2.



X = Br, Cl<sub>2</sub> = 2,4-Cl<sub>2</sub> (**5a**); X = I, Cl<sub>2</sub> = 2,5-Cl<sub>2</sub> (**5b**); X = I, Cl<sub>2</sub> = 3,4-Cl<sub>2</sub> (**5c**).

regioselectivity of reduction of trichlorobiphenyls **1–4** with 2-propanol in basic medium catalyzed by Pd/C (Scheme 1).

The choice of the substrates was based on the fact that they were the least chlorinated components of Sovol and Sovtol commercial mixtures and the major components of the Triklorbifenil mixture. Moreover, trichlorinated biphenyls always contain differently substituted benzene rings which is important for the investigation of regularities of catalytic reduction of polychlorinated biphenyls. The reaction was stopped at incomplete conversion to determine the major product of the reduction of a single chlorine group.

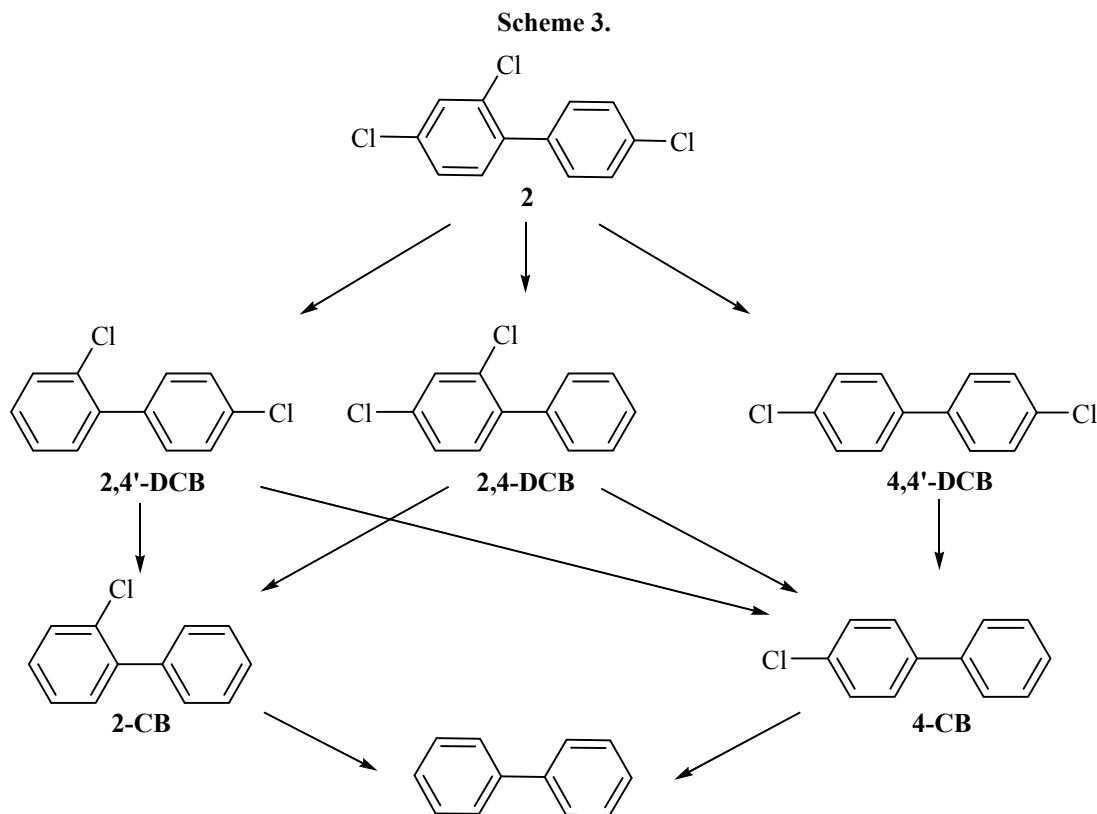
Individual congeners of polychlorinated biphenyls **2–4** were synthesized via the Suzuki reaction [11] from polyhalogenated benzenes **5** and 4-chlorophenylboronic acid **6** (Scheme 2). Acyclic diaminocarbene complex of palladium (complex **7**) was used as the catalyst [37–40].

Hydrodechlorination reactions of isomeric trichlorobiphenyls are illustrated in Scheme 3 by these of compound **2**. The considered reactions are complex processes involving several sequential and parallel stages. The first stage of the process consists in the

competing hydrodechlorination of one of the three nonequivalent chlorine atoms in the substrate to form three isomeric dichlorobiphenyls (**DCB**). The second hydrodechlorination stage yields isomeric monochlorobiphenyls (**CB**). The final product of hydrodechlorination is biphenyl.

Reduction of isomeric trichlorobiphenyls with 10% palladium on active carbon (Pd/C) was performed under conditions adopted from [32], the first report to describe the use of such system for hydrodechlorination of polychlorinated biphenyls. The experiments at low conversion of the substrates were used to elucidate the regioselectivity of the first stage of hydrodechlorination, whereas the experiments at high conversion served to optimize the conditions of complete reduction of the substrates into biphenyl. The conversion was adjusted by changing the reaction duration or the catalyst amount.

Chromato–mass spectrometry (GLC–MS) was used as the primary method to investigate the regioselectivity. That highly sensitive method allowed group identification of the peaks corresponding to isomeric di- and monochlorinated biphenyls. Identification of the individual isomers involved comparison of



the retention times of the reaction mixture components with those of the references (either commercially available or synthesized).

Regioselectivity of hydrodechlorination of trichlorobiphenyls is the ratio of the accumulation rates of the corresponding dichlorobiphenyls in the reaction mixture under conditions preventing their deeper reduction (for example, at low conversion, 3–7% in this work). It was determined from the areas of the peaks of the corresponding dichlorobiphenyls. That method could not be applied for 2,4,5-trichlorobiphenyl **1** and 3,4,4'-trichlorobiphenyl **4**, since some of the formed products (2,4- and 2,5-dichlorobiphenyls for compound **1**; 3,4- and 3,4'-dichlorobiphenyls for compound **4**) exhibited practically equal retention times. The attempts to elaborate the conditions of their separation by chromatography failed. Therefore, the data on regioselectivity of hydrodechlorination of isomeric trichlorobiphenyls were limited to congeners **2** and **3** (Scheme 4).

The obtained results suggested that chlorine atoms in the *para* or *meta* position of the more substituted benzene ring were the most reactive sites of the substrate.

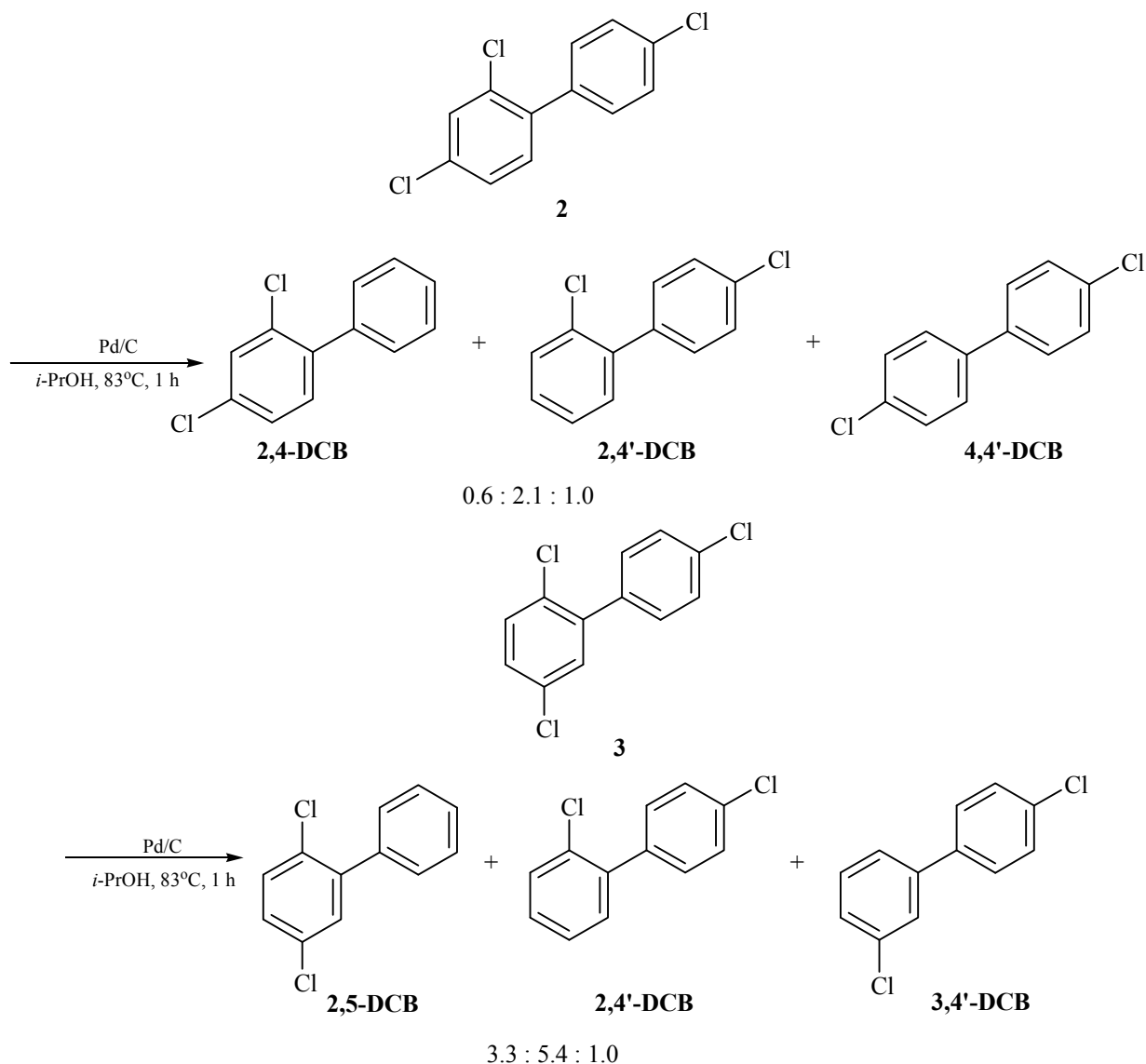
The obtained data contradicted the common regularities of anion-radical reactions. In the case of intermediate formation of anion-radicals of polyhaloarenes,

the reaction occurs predominantly at the halogen atom in the *ortho* position to the substituent, irrespectively of the sign of the substituent electronic effects [25, 29, 30, 41]. At the same time, the opposite regioselectivity has been revealed for the metal-catalyzed reactions involving the coordinated oxidative addition of the aryl halide to the metal: the *ortho*-substituents decelerate the process [41, 42] (as was observed in this study). Hence, it was suggested that Pd/C-catalyzed hydrodechlorination of polychlorinated biphenyls with 2-propanol in basic medium occurred via dehydration of 2-propanol on the catalyst, followed by catalytic hydrogenation of the chlorinated substrate.

That was additionally confirmed by the investigation of reduction of congener **3** with 2-propanol enriched with deuterium at the hydroxy group (i.e. a mixture of *i*-PrOH and *i*-PrOD). Mass-spectrometric analysis of the isotopic distribution of hydrogen in the reduction products revealed that the content of deuterium in the hydrodechlorination reaction products exceeded its natural occurrence. The enrichment of 2,4',5-trichlorobiphenyl hydrodechlorination products with deuterium was calculated as follows:

$$\% \text{ D} = \frac{I_{\text{rel(D)}} - I_{\text{rel(H)}}}{100 - I_{\text{rel(H)}}} \times 100\%, \quad (1)$$

Scheme 4.



where  $I_{\text{rel(D)}}$  and  $I_{\text{rel(H)}}$  being the relative intensities of the  $[M + 1]/[M]$  peaks for the compounds prepared using deuterium-enriched and conventional 2-propanol, respectively.

Enrichment of 2-propanol with deuterium was performed using two different procedures (cf. Experimental). The data on the reduction products analysis are collected in Tables 1 and 2. The enrichment of the reduction products with deuterium contained exclusively in the hydroxy group of the alcohol confirmed the reaction pathway via the dehydration of 2-propanol.

#### EXPERIMENTAL

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker Avance II+ spectrometer [400.13 MHz ( $^1\text{H}$ )

and 100.61 MHz ( $^{13}\text{C}$ )] in  $\text{CDCl}_3$ . The chemical shifts were measured relative to the residual protons and carbon atoms of the solvent. Gas-liquid chromatography (GLC) analysis was performed using a Khromatel Kristall 5000.2 instrument equipped with a flame ionization detector and a VRKh-1 capillary column (10 m  $\times$  0.53 mm  $\times$  2.65  $\mu\text{m}$ ). Chromato-mass spectrometry analysis was performed using a Shimadzu GCMS QP-2010 SE instrument under the following conditions: EI at 70 eV, scanning over  $m/z$  50–500, detector temperature 220°C, Rtx-5MS column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ ), argon as the carrier gas (0.8 mL/min).

Inorganic chemicals (“chemically pure or “analytically pure” grade) were purchased from Vekton and Merck. Solvents (“chemically pure or “analytically

**Table 1.** Calculation of enrichment with deuterium of the products of congener **3** reduction with *i*-PrOD prepared via method *a*<sup>a,b</sup>

Reduction product	$I_{\text{rel(D)}}$	$I_{\text{rel(H)}}$	$I_{\text{rel(D)}} - I_{\text{rel(H)}}$	% D
2,5-Dichlorobiphenyls	24.09±0.16	12.45±0.08	11.64±0.18	13.3±0.2
2,4'-Dichlorobiphenyls	28.80±0.90	13.23±0.41	15.57±0.99	17.9±1.1
3,4'-Dichlorobiphenyls	36.40±1.09	14.57±0.44	21.83±1.18	25.6±1.3

<sup>a</sup> Deuterium-enriched 2-propanol was prepared using method *a*. <sup>b</sup> Conversion of congener **3** was 0.6%.

**Table 2.** Calculation of enrichment with deuterium of the products of congener **3** reduction with *i*-PrOD prepared via method *b*<sup>a,b</sup>

Reduction product	$I_{\text{rel(D)}}$	$I_{\text{rel(H)}}$	$I_{\text{rel(D)}} - I_{\text{rel(H)}}$	% D
2,5-Dichlorobiphenyls	15.86±0.10	12.45±0.08	3.41±0.13	3.9±0.2
2,4'-Dichlorobiphenyls	17.14±0.90	13.23±0.41	3.91±0.67	4.5±0.8
Biphenyl	23.62±0.73	13.19±0.13	10.43±0.74	12.0±0.8

<sup>a</sup> Deuterium-enriched 2-propanol was prepared using method *a*. <sup>b</sup> Conversion of congener **3** was 97%.

pure” grade) were used as received. Commercial halogenated benzenes, 4-chlorophenylboronic acid, 4,4'-dibromobiphenyl, 2,4-dichlorobiphenyl, 3,4-dichlorobiphenyl, and 2,4,5-trichlorobiphenyl (Vekton) were used as received; their purity was confirmed by <sup>1</sup>H NMR and GLC. The catalyst for Suzuki reaction was prepared as described elsewhere [37–40]. The catalyst for hydrodechlorination reactions (10% palladium on active carbon) was purchased from Acros Organics.

**4,4'-Dichlorobiphenyl** [43]. A mixture of 624 mg (2 mmol) of 4,4'-dibromobiphenyl and 2 g (20 mmol) of CuCl in 10 mL of anhydrous DMF was refluxed during 8 h at stirring. The solvent was distilled off at a water-jet pump vacuum, and the residue was extracted with chloroform. The extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated. The obtained crystals were recrystallized from 96% ethanol. Yield 63% (290 mg), colorless crystals, mp 151–152°C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.43 and 7.50 (8H, AA'XX' system,  $J = 8.6$  Hz). <sup>13</sup>C NMR spectrum,  $\delta_{\text{C}}$ , ppm: 128.19 (C<sup>2,6,2',6'</sup>), 129.08 (C<sup>3,5,3',5'</sup>), 133.80 (C<sup>4,4'</sup>), 138.47 (C<sup>1,1'</sup>).

**2,4,4'-Trichlorobiphenyl** [44]. A 15 mL screw-top glass tube was loaded with 4 mL of 96% ethanol, 226 mg (1 mmol) of 1-bromo-2,4-dichlorobenzene, 172 mg (1.1 mmol) of 4-chlorophenylboronic acid, and 207 mg (1.5 mmol) of anhydrous K<sub>2</sub>CO<sub>3</sub>. The tube was put in an oil bath heated to 78°C. The reaction mixture was stirred during 3 min, and then 0.7 mg (0.0012 mmol) of acyclic diaminocarbene complex of palladium **7** in

0.5 mL of ethanol was added. The tube was tightly screwed and stirred during 2.5 h at 83°C. The mixture was then cooled to ambient, 10 mL of water was added, and the reaction product was extracted with a 2 : 1 hexane–dichloromethane mixture (3×20 mL), the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated, and the residue was weighed and analyzed by <sup>1</sup>H NMR and GLC. Yield 252 mg (98%), mp 56°C (methanol). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.25 d (1H, H<sup>6</sup>,  $J = 8.2$  Hz), 7.32 d.d (1H, H<sup>5</sup>,  $J = 8.2, 2.0$  Hz), 7.37 and 7.43 (4H, AA'XX' system, H<sup>2',3',5',6'</sup>,  $J = 8.5$  Hz), 7.51 d (1H, H<sup>3</sup>,  $J = 2.0$  Hz).

**2,5,4'-Trichlorobiphenyl** [45] was prepared similarly from 546 mg (2 mmol) of 1-iodo-2,5-dichlorobenzene and 344 mg (2.2 mmol) of 4-chlorophenylboronic acid. Yield 508 mg (98.6%), crude product was recrystallized from methanol, yield 420 mg (81.5%), purity >99.6% (GLC–MS), mp 66°C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.30 d.d (1H, H<sup>4</sup>,  $J = 8.5, 2.5$  Hz), 7.33 d (1H, H<sup>6</sup>,  $J = 2.5$  Hz), 7.39 and 7.43 (4H, AA'XX' system, H<sup>2',3',5',6'</sup>,  $J = 8.6$  Hz), 7.42 d (1H, H<sup>3</sup>,  $J = 8.6$  Hz). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 128.48 (C<sup>2',6'</sup>), 128.82 (C<sup>4</sup>), 130.63 (C<sup>3',5'</sup>), 130.79 (C<sup>2</sup>), 130.99 (C<sup>6</sup>), 131.14 (C<sup>3</sup>), 132.73 (C<sup>5</sup>), 134.31 (C<sup>4'</sup>), 136.55 (C<sup>1</sup>), 140.76 (C<sup>10</sup>).

**3,4,4'-Trichlorobiphenyl** [46] was prepared similarly from 410 mg (1.5 mmol) of 1-iodo-3,4-dichlorobenzene and 258 mg (1.65 mmol) of 4-chlorophenylboronic acid. Crude product yield 359 mg (92.9%), mp 88–89°C (methanol). <sup>1</sup>H NMR spectrum,

$\delta$ , ppm: 7.39 d.d (1H, H<sup>6</sup>,  $J = 8.4, 2.1$  Hz), 7.44 and 7.49 (4H, AA'XX' system,  $J = 8.6$  Hz), 7.52 (1H, H<sup>5</sup>,  $J = 8.4$  Hz), 7.65 d (1H, H<sup>2</sup>,  $J = 2.1$  Hz). <sup>13</sup>C NMR spectrum,  $\delta_c$ , ppm: 126.18 (C<sup>6</sup>), 128.20 (C<sup>3',5'</sup>), 128.81 (C<sup>4</sup>), 129.20 (C<sup>2',6'</sup>), 130.81 (C<sup>5</sup>), 131.84 (C<sup>4</sup>), 133.03 (C<sup>3</sup>), 134.35 (C<sup>4</sup>), 137.21 (C<sup>1</sup>), 139.98 (C<sup>1</sup>).

**2,4'-Dichlorobiphenyl** [47] was prepared similarly from 192 mg (1 mmol) of 2-bromochlorobenzene and 172 mg (1.1 mmol) of 4-chlorophenylboronic acid. Crude product yield 198 mg (89%), mp 44–45°C (*n*-hexane). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.28–7.34 m (3H, H<sup>4,5,6</sup>), 7.41 and 7.43 (4H, AA'XX' system,  $J = 8.7$  Hz), 7.48–7.52 m (1H, H<sup>3</sup>). <sup>13</sup>C NMR spectrum,  $\delta_c$ , ppm: 126.89 (C<sup>5</sup>), 128.27 (C<sup>2',6'</sup>), 128.82 (C<sup>4</sup>), 130.04 (C<sup>6</sup>), 130.77 (C<sup>3',5'</sup>), 131.16 (C<sup>3</sup>), 132.49 (C<sup>2</sup>), 133.77 (C<sup>4</sup>), 137.82 (C<sup>1</sup>), 139.40 (C<sup>1</sup>).

#### Determination of regioselectivity of reduction.

The reaction was performed with a small amount (3–4 mg) of a substrate with purity of at least 99% in 2-propanol medium (1–1.5 mL) in the presence of excess of solid alkali (NaOH or KOH) and the required amount of Pd/C catalyst, refluxing the mixture on an oil bath (83°C). 0.1–0.3 mL of the reaction mixture was sampled, diluted with 1–2 mL of water, and extracted with 1–4 mL of a 2 : 1 hexane–methylene chloride mixture. The organic layer was sampled, dried over sodium sulfate, and analyzed by means of GLC–MS. The regioselectivity was determined from the results of the experiments with the trichlorobiphenyl conversion not exceeding 7%.

**Preparation of deuterium-enriched isopropanol (CH<sub>3</sub>)<sub>2</sub>CHOD.** *a.* 0.26 g of Na was dissolved in 7.5 mL of *i*-PrOH at boiling. Excess of *i*-PrOH was distilled off at a vacuum as azeotrope with *n*-hexane and then as azeotrope with toluene; the obtained *i*-PrONa was introduced in the reaction with D<sub>2</sub>O (D content at least 99.8%). The prepared suspension of NaOD in *i*-PrOD was mixed with anhydrous 2-propanol and used in the reaction of hydridechlorination of congener **3**.

*b.* 0.70 g of Na was dissolved in 1.5 mL of *i*-PrOH at boiling. The reaction mixture was cooled down, and 90 mg of D<sub>2</sub>O (D content at least 99.8%) was added. The obtained mixture was used for hydridechlorination of congener **3**.

#### ACKNOWLEDGMENTS

This study was financially supported by St. Petersburg State University (grant no. 12.37.214.2016).

The experiments were performed using the equipment of Resource Centers of St. Petersburg State University: “Magnetic Resonance Methods” and “Education Resource Center for Chemistry field.”

#### REFERENCES

- Zanaveskin, L.N. and Aver'yanov, V.A., *Russ. Chem. Rev.*, 1998, vol. 67, no. 8, p. 713.
- Gorbunova, T.I., Saloutin, V.I., and Chupakhin, O.N., *Russ. Chem. Rev.*, 2010, vol. 79, no. 6, p. 511. doi 10.1070/RC2010v079n06ABEH004047
- Robinson, G.K. and Lenn, M.J., *Biotechnol. Gen. Engineer. Rev.*, 1994, vol. 12, p. 139. doi 10.1080/02648725.1994.10647911
- Praveckova, M., Brennerova, M.V., Holliger, C., Alencastro, F.D., and Rossi, P., *Front. Microbiol.*, 2016, vol. 7, p. 1. doi 10.3389/fmicb.2016.00933
- Ostanina, N.Yu., Dul'tseva, L.D., Suvorov, A.L., and Chupakhin, O.N., *Russ. J. Appl. Chem.*, 2002, vol. 75, no. 5, p. 814. doi 10.1023/A:1020379016869
- Zabelina, O.N., Gorbunova, T.I., Pervova, M.G., Kirichenko, V.E., Zapevalov, A.Ya., Saloutin, V.I., and Chupakhin, O.N., *Russ. J. Appl. Chem.*, 2004, vol. 77, no. 9, p. 1523. doi 10.1007/s11167-005-064-y
- Zabelina, O.N., Pervova, M.G., Kirichenko, V.E., Yatluk, Yu.G., and Saloutin, V.I., *Russ. J. Appl. Chem.*, 2006, vol. 79, no. 5, p. 791. doi 10.1134/S1070427206050181
- Gorbunova, T.I., Pervova, M.G., Trushina, E.B., Pavlyshko, S.V., Zapevalov, A.Ya., and Saloutin, V.I., *Russ. J. Appl. Chem.*, 2012, vol. 85, no. 10, p. 1622. doi 10.1134/S1070427212100254
- Gorbunova, T.I., Pervova, M.G., Saloutin, V.I., and Chupakhin, O.N., *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 1, p. 138. doi 10.1134/S1070363212010227
- Gorbunova, T.I., Subbotina, Yu.O., Saloutin, V.I., and Chupakhin, O.N., *Russ. J. Gen. Chem.*, 2014, vol. 84, no. 3, p. 486. doi 10.1134/S107036321403013X
- Khaibulova, T.Sh., Boyarskaya, I.A., Polukeev, V.A., and Boyarskii, V.P., *Russ. J. Gen. Chem.*, 2016, vol. 86, no. 10, p. 2318. doi 10.1134/S1070363216100121
- Lanina, S.A., Boyarskii, V.P., Zhesko, T.E., Nikiforov, V.A., and Bart, T.Ya., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 1, p. 127. doi 10.1134/S1070363208010210
- Zhesko, T.E., Boyarskii, V.P., Lanina, S.A., Nikitina, A.G., and Tereshchenko, G.F., *Petroleum Chem.*, 2007, vol. 47, no. 4, p. 268. doi 10.1134/S0965544107040068
- Boyarskii, V.P., Zhesko, T.E., Lanina, S.A., and Tereshchenko, G.F., *Russ. J. Appl. Chem.*, 2007, vol. 80, no. 7, p. 1090. doi 10.1134/S1070427207070154
- Sajiki, H., Kume, A., Hattori, K., Nagase, H., and Hirota, K., *Tetrahedron Lett.*, 2002, vol. 43, p. 7251. doi 10.1016/S0040-4039(02)01620-9

16. Kume, A., Monguchi, Y., Hattori, K., Nagase, H., and Sajiki, H., *Appl. Catal. (B)*, 2008, vol. 81, p. 274. doi 10.1016/j.apcatb.2007.12.019
17. Ishihara, S., Idob, A., Monguchia, Y., Nagase, H., and Sajiki, H., *J. Hazard. Mater.*, 2012, vols. 229–230, p. 15. doi 10.1016/j.jhazmat.2012.05.005
18. Ido, A., Ishihara, S., Kume, A., Nakanishi, T., Monguchi, Y., Sajiki, H., and Nagase, H., *Chemosphere*, 2013, vol. 90, p. 57. doi 10.1016/j.chemosphere.2012.06.074
19. Yanga, B., Denga, S., Yua, G., Zhang, H., Wuc, J., and Zhuo, Q., *J. Hazard. Mater.*, 2011, vol. 189, p. 76. doi 10.1016/j.jhazmat.2011.02.001
20. De Vor, R., Carvalho-Knighton, K., Aitken, B., Maloney, P., Holland, E., Talalaj, L., Fidler, R., Elsheimer, S., Clausen, C.A., and Geiger, C.L., *Chemosphere*, 2008, vol. 73, p. 896. doi 10.1016/j.chemosphere.2008.07.006
21. Agarwal, S., Al-Abed, S.R., and Dionysiou, D.D., *Environ. Sci. Technol.*, 2007, vol. 41, p. 3722. doi 10.1021/es062886y
22. Agarwal, S., Al-Abed, S.R., Dionysiou, D.D., and Graybill, E., *Environ. Sci. Technol.*, 2009, vol. 43, no. 3, p. 915. doi 10.1021/es802538d
23. Mekhaev, A.V., Butin, F.N., Pervova, M.G., Taran, O.P., Simakova, I.L., and Parmon, V.N., *Russ. J. Org. Chem.*, 2014, vol. 50, no. 6, p. 900. doi 10.1134/S1070428014060244
24. Boyarskii, V.P., Zhesko, T.E., and Tvorogov, K.E., *Russ. J. Org. Chem.*, 2007, vol. 43, no. 12, p. 1760. doi 10.1134/S1070428007120044
25. Khaibulova, T.S., Boyarskaya, I.A., Larionov, E., and Boyarskiy, V.P., *Molecules*, 2014, vol. 19, no. 5, p. 5876. doi 10.3390/molecules19055876
26. Gorbunova, T.I., Pervova, M.G., Saloutin, V.I., and Chupakhin, O.N., *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 1, p. 138. doi 10.1134/S1070363212010227
27. Gorbunova, T.I., Subbotina, Yu.O., Saloutin, V.I., and Chupakhin, O.N., *Russ. J. Gen. Chem.*, 2014, vol. 84, no. 3, p. 486. doi 10.1134/S107036321403013X
28. Boyarskii, V.P., Sangaranarayanan, M.V., Khaibulova, T.Sh., and Boyarskaya, I.A., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 4, p. 800. doi 10.1134/S1070363210040201
29. Muthukrishnan, A., Sangaranarayanan, M.V., Boyarskiy, V.P., and Boyarskaya, I.A., *Chem. Phys. Lett.*, 2010, vol. 490, nos. 4–6, p. 148. doi 10.1016/j.cplett.2010.03.042
30. Muthukrishnan, A., Boyarskiy, V., Sangaranarayanan, M.V., and Boyarskaya, I., *J. Phys. Chem. (C)*, 2012, vol. 116, no. 1, p. 655. doi 10.1021/jp2066474
31. Monguchi, Y., Kume, A., Hattori, K., Maegawa, T., and Sajiki, H., *Tetrahedron*, 2006, vol. 62, p. 7926. doi 10.1016/j.tet.2006.05.025
32. Ukisu, Y., Iimura, S., and Uchida, R., *Chemosphere*, 1996, vol. 33, no. 8, p. 1523. doi 10.1016/0045-6535(96)00290-1
33. Ukisu, Y. and Miyadera, T., *J. Mol. Catal. (A)*, 1997, vol. 125, p. 135. doi 10.1016/S1381-1169(97)00092-7
34. Ukisu, Y. and Miyadera, T., *Appl. Catal. (B)*, 2003, vol. 40, p. 141. doi 10.1016/S0926-3373(02)00148-0
35. Ukisu, Y., *Appl. Catal. (A)*, 2008, vol. 349, p. 229. doi 10.1016/j.apcata.2008.07.040
36. Ukisu, Y., *Reac. Kinet. Mech. Cat.*, 2010, vol. 100, p. 93. doi 10.1007/s11144-010-0176-0
37. Miltsov, S.A., Karavan, V.S., Boyarskiy, V.P., Gómez de Pedro, S., Alonso-Chamarro, J., and Puyol, M., *Tetrahedron Lett.*, 2013, vol. 54, no. 10, p. 1202. doi 10.1016/j.tetlet.2012.12.060
38. Ryabukhin, D.S., Sorokoumov, V.N., Savicheva, E.A., Boyarskiy, V.P., Balova, I.A., and Vasilyev, A.V., *Tetrahedron Lett.*, 2013, vol. 54, no. 19, p. 2369. doi 10.1016/j.tetlet.2013.02.086
39. Kras'ko, S.A., Zlotskii, S.S., and Boyarskiy, V.P., *Russ. J. Gen. Chem.*, 2015, vol. 85, no. 11, p. 2541. doi 10.1134/S1070363215110079
40. Savicheva, E.A., Kurandina, D.V., Nikiforov, V.A., and Boyarskiy, V.P., *Tetrahedron Lett.*, 2014, vol. 55, no. 13, p. 2101. doi 10.1016/j.tetlet.2014.02.044
41. Khaibulova, T.Sh., Boyarskaya, I.A., and Boyarskiy, V.P., *Russ. J. Org. Chem.*, 2013, vol. 49, no. 3, p. 360. doi 10.1134/S1070428013030081
42. Kurandina, D.V., Eliseenkova, E.V., Khaibulova, T.Sh., Petrov, A.A., and Boyarskiy, V.P., *Russ. J. Gen. Chem.*, 2015, vol. 85, no. 10, p. 2277. doi 10.1134/S1070363215100096
43. Said, K. and Salem, R.B., *Adv. Chem. Eng. Sci.*, 2016, vol. 6, no. 2, p. 111. doi 10.4236/aces.2016.62013
44. Kylmäälä, T., Kuuloja, N., Xu, Y., Rissanen, K., and Franzén, R., *Eur. J. Org. Chem.*, 2008, no. 23, p. 4019. doi 10.1002/ejoc.200800119
45. Kania-Korwel, I., Parkin, S., Robertson, L.W., and Lehmler, H.-J., *Chemosphere*, 2004, vol. 56, no. 8, p. 735. doi 10.1016/j.chemosphere.2004.04.035
46. Kania-Korwel, I. and Lehmler, H.-J., *Chemosphere*, 2001, vol. 45, p. 137. doi 10.1016/S0045-6535(00)00546-4
47. Ullah, E., McNulty, J., and Robertson, A., *Eur. J. Org. Chem.*, 2012, no. 11, p. 2127. doi 10.1002/ejoc.201200160