ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 1, pp. 138–143. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © T.I. Gorbunova, M.G. Pervova, V.I. Saloutin, O.N. Chupakhin, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 1, pp. 142–147.

Reactivity Features of Polychlorobiphenyl Congeners in the Nucleophilic Substitution Reactions

T. I. Gorbunova, M. G. Pervova, V. I. Saloutin, and O. N. Chupakhin

Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences,
ul. S. Kovalevskoi 22, Yekaterinburg, 620990 Russia
e-mail: gorbunova@ios.uran.ru

Received October 28, 2010

Abstract—Groups of congeners and individual congeners of polychlorobiphenyls contributing to the composition of the technical mixture “Sovol” (PCB 60, PCB 64, PCB 70, PCB 74, PCB 97, PCB 101, PCB 105, PCB 110, PCB 118, PCB 138, PCB 149, PCB 156, and PCB 163) were synthesized by the reaction of aryl–aryl coupling. The interaction of the congeners with sodium methoxide was performed and their complete conversion was proved. By means of gas chromatography–mass spectrometry the PCBs methoxy derivatives were identified. The data on the reactivity of the individual polychlorobiphenyl congeners were precised.

DOI: 10.1134/S1070363212010227

The problem of disposal of technogenic polychlorinated biphenyls (PCBs) is still relevant, since there is no universal method of disposal of this toxic material. At the same time, the previously developed methods of chemical treatment of PCBs continue to be improved, which brings new positive results. For example, the use of the nanosized Pd and/or Fe catalysts in the processes of reductive dehalogenation of the PCB congeners in some cases leads to comprehensive conversion (100%) of the principal compounds [1–8]. As a rule, the dehydrohalogenation of the highly chlorinated congeners results in a mixture of rather less chlorinated biphenyls, and these methods can serve as a preliminary stage to biodegradation of the chlorinated products and the subsequent removal of chlorine atoms from the substrate.

The stage of preliminary preparation of PCBs for disposal can also be performed using reactions of nucleophilic substitution of chlorine atoms in the PCB congeners [9].

We have shown previously that in the reaction of technical mixtures of the PCBs of “Sovol” brand with sodium methoxide the most reactive congeners are hexa- and pentachlorobiphenyls, while tetra- and trichlorobiphenyls are less reactive [10]. In this reaction the hexachlorobiphenyls (PCB 128, PCB 132, PCB 138, PCB 149, PCB 153, and PCB 156) were transformed into di- and trimethoxy derivatives, the pentachlorobiphenyls (PCB 82, PCB 85, PCB 87, PCB 91, PCB 95, PCB 97, PCB 99, PCB 101, PCB 105, PCB 110, and PCB 118), into mono-, di- and trimethoxy derivatives (to a low extent), tetrachlorobiphenyls (PCB 41, PCB 47, PCB 49, PCB 56, PCB 60, PCB 64, PCB 66, PCB 70, and PCB 74), into mono- and dimethoxy derivatives (to a low extent), trichlorobiphenyls (PCB 28 and PCB 33) into monomethoxy derivatives (partially). Using the method of internal normalization in the gas chromatographic (GC) analysis with a flame ionization detector (FID) we found that the amount of the congeners non-reacted with sodium methoxide, mostly three- and tetrachlorobiphenyls, was 8–15%.

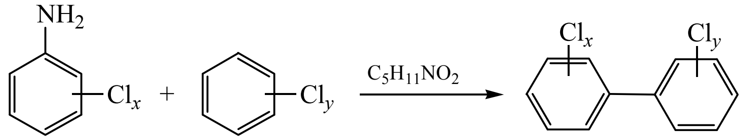
Given that Sovol is a mixture of 30 PCB congeners [11,12], the results of the study [10] are approximate and practically do not give information on the most reactive C–Cl bonds in the structures of individual chlorinated biphenyls within a single series of isomers. The error in determining the number and types of methoxy derivatives of PCBs in [10] appears both due to the different responses of the flame-ionization detector to the components of the initial and final products, and due to the coincidence in the retention times on the GC column at elution of some derivatives.

The aim of this work was the synthesis of certain groups of PCB congeners present in the technical mixture Sovol, and the study of their reactivity in the reaction with sodium methoxide.

A complete list of the methods of synthesis of the PCB congeners by the aryl–aryl coupling is given in [13]. Among these methods, the most common are the name reactions developed by Ullmann, Suzuki, Sonogashira, Gomberg–Bachmann–Hey, and Cadogan. The first three require special reagents and catalysts for their implementation, but two latter reactions proceed through the standard step diazotization of (polychloro) arylamines with subsequent condensation of diazonium salts with (polychloro) benzenes, and are the most suitable for laboratory studies.

For the synthesis of the groups of PCB congeners, we used the method proposed in [14]. As the diazotizing agent we used isoamyl nitrite, the objects for the diazotization are various polychloroanilines, second components of the condensation are the polychlorobenzenes differing by the number and location of the chlorine atoms in the aromatic ring. Synthesis of PCB congeners was carried out along the formal Scheme 1.

Scheme 1.



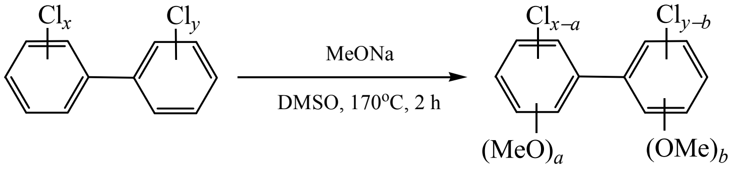
$x = 0–5, y = 1–5; x + y = 1–10.$

The data obtained on the synthesis of congeners are listed in the table. Note that the condensation reaction of diazonium salts with polychlorobenzenes proceed by free-radical mechanism, therefore only the congeners **II** and **III** obtained from the polychlorobenzenes of symmetrical structure relative to virtual symmetry axis were isolated in the individual state (except for 1,2-dichlorobenzene). In the other cases the condensation resulted in a mixture of congeners **I**, **IV**–**VI**.

The identification of the obtained groups of PCB congeners was performed by means of GC with mass-spectrometric detector (MSD) and FID, using the data of [11,15,16]. The quantitative estimation was carried out by the method of internal normalization.

The interaction of the obtained groups of congeners with sodium methoxide was effected under the conditions described in [10] along the Scheme 2. The composition of the resulting mixtures of the PCB methoxy derivatives is shown in the table.

Scheme 2.



$x + y = 4–6; a + b = 1–3.$

Tetrachlorobiphenyls **I** and **II** react with sodium methoxide to form a mixture of mono-and dimethoxy derivatives. Moreover, the PCB congeners containing three chlorine atoms in one aromatic ring and one chlorine atom in the other (compound **I**) give mostly monomethoxy derivatives (71.2%). It is obvious that PCB 74 and PCB 60, having chlorine atoms in 4,4-positions [10], are the most capable to transform into dimethoxy derivatives, while PCB 64 and PCB 63 (total content 61.0% in the initial mixture) mainly form monomethoxy derivatives.

Under similar conditions, PCB 70 (Fig. 1) preferably gives dimethoxy derivatives (72.1%) (Fig. 2), which is caused by almost equal reactivity of the chloro-substituted rings with the same number of chlorine atoms. The “Rules of selectivity” formulated in [17] for the tetrachlorinated PCB congeners with the

Physicochemical data of PCB congeners. The results of their reactions with sodium methoxide

Comp. no.	Condensation components		Condensation results[a]	Yield, %	bp, °C (mm Hg)	Methoxy-derivative type	Methoxy-derivative content, %
	polychloroaniline	polychlorobenzene					
I	4-Chloroaniline	1,2,4-Trichlorobenzene	**PCB 64** (38%), PCB 63 (23%), **PCB 74** (23%), **PCB 60** (13%)	41	154–161 (2–3)	$C_{12}H_6Cl_3OCH_3$ $C_{12}H_6Cl_2(OCH_3)_2$	71.2 28.8
II	3,4-Dichloroaniline	1,4-Dichlorobenzene	**PCB 70** (100%)	32	168–173 (4–5)	$C_{12}H_6Cl_3OCH_3$ $C_{12}H_6Cl_2(OCH_3)_2$	27.9 72.1
III	2,4,5-Trichloroaniline	1,4-Dichlorobenzene	**PCB 101** (100%)	42	196–213 (2–3)	$C_{12}H_5Cl_4OCH_3$ $C_{12}H_5Cl_3(OCH_3)_2$	87.2 12.8
IV	3,4-Dichloroaniline	1,2,4-Trichlorobenzene	**PCB 110** (38%), PCB 107 (21%), **PCB 118** (25%), **PCB 105** (13%)	36	193–215 (2–3)	$C_{12}H_5Cl_3(OCH_3)_2$ $C_{12}H_5Cl_2(OCH_3)_3$	88.8 11.2
V	2,4,5-Trichloroaniline	1,2-Dichlorobenzene	**PCB 97** (48%), **PCB 118** (51%)	43	152–158 (3–4)	$C_{12}H_5Cl_4OCH_3$ $C_{12}H_5Cl_3(OCH_3)_2$	68.0 32.0
VI	2,4,5-Trichloroaniline	1,2,4-Trichlorobenzene	**PCB 149** (21%), PCB 146 (21%), **PCB 153** (34%), **PCB 138** (22%)	36	202–218 (2–3)	$C_{12}H_4Cl_5OCH_3$ $C_{12}H_4Cl_4(OCH_3)_2$ $C_{12}H_4Cl_3(OCH_3)_3$	25.3 66.3 8.4
VII	3,4-Dichloroaniline	1,2,3,4-Tetrachlorobenzene	**PCB 156** (100%)	56	199–212 (2–3)	$C_{12}H_4Cl_5OCH_3$ $C_{12}H_4Cl_4(OCH_3)_2$ $C_{12}H_4Cl_3(OCH_3)_3$	62.9 15.2 21.9
VIII	3,4-Dichloroaniline	1,2,4,5-Tetrachlorobenzene	PCB 163 (100%)	51	197–205 (2–3)	$C_{12}H_4Cl_4(OCH_3)_2$ $C_{12}H_4Cl_3(OCH_3)_3$	12.5 87.5

[a] PCB congeners in the mixtures are listed in order of their elution from the weakly polar column HP-5, *bold* letters indicate the congeners present in “Sovol.”

same number of chlorine atoms in the rings show that the preferred points of attack in PCB 70 (2,5,3',4'-tetrachlorobiphenyl) by the nucleophile are the C^5 and $C^{3'}$ atoms. We noted earlier that the reactivity of PCB 70 is low [10], nevertheless it suffers deeper transformations in the reaction with sodium methoxide than the mixture of PCB 64, PCB 63, PCB 74, and PCB 60.

Among the synthesized pentachlorinated PCB congeners, the highest conversion showed a mixture of PCB 110, PCB 107, PCB 118, and PCB 105 (**IV**): no monomethoxy derivatives was found, the product contained mainly dimethoxy derivatives (88.8%). Note the similarity of distribution of chlorine atoms over the rings in these components of the mixture: three chlorine atoms are in one aromatic ring and two in another. In the PCB 110 and PCB 107 one chlorine atom is in *para*-position, and in the PCB 118 and PCB 105 both *para*-positions (4 and 4') are occupied by chlorine atoms. The mixture of PCB 97 and PCB 118 at approximately the same ratio of the congeners in the initial mixture **V** forms monomethoxy derivatives predominantly (68.0%) in the reaction with sodium methoxide, the rest is dimethoxy trichlorobiphenyls. Therefore, PCB 118 does not contribute to the formation of trimethoxy derivatives from the mixture **IV** of PCB 110, PCB 107, PCB 118 and PCB 105. These types of methoxy derivatives are formed

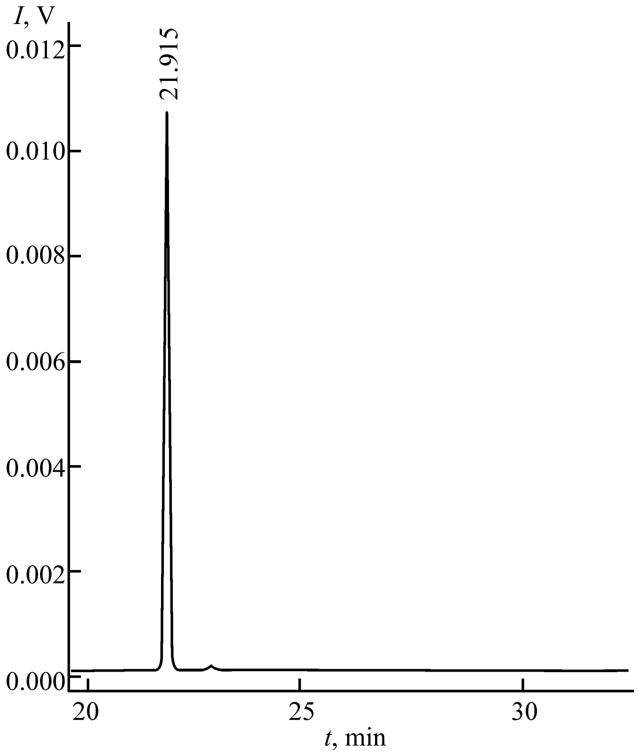


Fig. 1. Chromatogram of PCB 70 congener.

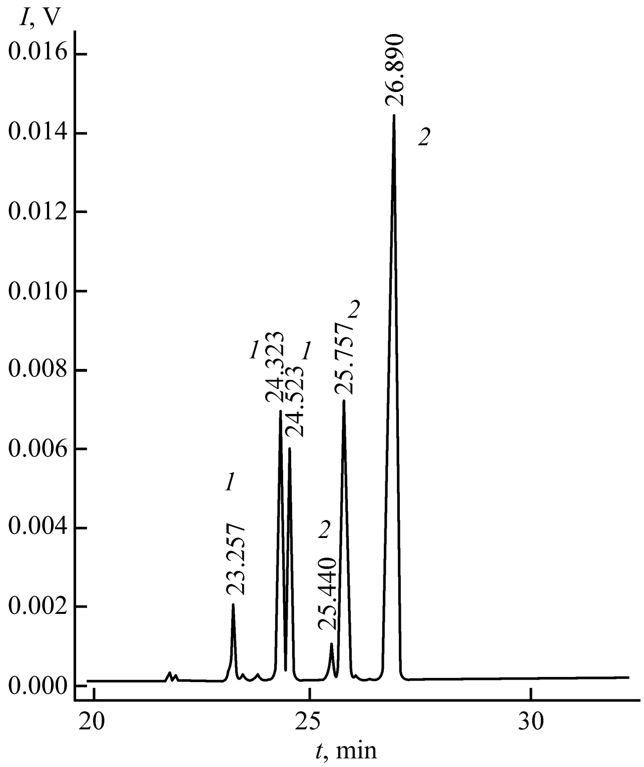


Fig. 2. Chromatogram of a mixture of methoxy-derivatives formed from PCB 70: (*1*) monomethoxy-derivatives and (*2*) dimethoxy derivatives.

probably from PCB 110, PCB 107, and PCB 105. Previously we have already noted that PCB 105 is one of the most reactive congeners of the "Sovol" mixture in the reaction with sodium methoxide [10].

Individual PCB 101 (**III**) under similar conditions forms preferably monomethoxy derivatives (87.2%). Considering the data on the carboxylation of PCB congeners [18], we may assume that the mono- and dimethoxy derivatives based on the PCB 101 (2,4,5,2',5'-pentachlorobiphenyl) are formed through the attack of the nucleophile only on the most substituted ring.

We failed to obtain more detailed information on the reactivity of pentachlorobiphenyls.

While studying transformation of the hexachlorinated PCB congeners **VI** and **VII**, we found that the crucial role in their reaction with sodium methoxide plays the distribution of chlorine atoms over the aromatic rings of biphenyl. Thus, a mixture of PCB 149, PCB 146, PCB 153, and PCB 138 (Fig. 3) under the reaction conditions undergoes complete conversion to form a mixture of mono-, di-, and trimethoxy-derivatives, the dimethoxylated products prevailing (66.3%) (Fig. 4). Therewith, the PCB congeners 149, PCB 146, PCB 153, and PCB 138 have three chlorine atoms in each ring. In the structure of PCB 156 four atoms of chlorine are in one ring (2,3,4,5-), and two in another (2',3'-). This compound forms predominantly monomethoxy derivative (62.9%).

To understand the low reactivity of PCB-156, we synthesized its isomer, PCB 163 (2,3,5,6,2',3'-hexachlorobiphenyl), and showed that in the reaction with sodium methoxide this congener is transformed exhaustively into a mixture of di- and trimethoxy-derivatives, in which trimethoxytrichlorobiphenyls dominate (87.5%). Consequently, there is a number monomethoxy derivatives based on the PCB 156, which cannot be transformed further owing to steric factors.

It was shown previously that hexachlorobiphenyls, the components of the technical mixture "Sovol," form in the reaction with sodium methoxide di- and trimethoxy-derivatives, while monomethoxy derivatives were not detected [10]. This fact evidences that several methoxy derivatives obtained from different congeners eluted jointly.

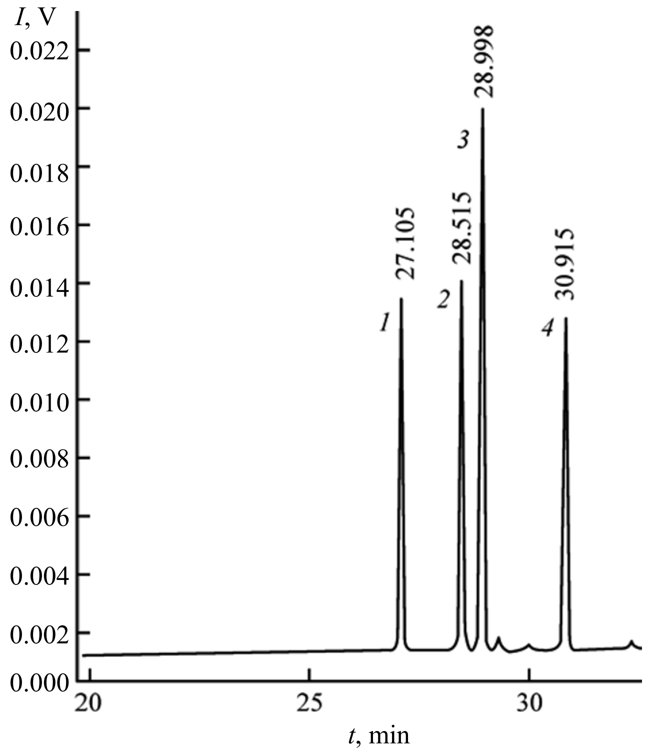


Fig. 3. Chromatogram of a mixture of the congeners (*1*) PCB149, (*2*) PCB 146, (*3*) PCB 153, and (*4*) PCB 138.

For all the compounds obtained mass spectra were recorded. The data obtained are completely consistent with the data of [10].

The results of this study made it possible to clarify some aspects of the reactivity of PCB congeners in the nucleophilic substitution. All the synthesized PCB congeners react exhaustively with sodium methoxide. The PCB-70 (with two chlorine atoms in each ring) is more reactive than the mixture of PCB 64, PCB 63, PCB 74, and PCB 60 (all have three chlorine atoms in one ring and one in another). Among the synthesized pentachlorobiphenyls (all have three chlorine atoms in one ring and two in another) more profound transformations occur in a mixture of PCB 110, PCB 107, PCB 118, and PCB 105, compared with individual PCB 101 or a mixture of PCB 97 and PCB 118. A crucial role in the reaction of hexaclorinated PCB congeners plays the steric factor. The mixture of PCB 149, PCB 146, PCB 153, and PCB 138 (all have three chlorine atoms in each ring) is more reactive compared with PCB 156 (with four chlorine atoms in one ring and two in another). But even more profound transformations suffers PCB 163 (also has four chlorine atoms in one ring and two in another). Its high

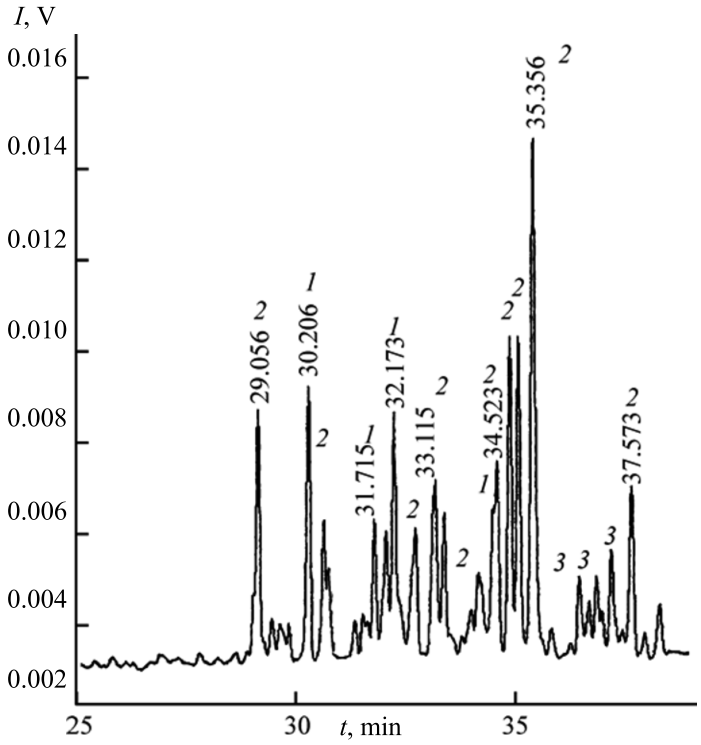


Fig. 4. Chromatogram of a mixture of methoxy-derivatives formed from a mixture of PCB 149, PCB 146, PCB 153, and PCB 138: (*1*) monomethoxy, (*2*) dimethoxy, and (*3*) trimethoxy derivatives.

reactivity is due to a significant redistribution of electron density at the unequal substitution in the aromatic rings and a sterically favorable arrangement of chlorine atoms in the most substituted ring.

EXPERIMENTAL

The reaction progress monitoring and quantifying were performed using a Shimadzu GC-17A gas chromatograph with FID, quartz capillary column MDN 5S 30 m × 0.25 mm, the stationary phase of film thickness 0.25 mm (the phase is polymethylsiloxane with 5% of grafted phenyl groups). Carrier gas nitrogen, the split ratio 1:30. The column initial temperature 100°C (isotherm 1 min), programmed heating is 10°C min^{-1} to 200°C and then 2°C min^{-1} to 300°C. Evaporator temperature 250°C, detector temperature 280°C.

To identify the reaction products a Fisons MD 800 gas chromatography–mass spectrometer was used with MSD system, quartz capillary column HP-5 25m × 0.25mm, film of stationary phase 0.25 mm thick (polymethylsiloxane, 5% of grafted phenyl groups). Carrier gas helium, the split ratio :20. Initial column temperature 100°C (isotherm 1 min), programmed heating is 10°C min^{-1} to 200°C and then 2°C min^{-1} to 300°C, evaporator temperature 250°C. Electronic ionization 70 eV, scan rate 1 s^{-1} of the full ion current in the mass range 20–700 amu.

Synthesis of PCB congeners. To 0.025 mol of a polychloroaniline was added 0.25 mol of a polychlorobenzene, the mixture was heated with stirring to 120–130°C, within 1 h 0.05 mol of isoamyl nitrite was added dropwise, and the mixture was stirred for 15–18 h at 130°C. Then the polychlorobenzene excess was distilled off, the residue was dissolved in hexane and 2–3 times filtered through a layer of Al_2O_3 (neutral, activity II by Brockmann). Hexane was evaporated, the residue was distilled in a vacuum of an oil pump.

Methods of performing reactions of the synthesized PCB congeners with sodium methoxide are described in [10].

ACKNOWLEDGMENTS

This work was supported by the Ural Branch of Russian Academy of Sciences (project no. 09-C-3-1016) and the Russian Foundation for Basic Research (project no. 08-03-99045).

REFERENCES

1. Korte, N.E., West, O.R., Liang, B.Gu, Zutman, J.L., and Fernando, Q., *Waster Manag*., 2002, vol. 22, p. 343.
2. Zhang, W.-X., *J. Nanoparticle Res*., 2003, no. 5, p. 323.
3. Lowry, G.V. and Johnson, K.M., *Environ. Sci. Technol*., 2004, vol. 38, p. 5208.
4. Lorenc-Grabowska, E., Yperman, J., Gryglewicz, G., Hoste, S., and Carieer, R., *Fuel*, 2006, vol. 85, p. 374.
5. Sun, Y., Takaoka, M., Takeda, N., Matsumoto, T., and Oshita, K., *Chemosphere*, 2006, vol. 65, p. 183.
6. Agarwal, S., Al-Abed, S.R., and Dionysiou, D.D., *Environ. Sci. Technol*., 2007, vol. 41, p. 3722.
7. Li, A., Tai, C., Zhao, Z., Wang, Y., Zhang, O., Jiang, G., and Hu, J., *Environ. Sci. Technol*., 2007, vol. 41, p. 6841.
8. Venkatachalam, K., Arzuaga, X., Chopra, N., Gavalas, V.G., Xu, J., Bhattacharyya, D., Henning, B., and Bachas, L.G., *J. Hazard. Mater*., 2008, vol. 159, p. 483.
9. Gorbunova, T.I., Saloutin, V.I., and Chupakhin, O.N., *Usp. Khim*., 2010, vol. 79, no. 6, p. 565.
10. Zabelina, O.N., Gorbunova, T.I., Pervova, M.G., Kirichenko, V.E., Zapevalov, A.Ya., Saloutin, V.I., and Chupakhin, O.N., *Zh. Prikl. Khim*., 2004, vol. 747, no. 9, p. 1533.
11. Kirichenko, V.E., Pervova, M.G., Promyshlennikova, E.P., and Pashkevich, K.I., *Analitika i Kontrol'*, 2000, vol. 4. no. 1, p. 41.
12. Piterskikh, I.A., Kirichenko, V.E., Pervova, M.G., and Kandakova, V.V., *Zavod. Lab. Diagnostika Materialov,* 2001, vol. 67. no. 8, p. 63.
13. Stanforth, S.P., *Tetrahedron*, 1998, vol. 54, p. 263.
14. Mullin, M.D., Pochini, C.M., McCrindle, S., Romkes, M., Safe, S.H., and Safe, L.M., *Environ. Sci. Technol*., 1984, vol. 18, no. 6, p. 468.
15. Frame, G.M., *Fresenius. J. Anal. Chem*., 1997, vol. 357, p. 714.
16. Hillery, B.R., Girard, J.E., Schants, M.M., and Wise, S.A., *Fresenius. J. Anal. Chem*., 1997, vol. 357, p. 723.
17. Hetflejš, J., Czakóová, M., Řeřicha, R., and Včelák, J., *Chemosphere*, 2001, vol. 44, p. 1521.
18. Boyarsky, V.P., Zhesko, T.E., Lanina, S.A., and Nikiforov, V.A., *Organohal. Comp*., 2001, vol. 54, p. 226.