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Reaction of Polychlorinated Biphenyls and Benzenes with Neopentyl Glycol

M. G. Pervova, T. I. Gorbunova, M. A. Samorukova, 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

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Abstract—The reactions of a mixture of 1,2,3- and 1,2,4-trichlorobenzene and polychlorinated biphenyls congeners of the industrial mixture Sovol with neopentyl glycol in the presence of alkali in DMSO medium was studied. In the conditions of nucleophilic substitution the aromatic compounds are converted completely. Using the method of gas chromatography with flame ionization and mass spectrometric detectors the structure of all synthesized compounds was studied and the following series of increasing reactivity of the polychlorinated biphenyls congeners was revealed: tetra- < penta- < hexachlorobiphenyls. The process can serve as a preliminary step of the preparation of industrial waste for the subsequent biological degradation.

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Methods of partial dechlorination of toxic chlorinated aromatic compounds through the reaction of nucleophilic substitution of chlorine atoms by different nucleophiles occupy a leading position in the list of the methods of industrial waste disposal. With respect to polychlorinated biphenyls (PCBs), which according to the Stockholm Convention (2001) should be completely destructed to year 2025, a number of methods of replacing dechlorination has been developed, including replacement of aromatic chlorine atoms by the hydroxy, alkoxy, and carboxy groups and the fluorine atoms [1]. The development of this group of methods is of great importance because of the possibility of a significant decrease in the chlorine content in chlorinated aromatic substrates by implementing some simple laboratory technique. The resulting low-chlorinated PCB congeners are the pre-compounds for the following biological degradation or the intermediates for the other chemical processes of neutralization.

A criterion in the selection of the process of substitution of chlorine atoms in the PCB structures by other groups in order to use the resulting compounds for biodegradation is the kind of interaction that leads to congeners with fewer chlorine atoms, as it is known that highly-chlorinated PCB congeners (penta-, hexa-, heptachlorobiphenyls, etc.) are not decomposed by the most of bacteria strains [2, 3].

Previous investigations of the reaction of industrial PCB mixture Sovol containing tri-, tetra-, penta-, and hexachlorobiphenyls with the alkali metals alkoxylates/alcohol in the presence of alkali in DMSO showed that in none of the cases a complete conversion was achieved of the original PCB mixture [4,5]. In the reaction with MeONa (DMSO, 153°C, 4 h) the unreacted congeners content amounted to 10%. In the reaction of the Sovol mixture with other sodium alkoxylates in DMSO the unreacted congeners content increased with increasing length of alkoxy groups: 5% (EtO^-), 6% (PrO^-), 22% (n-BuO^-), 65% (s-BuO^-), and in the reaction of industrial PCB with t-BuO^- the alkoxy derivatives were not detected. In all the cases, the most reactive congeners were hexa- and pentachlorobiphenyls, tetra- and trichlorobiphenyls are less reactive. The hexachlorobiphenyls in the Sovol composition transformed mainly into the di- and trialkoxyderivatives, pentachlorobiphenyls, in mono-, di- and trialkoxyderivatives (insignificantly), tetrachlorobiphenyls, in mono- and dialkoxyderivatives (insignificantly), trichlorobiphenyls, in monoalkoxyderivatives (partially). Tetrachlorobiphenyls such as PCB 44 and PCB 52 in all reactions with alkoxides remained unchanged.

The processes of nucleophilic substitution of chlorine atoms in the industrial PCB by an alkoxy

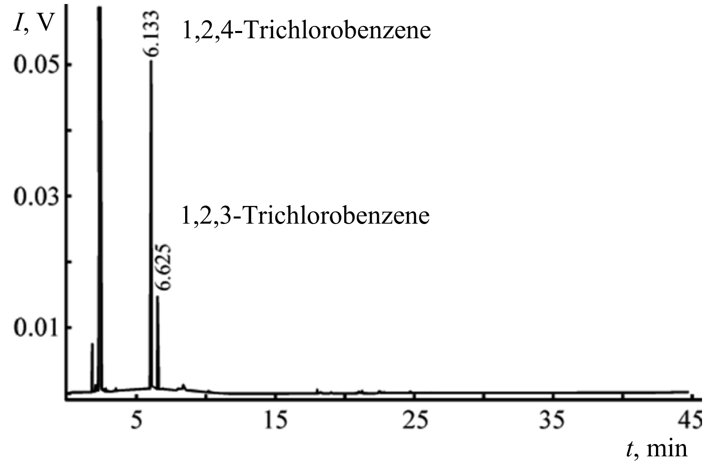


Fig. 1. Chromatogram of a mixture of trichlorobenzenes.

group of a dihydric alcohols were poorly studied previously. Examples are known of the reaction of a mixture of PCB with higher polyethylene glycols in the presence of KOH resulting according to the elemental analysis in the formation of mono- [6] or dipolyethylene glycol PCB derivatives [7]. The reactivity of polychlorobenzene congeners has not been studied.

The aim of this work was to study the reactivity of the congeners of the industrial PCB mixture Sovol with 2,2-dimethyl-1,3-propanediol (neopentyl glycol) in the presence of alkali.

Study of the resulting mixture obtained in the reaction of Sovol with neopentyl glycol in the presence of NaOH in the medium of the same glycol by gas chromatography with flame ionization detector (GC-FID) did not register any reaction product.

Chemical modification of the industrial mixture Sovol with the dihydric alcohol neopentyl glycol with the addition of NaOH was carried out in the conditions described in [4]: the reaction medium is DMSO, temperature 150°C, the total time 11 h. The result of this process, according to GC-FID is 100% conversion of the Sovol mixture, which is the first example of a complete transformation of an artifical mixture of PCBs under the influence of alcohol in alkaline conditions. The optimum temperature and time of this reaction were determined by analysis of samples taken from the reaction mixture every 30 minutes.

To identify the components of a complex mixture of the Sovol reaction products with neopentyl glycol in the presence of NaOH, we carried out a blank experiment: the reaction of neopentyl glycol with a mixture of DMSO and NaOH at 150°C for 2 h. The study of the fractions isolated from the reaction mixture by GC-FID and GC with mass spectrometric detector (GC-MSD) using NIST05 mass spectra database showed that under these reaction conditions the neopentyl glycol forms MeOH, *i*-BuOH, and 2-methyl-1,3-butadiene.

As a model of the process carried out to identify the reaction products of Sovol with neopentyl glycol in the presence of alkali was implemented the reaction of a mixture of 1,2,3- and 1,2,4-trichlorobenzene, the components of the industrial PCB mixture Sovtol-10, in similar conditions. The resulting mixture of trichlorobenzene derivatives was studied by GC-FID (Figs. 1, 2) and GC-MSD. Analytical data are given in Table 1.

The main pathway of the reaction of 1,2,3- and 1,2,4-trichlorobenzene mixture with neopentyl glycol in DMSO in the presence of NaOH is the substitution of one chlorine atom by neopentyl glycol residue: the content of monoalkoxylation product **IV** is 54.2%. Competing processes are hydrolysis (**I**, 21.1%), replacement of two vicinal chlorine atoms by one molecule of the neopentyl glycol (**VI**, 12.4%), and replacement of two chlorine atoms by two neopentyl glycol groups (**V**, 7.0%). The content of other products (**II** and **III**) is low (0.7 and 2.9% respectively). The formation of ethers **VII** (1.4%) is due to the implementation of the Williamson reaction mechanism [8] at a ratio of ArX:ROH equal to 2:1 [ArX is any of trichlorobenzenes, R = $CH_2(CH_2OH)C(CH_3)_2$].

Structures of compounds **I–VII** were confirmed by GC-MSD. The mass spectra contain molecular ions, the fragment ions correspond to the structures of

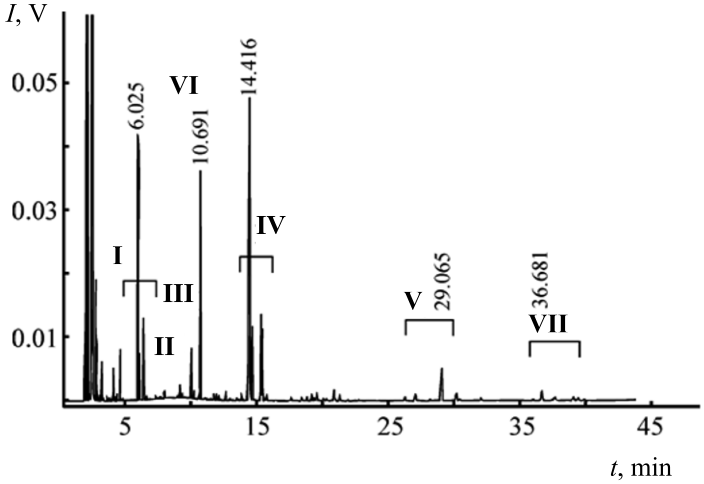
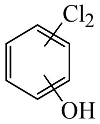
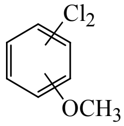
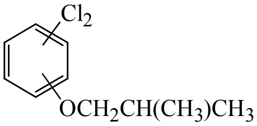
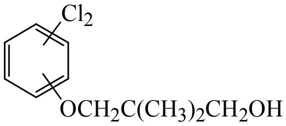
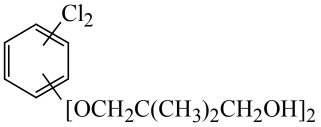
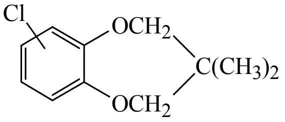
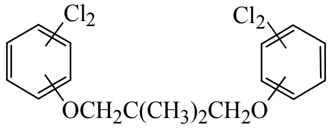


Fig. 2. Chromatogram of reaction products of trichlorobenzene with neopentyl glycol and NaOH in DMSO (numbers correspond to the reaction products listed in Table 1).

Table 1. The results of the reaction of a mixture of 1,2,3- and 1,2,4-trichlorobenzenes with neopentyl glycol in the presence of sodium hydroxide in DMSO

Comp. no.	Structure of the reaction product	M^+, m/z (I_{rel}, %)	Retention time, t, min	Content in the mixture, % [a]
I		162 (100)	5.93–6.37	21.1
II		176 (100)	9.14–9.20	0.7
III		218 (20)	9.99–10.19	2.9
IV		248 (15)	14.41–15.74	54.2
V		316 (25)	27.06–30.17	7.0
VI		212 (80)	10.69	12.4
VII		392 (50)	36.68–40.01	1.4

[a] Estimation of the content of reaction products is carried out by the method of internal normalization.

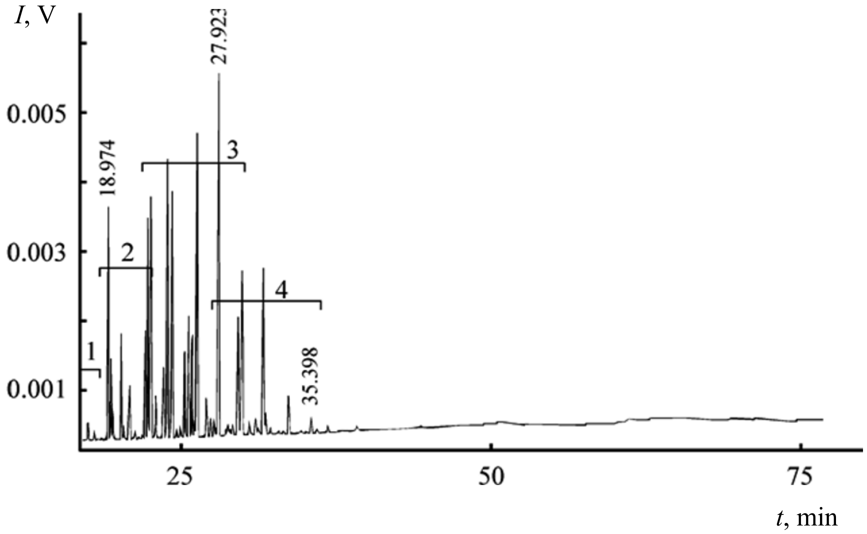


Fig. 3. Chromatogram of the initial PCB mixture: (1) trichlorobiphenyls, (2) tetrachlorobiphenyls, (3) pentachlorobiphenyls, and (4) hexachlorobiphenyls.

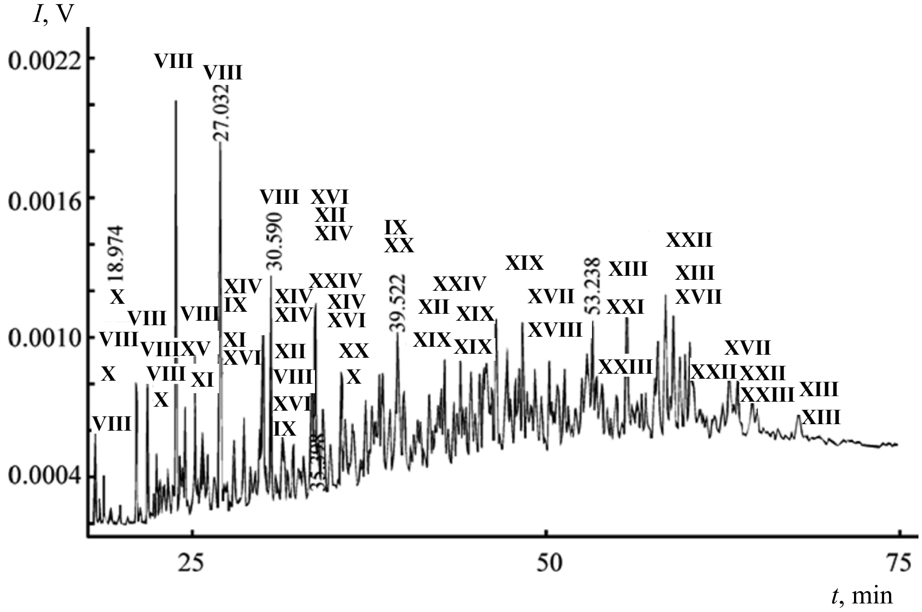


Fig. 4. Chromatogram of reaction products of PCB with neopentyl glycol and NaOH in DMSO (numbers correspond to the reaction products shown in the scheme and in Table 2).

respective compounds. Because of the similarity of the fragmentation direction of isomeric products **I–VII** under electronic ionization, it was impossible to establish the exact location of the chlorine atoms and functional groups in the aromatic ring.

Based on the data on the reactivity of trichlorobenzene, a mixture of products of the interaction of industrial PCBs with neopentyl glycol and NaOH in DMSO was similarly studied, and it was found that under the reaction conditions the mixture of Sovol congeners undergoes a more profound transformation in comparison with trichlorobenzene (Fig. 3, 4, and the scheme). The analysis of reaction products by GC-FID and GC-MSD showed that the composition of the mixtures obtained is rather complicated, the number of peaks in the chromatograms increased significantly, and their relative intensities decreased. In many cases there are the co-eluted compounds (Fig. 4), and the mass spectra correspond to the mixtures. About 30 new types of PCB derivatives were obtained, which differ both in the number of the remaining chlorine

Table 2. Results of reaction of a Sovol mixture with neopentyl glycol in the presence of NaOH in DMSO

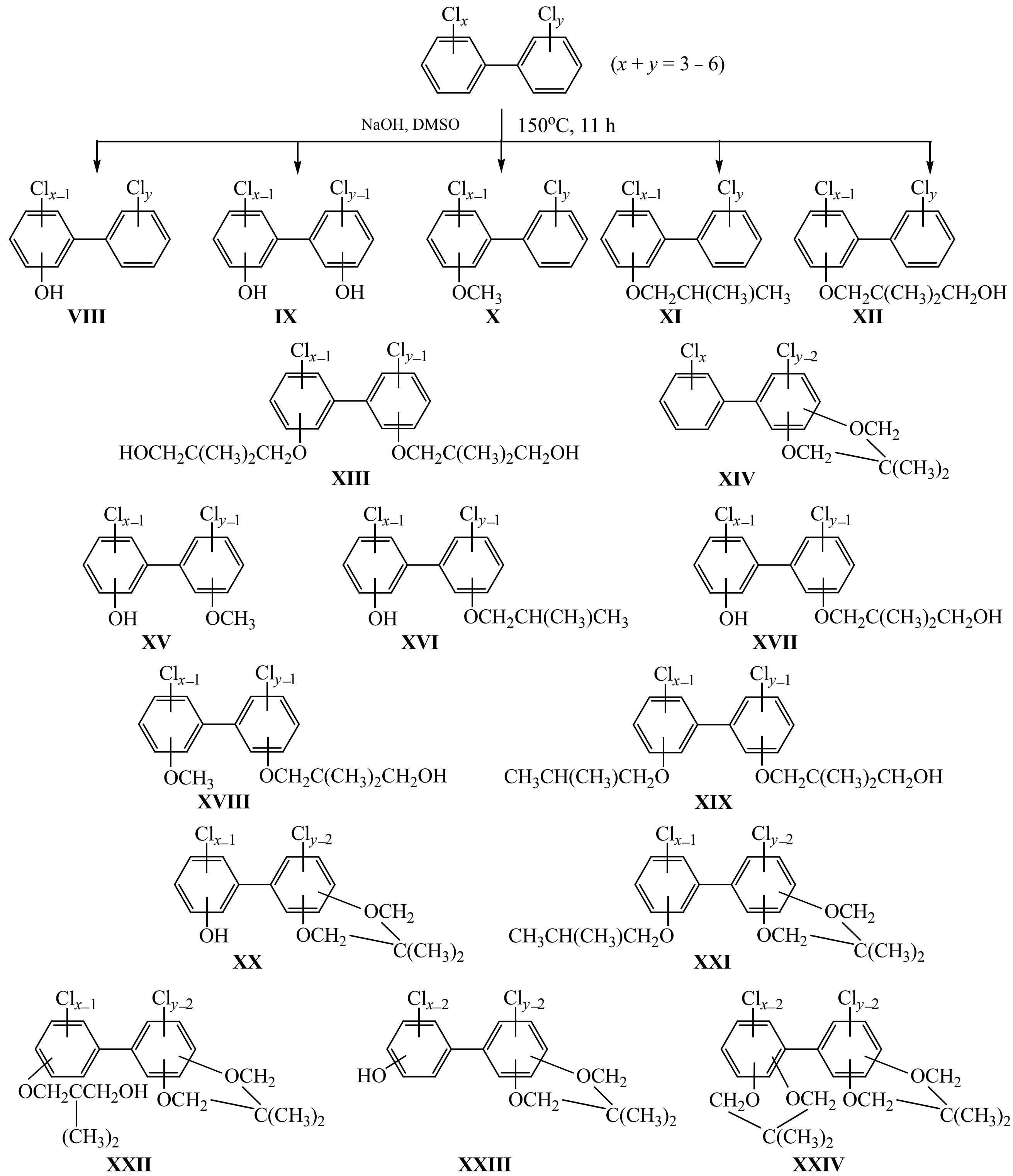
Run no.	Congeners of the Sovol mixture[a]	Products	M^+, m/z (I_{rel}, %)	Content in the mixture,% [b]
1	Trichlorobiphenyls: PCB 28, PCB 33, PCB 22	**X**	252 (100)	1.9
		XI	294 (25)	<0.1
		XII	324 (23)	0.1
2	Tetrachlorobiphenyls: PCB 41, PCB 44, PCB 47, PCB 49, PCB 52, PCB 56, PCB 60, PCB 64, PCB 66, PCB 70, PCB 74	**VIII**	272 (100)	2.6
		X	286 (100)	<0.1
		XI	328 (22)	1.5
		XII	358 (25)	3.2
		XIII	426 (23)	4.7
		XIV	322 (100)	5.2
		XVII	340 (20)	1.2
		XIX	396 (21)	1.9
3	Pentachlorobiphenyls: PCB 82, PCB 85, PCB 87, PCB 91, PCB 95, PCB 97, PCB 99, PCB 101, PCB 105, PCB 110, PCB 118	**VIII**	306 (100)	19.5
		X	320 (100)	0.1
		XIII	460 (21)	0.4
		XIV	356 (100)	3.5
		XV	302 (100)	1.7
		XVI	344 (24)	4.7
		XVII	374 (20)	11.2
		XVIII	388 (19)	1.6
		XIX	430 (15)	3.5
		XX	338 (100)	0.6
		XXI	394 (52)	2.6
		XXII	424 (45)	10.7
4	Hexachlorobiphenyls: PCB 128, PCB 132, PCB 138, PCB 149, PCB 153, PCB 156	**IX**	322 (100)	4.9
		XVII	408 (15)	1.5
		XX	372 (100)	6.0
		XXIII	422 (100)	2.4
		XXIV	368 (100)	2.8

[a] The numbering of PCB congeners is given in accordance with the recommendations of IUPAC [11]. [b] The content of the reaction products was estimated using the method of internal normalization.

atoms and the nature of the substituents (Table 2). All congeners of the Sovol mixture completely transformed under the reaction conditions.

The main contribution to the product mixture the hydroxy-PCB (52.1%) consist of hydroxy-PCB, about half of them are the products of replacement of chlorine atoms only by the hydroxy groups (**VIII, IX,** 31.9%), the other part (20.2%) includes the compounds of mixed type with hydroxy- and alkoxy-substituents (**XV–XVII**). The registered alkoxy substituents comprise methoxy (**X**), iso-butoxy (**XI**), and neopentylglycoloxy (2,2-dimethyl-3-hydroxypropyl) (**XII**) groups. In addition, there are derivatives formed at the substitution by one molecule of neopentyl glycol of two vicinal chlorine atoms in one (**XIV**) or two (**XXIV**) PCB rings, etc. The products of the reaction of PCB congeners similar to compounds **VII** were not registered in the resulting mixtures.

Trichlorobiphenyls react with neopentyl glycol in the presence of NaOH affording only mono-derivatives, including those based on the products of disproportionation of the neopentyl glycol (methanol



and *i*-BuOH). Tetrachlorobiphenyls undergo both mono- and disubstitution. Pentachlorobiphenyls under the reaction conditions transformed into mono-, di-, and trisubstituted products, reducing the amount of chlorine atoms significantly, taking into account the fact that they constitute the basic fraction (50%) in the industrial PCB mixture Sovol [9, 10]. Hexachlorobiphenyls suffered an even deeper substitution, forming products from di- to tetra-substitution. The order of reactivity of the congeners in the nucleophilic substitution is consistent with that in the processes studied previously [4, 5].

To reveal the structure of the resulting products **VIII–XXIV** we studied the mass spectra of all newly registered compounds. At the electronic ionization, each of the compounds **VIII–XXIV** gives a peak of molecular ion differing by intensity. The character of the molecular ion decay of these products coincides with the fragmentation of molecular ions of similar derivatives **I–VII** obtained from trichlorobenzene.

The direction of the fragmentation of molecular ions in the mass spectra of mono- and dineopentylglycol PCB derivatives **XII** and **XIII** is similar to the fragmentation described in [5] for alkoxy derivatives. All spectra contain the peaks of the molecular ions with the intensity 10–25%. The basic peaks are those corresponding to mono- and dihydroxy derivatives of PCB, formed at the splitting off a pentenol molecule (C_5H_9OH). Then successively Cl (HCl) and HCO groups split off. All mass spectra contain a peak at *m/z* 86 $[C_5H_9OH]^+$ with an intensity of 1%.

The mass spectra of compounds containing simultaneously methoxy and neopentylglycol (**XVIII**), *i*-butoxy and neopentylglycol (**XIX**), hydroxy and neopentylglycol groups (**XVII**) typically contain a peak of molecular ion with the intensity of 20–25%. The basic peaks are those corresponding to dihydroxy-derivatives of PCB. In all cases, the separation of pentenol (C_5H_9OH) initially occurs. At the fragmentation of *i*-butoxyneopentylglycol derivative **XIX** the butylene (C_4H_8) is eliminated, and at the fragmentation of methoxyneopentylglycol derivative **XVIII** a CH_3 group is removed. Then the decay characteristic of methoxy, *i*-butoxy, or hydroxy derivatives of PCB occurs.

For the mass spectra of compounds **XIV, XXIV** formed at the substitution of two vicinal chlorine atoms with one molecule of neopentyl glycol the presence is typical of the molecular ion peak, which is the basic one in almost all the mass spectra. Next successively two CH_3 groups split off, with a very low intensity of the peaks $[M - CH_3]^+$ and $[M - 2CH_3]^+$ (1–2%). The subsequent decay proceeds in two directions. To the first one the peaks correspond formed at splitting off the C_4H_9 group ($M - 57$), with intensity of up to 80%. In the second direction the peaks appear formed at removing a C_5H_8 group ($M - 68$), also with a high intensity (60–70%). During this process the ion is formed corresponding to polychlorohydroxybiphenyl. The subsequent decay in both directions occurs through the sequential splitting off the Cl atoms and HCO groups till the benzene ring collapses. A characteristic feature of the mass spectra of these derivatives is the presence of peaks with *m/z* 69 $[C_5H_9]^+$ and *m/z* 41 $[C_3H_5]^+$ with 40–70% intensity. There is also a peak with *m/z* 57 $[C_4H_9]^+$ with the intensity of 20–30%.

The mass spectra of compounds **XXI, XXII,** and **XXIII** include the peak of the molecular ion of a medium intensity (50%). In the mass spectra of derivative **XX** this peak is basic. At the decay of the derivatives **XXI, XXII,** and **XXIII** butene $[M - C_4H_8]$, pentenol $[M - C_5H_9OH]$, or CH_3 group are initially removed, respectively, to form the corresponding hydroxy derivative. The peak of the latter has the maximum intensity. Then, the decay occurs according to the above described scheme typical for the derivative **XIV**.

The results of the study can be summarized as follows:

– The results of the reactions of 1,2,3- and 1,2,4-trichlorobenzene and PCB congeners with neopentyl glycol and NaOH in the presence of DMSO are practically identical;

– The reaction of industrial PCB Sovol mixture with neopentyl glycol and NaOH in the presence of DMSO is the first example of an exhaustive conversion of all congeners in a nucleophilic substitution reaction with alcohol;

– The reactivity of groups of isomers of PCB congeners increases in the order: tetra-, penta-, hexachlorobiphenyls;

– The developed technique is potentially a way of preparation the PCB for the biodegradation.

EXPERIMENTAL

Monitoring the progress and quantitative estimation of the reactions were performed using a gas chromatograph Shimadzu GC-17A with a flame-ionization detector, quartz capillary column ZB-5 30 m × 0.25 mm with the film thickness of the stationary phase 0.25 mm (polydimethylsiloxane with 5% of grafted phenyl groups). Carrier gas nitrogen, the flow division 1:30.

Initial column temperature 100°C (isotherm 1 min), programming 10°C per minute to 200°C and then 2°C per minute to 300°C. The evaporator temperature 250°C, the detector temperature 280°C.

To identify the reaction products a gas chromatograph-mass spectrometer Agilent GC 7890A MSD 5975C inert XL EI/CI was used with a quartz capillary column HP-5 25 m × 0.25 mm, the film thickness of the stationary phase 0.25 μm (polydimethylsiloxane with 5% of grafted phenyl groups), and quadrupole mass spectrometric detector (GC-MSD). Scanning the full ion current in the mass range 20–1000 a.u. in the electronic ionization mode (70 eV). Carrier gas helium, split ratio 1:50. Initial column temperature 100°C (isotherm 1 min), programming 10°C per minute to 200°C and then 2°C per minute to 300°C (isotherm 40 min), the evaporator temperature 250°C, transition chamber 280°C, MS source 230°C, quadrupole 250°C.

Quantitative calculations were carried out by the method of internal normalization.

Blank experiment. 7.8 g of neopentyl glycol was heated (~120°C) with 3.0 g of NaOH while stirring to homogenization. Then 20 ml of DMSO was added and the mixture was stirred at 150°C for 2 h, then cooled and distilled, selecting the fraction with bp 82–130°C.

The technique of the reaction of trichlorobenzene, and industrial PCB mixture Sovol with neopentyl glycol and NaOH in the presence of DMSO is similar to that described in [4].

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