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Features of Polychlorinated Biphenyls Nitration

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Abstract—Nitration of mono-, di-, and trichlorobiphenyls has been studied. The nitration degree depends on the number of chlorine substituents; one to four nitro groups can be introduced. The conclusions have been confirmed by results of nitration of the “Trikhlorbifenil” technical mixture of polychlorinated biphenyls.

Keywords: polychlorinated biphenyls, nitration, gas chromatography, mass spectrometry

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A combination of different methods is generally utilized for neutralization of polychlorinated biphenyls, large-scale industrial waste; development of such methods has remained a topical problem nowadays. In particular, the thermal, pyrotechnical, electrochemical, biological, and chemical methods have been described (cf. [1, 2]). Hydrodechlorination [3] has been recognized as the most important chemical method of polychlorinated biphenyls neutralization, whereas other processes (substitutive dechlorination, oxidation, etc.) has been less developed.

The sulfonation reaction has been the most studied electrophilic substitution process involving polychlorinated biphenyls [4–7]. However, these studies have been performed using the industrial samples, and their results has been patented. Reactivity of individual polychlorinated biphenyls towards sulfonation has not been studied.

General features of nitration of the Sovol industrial mixture {containing tri- (2%), tetra- (20%), penta- (55%), hexa- (18%), and heptachlorinated (2%) biphenyls [8, 9]} have been studied earlier [10]. Further GC–MS study [11] has revealed that tetrachlorinated biphenyls yield exclusively dinitro derivatives (16%), pentachlorinated biphenyls are transformed into mononitro (9%) and dinitro (51%) derivatives, hexachlorinated biphenyls afford the mononitro (12%) and dinitro (7%) derivatives under conditions of the nitration reaction, whereas nitro derivatives of tri- and heptachlorinated biphenyls have not been detected in the reaction mixture.

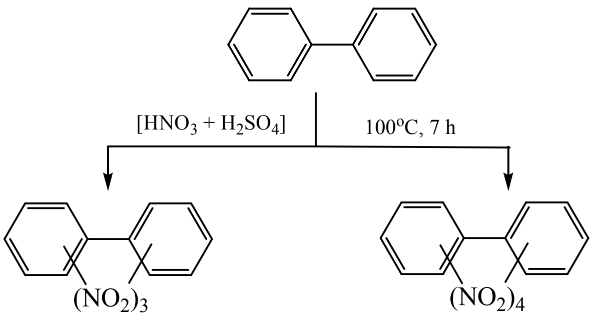
The results of earlier studies have not allowed prediction of reactivity of mono-, di-, and trichlorinated biphenyls. However, the relevant information is of practical importance, since these compounds are components of the industrial polychlorinated biphenyls mixtures such as Arochlor 1016, Arochlor 1242, Arochlor 1248, Kanechlor 300, Kanechlor 400, etc. [11]. Nitration of such industrial mixtures followed by reduction can yield the amino derivatives, valuable intermediates of polycondensation reaction or production of benzidine type dyes.

In view of the above, in this work we studied nitration of individual chlorinated biphenyls.

Mononitro [12, 13] and dinitro [14] derivatives of biphenyl have been described. The mononitro derivatives are commonly prepared indirectly from the mononuclear derivatives [13] rather than via direct nitration of biphenyls. A method of 4-nitrobiphenyl production with the yield of 84% upon biphenyl treatment with a mixture of sodium nitrite and an acid (the elemental formula $CH_{0.35}O_{0.35}S_{0.14}$) at room temperature has been described in [15]. Biphenyl treatment with the conventional nitrating mixture has afforded 4,4'-dinitrobiphenyl [14] and 3,5,4'-trinitro-4-hydroxybiphenyl [16]. The products of deeper nitration of biphenyl have not been found in the reaction mixture.

In order to simplify GC–MC identification of nitro derivatives of chlorinated biphenyls, we first studied nitration of unsubstituted biphenyl. The substrate was completely converted under the chosen reaction

Scheme 1.



Ia (4.2%) **Ib** (95.8%)

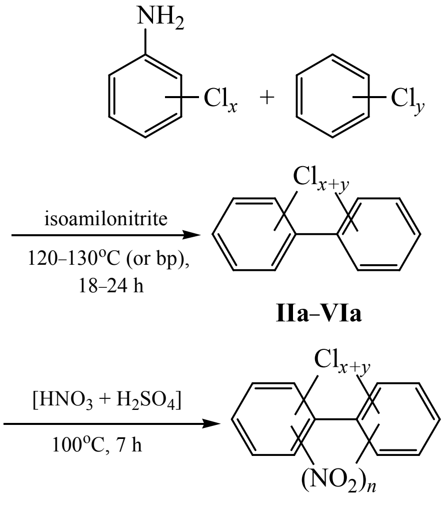
conditions to yield products of deeper nitration than were generally reported in the literature (Scheme 1). Tetranitrobiphenyls **Ib** (four isomers) were the major products, whereas content of the single trinitrobiphenyl isomer **Ia** in the products mixture was lower.

Introduction of a chlorine atom in biphenyl structure significantly affected its reactivity in the nitration process. In particular, 3-chlorobiphenyl **IIa** (prepared from 3-chloroaniline and benzene via the Gomberg–Bachmann reaction [17–19]; PCB 2 according to the BZ nomenclature accepted by IUPAC [17]) gave mainly trinitrochlorobiphenyls **IIb** (eight isomers) and smaller amounts of tetranitrochlorobiphenyls **IIc** (two isomers) (Scheme 2); the conversion of compound **IIa** was of 100%.

The result of nitration of dichlorobiphenyls depended on the substituents location. When the chlorine atoms were located in the different aromatic rings (in particular, nitration of a mixture of 2,4'-dichlorobiphenyl PCB 8, 3,4'-dichlorobiphenyl PCB 13, and 4,4'-dichlorobiphenyl PCB 15 was studied), the reaction mainly gave the dinitro derivatives **IIIb** (eight isomers) (Scheme 2). When the two chlorine atoms were located at the same aromatic ring (3,4-dichlorobiphenyl PCB 12, **IVa**), the reaction afforded trinitrodichlorobiphenyls **IVc** (five isomers) (Scheme 2). Tetranitrodichloro derivatives and the starting compounds were not detected in the mixtures.

Nitration of the trichlorobiphenyls with the chlorine atoms located in the same aromatic ring (2,3,4-trichlorobiphenyl PCB 29, **Va** and 2,4,6-trichlorobiphenyl PCB 30, **VIa**) gave the dinitrotrichlorobiphenyls as the major products: **Vb** (six isomers) and **VIb** (three isomers), respectively (Scheme 2). The minor reaction products were trinitro derivatives **Vc** (three isomers) and **VIc** (three isomers), respectively; conversion of the starting substrates was complete.

Scheme 2.



IIa–VIa

IIb, IIc–IVb, IVc

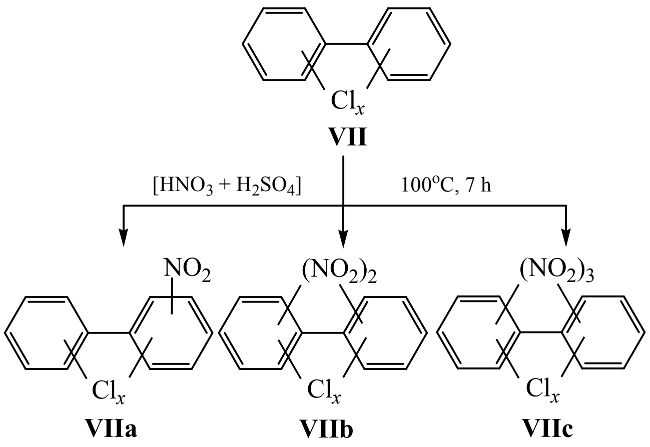
II, $x = 1$ (*m*-Cl), $y = 0$, $n = 3$ (**b**, 79.9%), 4 (**c**, 20.1%); **III**, $x = 1$ (*n*-Cl), $y = 1$ (*o'*-, *m'*- or *p'*-), $n = 2$ (**b**, 90%), 3 (**c**, 10%); **IV**, $x = 2$ (*m*-, *p*-2Cl), $y = 0$, $n = 2$ (**b**, 19.9 %), 3 (**c**, 80.1%); **V**, $x = 3$ (*o, m, p*-3Cl), $y = 0$, $n = 2$ (**b**, 77.5%), 3 (**c**, 22.5%); **VI**, $x= 3$ (*o, o, p*-3Cl), $y = 0$, $n = 2$ (**b**, 98.8%), 3 (**c**, 1.2%).

Thus the investigation of nitration of mono-, di-, and trichlorobiphenyls showed that the increased number of chlorine substituents in biphenyl scaffold significantly decreased the fraction of deep nitration products.

One of the industrial mixtures of polychlorinated biphenyls widely used in Russia is the Trikhlorbifenil, utilized in power capacitors. Our analysis (gas chromatography with flame ionization detector and GC–MS) showed that the Trikhlorbifenil mixture used in this work (**VIIa**) was composed of di- (14%), tri- (48%), tetra- (30%), and pentachlorinated (4%) biphenyls. That composition roughly corresponded to the Arochlor 1242 mixture [20].

The nitration of the **VIIa** substrate resulted in its complete conversion according to Scheme 3 (the numbers of the isomers are given in parentheses). We found by GC–MS analysis dinitro derivatives **VIIc** of tri- and tetrachlorinated biphenyls as the major nitration products (Fig. 1), whereas the fraction of trinitro derivatives **VIId** of di- and trichlorinated biphenyls was relatively low. Hence, the outcome of nitration of the **VIIa** mixture coincided with the conclusions derived from the investigation of nitration of the individual di- and trichlorinated biphenyls **III–VIa**.

Scheme 3.



x	**VIIa**	**VIIb**	**VIIc**
2	–	5.9 (5)	4.7 (4)
3	0.3 (1)	56.4 (13)	3.3 (7)
4	1.7 (3)	21.4 (17)	–
5	0.7 (2)	0.5 (5)	–

To summarize, the direct nitration of polychlorinated biphenyls was a non-selective process, the reaction outcome being mainly affected by the spatial factors. The congeners with less of the electrophilic chlorine substituents in the biphenyl molecule underwent deeper nitration; one to four of nitro groups could be introduced in the substrate under the used reaction conditions.

The above-given quantitative data were obtained using gas chromatography with flame ionization detecting and internal normalization of the peak areas. Such analysis was subject to certain systematic errors due to the unequal sensitivity of the detector to the derivatives with different number of nitro groups and overlap of elution peaks of several products. Therefore, we further analyzed the reaction mixtures applying GC–MS technique; most of the recorded mass spectra of the nitro derivatives of polychlorinated biphenyls contained the molecular ion peaks.

The fragmentation of molecular ions of di- (**IVb**), tri- (**Ib**, **IIb**, and **IVc**), and tetranitro (**Ic** and **IIc**) derivatives occurred via two pathways. In the first case, the molecular ion peak was the strongest one in the spectrum; in the second case, the molecular ion peak intensity was below 1%, and the strongest one was the $[M – NO_2]$ ion peak. However, in both cases, the molecular ion fragmentation occurred via sequential elimination of the nitro groups giving rise to the signals of the $[M – OH]$, $[M – NO]$, $[M – NO_2]$, $[M – 2NO_2]$, etc ions of variable intensity.

The fragmentation of molecular ions of dinitro derivatives **IIIb** occurred via three pathways. Two of them were similar to the above described: (a) the molecular ion peak was absent, and the $[M – NO_2]$ ion peak was the strongest one (Fig. 1) and (b) the molecular ion peak was the strongest one (Fig. 2). In those cases, the molecular ion fragmentation occurred via sequential elimination of the nitro groups, followed by elimination of chlorine atoms. In the third case, an unusual signals pattern was observed: the intensity of the molecular ion peak was 5%, and the strongest signal belonged to the $[M – Cl]$ ion (Fig. 3). Further signals found in the spectrum were assigned to the $[M – Cl – NO]$, $[M – Cl – NO_2 – CO]$, and $[M – Cl – 2NO_2 – Cl]$ ions. Hence, the third fragmentation pathway occurred via sequential elimination of a chlorine atom, a nitro group, and another chlorine atom.

Mass spectra of the trinitro derivatives **IIIc** demonstrated the possibility of all three above-described fragmentation paths. Mass spectra of di- (**Vb** and **VIb**) and trinitro (**Vc** and **VIc**) derivatives of the trichlorobiphenyls (**Va** and **VIa**, respectively) evidenced two possible fragmentation pathways: (a) giving rise to the strongest $[M – Cl]$ ion peak, with the molecular ion peak intensity of 1–2% and (b) havng the molecular ion peak as the strongest one and proceeding with the formation of the $[M – O]$, $[M – NO]$, and $[M – NO_2]$ ions. The fragmentation of the nitro derivatives **VIIb–d** occurred similarly, via the two pathways yielding either the $[M – Cl]$ ion peak with 100% intensity and the molecular ion peak with 1–5% intensity or the molecular ion peak as the strongest one.

EXPERIMENTAL

Chromatograms of the starting compounds and the nitration products were recorded using a Shimadzu GC-2010Plus gas–liquid chromatograph equipped with a flame ionization detector. Other conditions were as follows: a GsBP-5MS quartz capillary column, PDMS with 5% of grafted phenyl groups as the stationary phase, length 30 m, inner diameter 0.25 mm, stationary phase film thickness 0.25 μm; nitrogen as carrier gas, split ratio 1 : 30; starting column temperature 40°C (3 min isotherm followed by heating to 280°C at a rate 10 deg/min), evaporator temperature 250°C, and detector temperature 300°C.

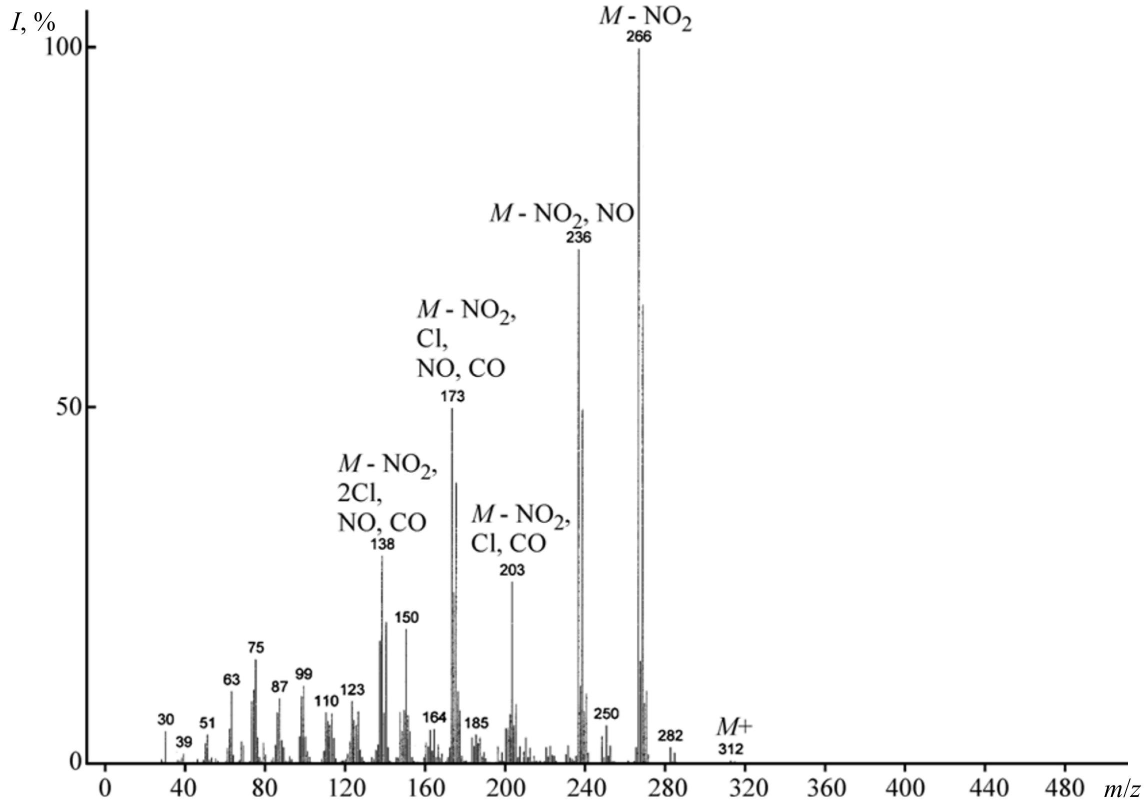


Fig. 1. Mass spectrum of dinitro derivatives **IIIb** [$(C_{12}H_6Cl_2(NO_2)_2]$] (the first type of molecular ion fragmentation).

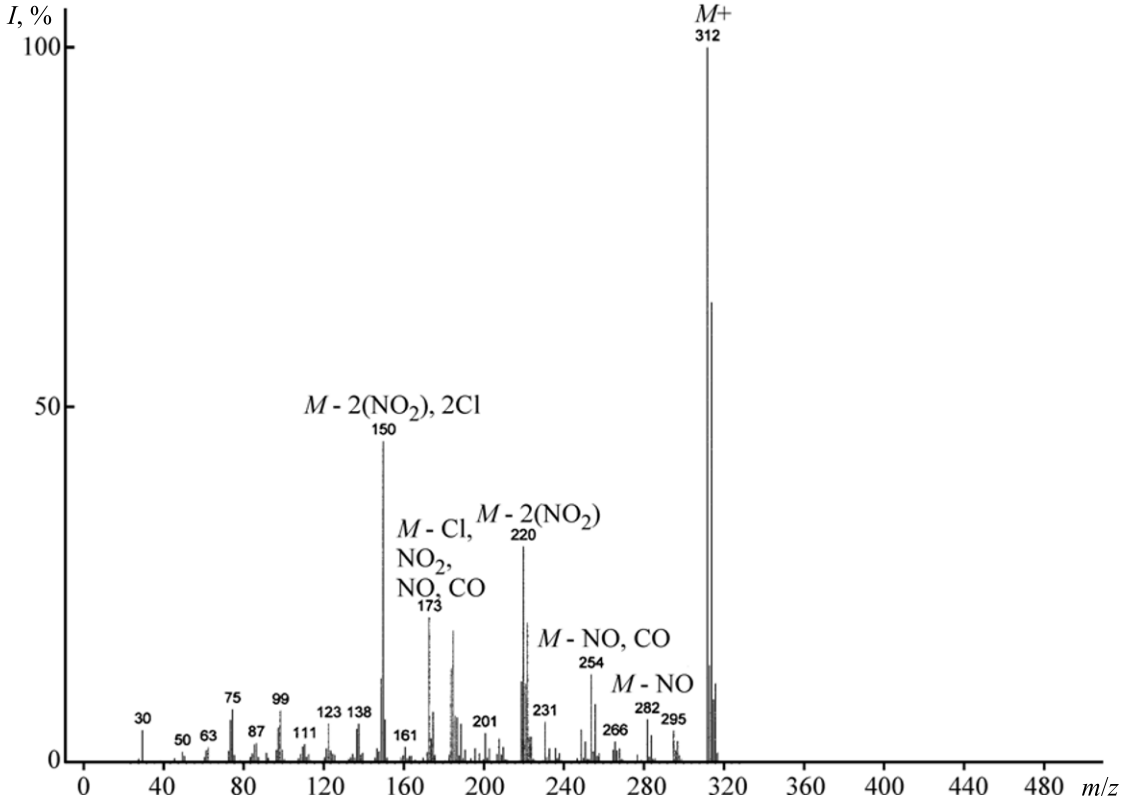


Fig. 2. Mass spectrum of dinitro derivatives **IIIb** [$(C_{12}H_6Cl_2(NO_2)_2]$] (the second type of molecular ion fragmentation).

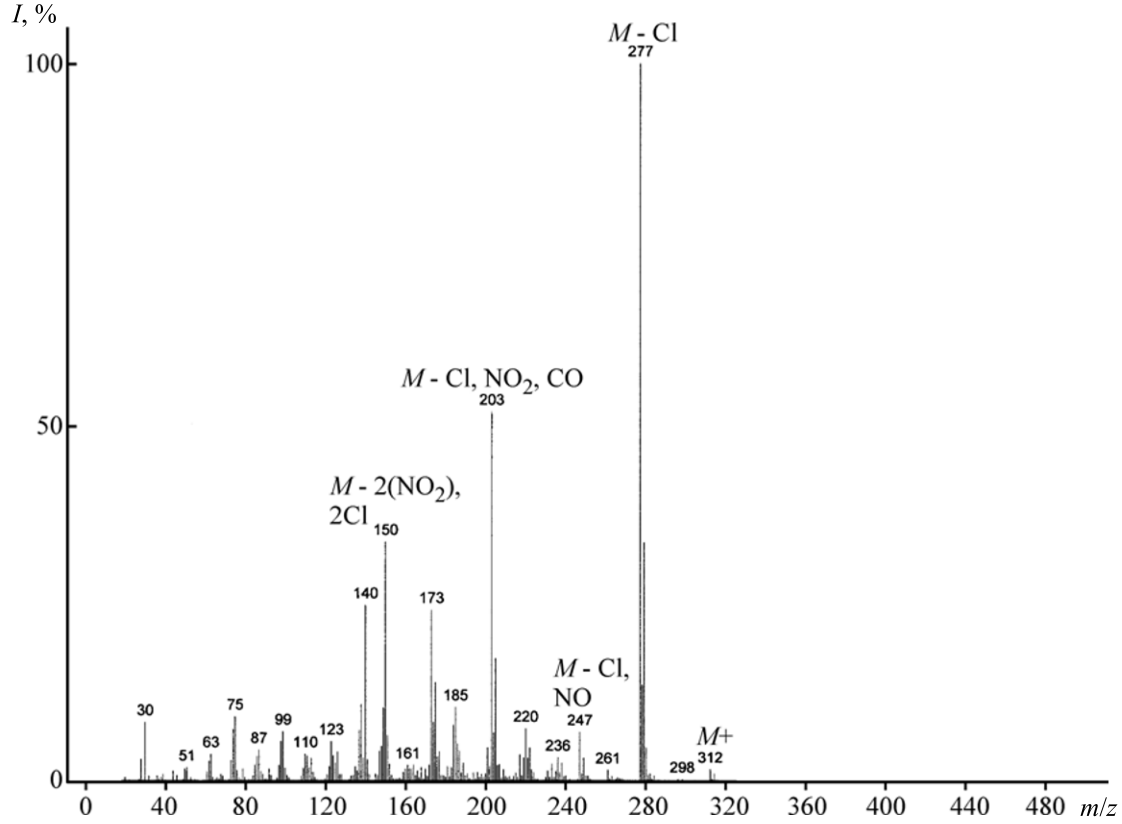


Fig. 3. Mass spectrum of dinitro derivatives **IIIb** [$(C_{12}H_6Cl_2(NO_2)_2)$] (the third type of molecular ion fragmentation).

Mass spectra of the products were obtained using an Agilent GC 7890A MSD 5975 C inert XL EI/CI tandem gas chromatograph–mass spectrometer instrument. Chromatography conditions were as follows: an HP-5MS quartz capillary column, PDMS with 5% of grafted phenyl groups as the stationary phase, length 30 m, inner diameter 0.25 mm, stationary phase film thickness 0.25 µm; helium as carrier gas, split ratio 1 : 50; starting column temperature 40°C (3 min isotherm followed by heating to 290°C at a rate 10 deg/min), evaporator temperature 250°C, transition chamber temperature 280°C, source temperature 230°C, and quadrupole temperature 250°C. Mass spectrum recording conditions were as follows: quadrupole detector, scanning over the whole ion current at mass range of 20–1000 Da; EI at 70 eV.

^{1}H NMR spectra were registered using a Bruker DRX-400 spectrometer at 400 MHz with reference to Me_4Si in CD_3OD. Elemental analysis was performed using a Perkin–Elmer CHN PE 2400 automated analyzer. IR spectra were registered using a Perkin–Elmer Spectrum One spectrophotometer.

^{1}H NMR spectra of the individual polychlorinated biphenyls **IIa** and **IVa**–**VIa** coincided with the reference data [17, 21]. The congeners mixture **IIIa** was a viscous yellow liquid, bp 173–182°C (5 mmHg). Structures of the compounds PCB 8, PCB 13, and PCB 15 constituting the mixture were confirmed by their mass spectra.

Nitration (*general procedure*). 11 mL of the nitrating mixture prepared from 5 mL of conc. HNO_3 and 6 mL of conc. H_2SO_4 on cooling was added dropwise to 0.001 mol of a biphenyl (or a polychlorinated biphenyl congener) at room temperature upon stirring. The reaction mixture was heated on a boiling water bath during 7 h at vigorous stirring. After cooling the mixture to ambient, the viscous organic layer or the solid reaction product was separated and washed with water several times. IR spectrum, ν, cm^{-1}: 2990–2996, 3008–3035 (C–H); 1332–1337, 1530–1536 (NO_2); 892–898 (C–Cl).

Mixture of nitro derivatives (IIb and IIc). Yield 91% (with respect to compound **IIb**). Found, %: C 44.06; H 2.01; Cl 10.67; N 13.15. $C_{12}H_7ClN_3O_6$. Calculated, %: C 44.40; H 2.17; Cl 10.92; N 12.94.

Mixture of nitro derivatives (IIIb and IIIc). Yield 97% (with respect to compound **IIIb**). Found, %: C 44.54; H 1.97; Cl 22.19; N 9.78. $C_{12}H_6Cl_2N_2O_4$. Calculated, %: C 46.03; H 1.93; Cl 22.65; N 8.95.

Mixture of nitro derivatives (IVb and IVc). Yield 92% (with respect to compound **IVc**). Found, %: C 33.73; H 2.25; Cl 17.87; N 9.14. $C_{12}H_5Cl_2N_3O_6$. Calculated, %: C 40.25; H 1.41; Cl 19.80; N 11.73.

Mixture of nitro derivatives (Vb and Vc). Yield 91% (with respect to compound **Vb**). Found, %: C 37.32; H 1.55; Cl 28.82; N 8.83. $C_{12}H_5Cl_3N_2O_4$. Calculated, %: C 41.47; H 1.45; Cl 30.60; N 8.06.

Mixture of nitro derivatives (VIb and VIc). Yield 97% (with respect to compound **VIb**). Found, %: C 40.75; H 1.35; Cl 30.24; N 8.04. $C_{12}H_5Cl_3N_2O_4$. Calculated, %: C 41.47; H 1.45; Cl 30.60; N 8.06.

Mixture of nitro derivatives (VIIb–VIId). Yield 95% (with respect to compound **VIIb**). Found, %: C 38.11; H 1.29; Cl 38.13; N 7.79. $C_{12}H_4Cl_4N_2O_4$. Calculated, %: C 37.73; H 1.06; Cl 37.12; N 7.33.

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