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A Methodology for Synthesis of Primary *o*-Phenylenebisphosphines and *o*-Chlorophenylphosphines

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Abstract — On the basis of the reaction of ethynediylbisphosphonates and chloroethynylphosphonates with classical donor alka-1,3-dienes, a general strategy for synthesis of *o*-bisphosphanylbenzenes and *o*-chlorophosphanylbenzenes, which includes two consecutive steps: Diels–Alder condensation → aromatization of the carbocyclic phosphonate (bisphosphonate) formed → reduction of the phosphonate groups, was developed. Convenient procedures are devised for aromatization of phosphorus-containing cyclohexa-1,4-dienes and for reduction of *o*-phenylenebisphosphonates and *o*-clorophenylphosphonates to primary phosphines. A series of new alkylsubstituted phosphonic chlorides were prepared, and a possibility of functionalization of methyl-substituted *o*-phenylenebisphosphonates and *o*-clorophenylphosphonates by the methyl groups is demonstrated.
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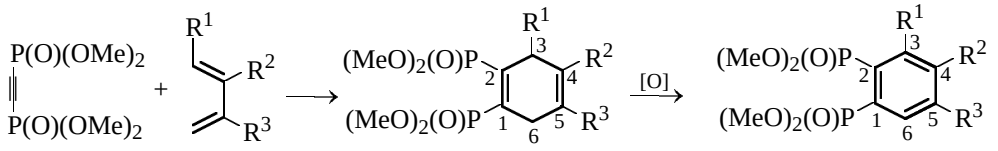
Primary ring-substituted *o*-bisphosphanylbenzenes are of special interest for the coordination chemistry as polydentate ligands [1]. The simplest representative of this class of compounds, 1,2-bisphosphanylbenzene, *o*-$C_6H_4(PH_2)_2$, has been prepared by reduction of corresponding *o*-bisphosphorylated arenes: tetraethyl *o*-phenylenebisphosphonate with LiAlH4 [2]; tetramethyl *o*-phenylenebisphosphonate with $LiAlH_4$/Me_3SiCl [3] or Ph_2SiH_2 [4], as well as *o*-phenylenebis(dichlorophosphane) *o*-$C_6H_4(PCl_2)_2$ by $LiAlH_4$ [5, 6]. Methods for formation of aromatic precursors are mostly complicated, give hardly separable mixtures, and, as a result, afford low yields. One of the methods involves substitution of halogens in 1,2-dihalobenzenes. For example, *o*-phenylenebisphosphonates can be synthesized by a photocatalytic reaction of dialkyl phosphites with 1-bromo-2-iodo- and 1-chloro-2-iodobenzene [7] and by photo- [8] or Ni(II)-catalyzed [9] reactions of trialkyl phosphites with the above-mentioned 1-iodo-2-halobenzenes or *o*-dichlorobenzene [3]. Another synthetic route to aromatic *o*-bisphosphines is based on nucleophilic substitution of halogens in 1-iodo-2-halobenzenes with Na, K, Li, or Ca phosphides. Depending on the phosphide used, secondary or tertiary *o*-bisphosphanylbenzenes have been obtained [10–22].

The Diels–Alder reaction provides an alternative synthetic route to *o*-phenylenebisphosphonates. Its classical form (donor diene and acceptor acetylene) has been realized in the reaction of ethynediylbisphosphonic acid with some active cyclic dienes (α-pyrone [23], cyclohexa-1,3-diene [24]) with a fixed *cis* configuration. The process involves thermal elimination of low-molecular compounds (CO_2, C_2H_4), resulting in ring aromatization. In the case of 1-phosphono-2-propynoic acid as dienophile [25], a high regioselectivity was noted in the reaction with 1-substituted butadienes. In all the cases, the initial Diels–Alder adduct was not registered, and compounds formed by subsequent aromatization of carbocyclic phosphonates were only described. We earlier reported [26, 27] that 2-chloro- and 2-bromoethynylphosphonates, like ethynediylbisphosphonates, are active dienophiles in reactions with donor alka-1,3-dienes (butadiene, isoprene, piperylene, and 2,3-dimethylbuta-1,3-diene).

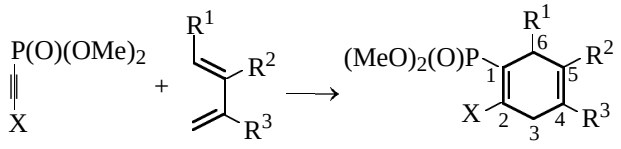
In this communication we consider in more details a general method for synthesis of phenylphosphonates and *o*-phenylenebisphosphonates, related dichlorides, phosphanylbenzenedicarboxylates, and primary phosphines, in which the *ortho* position of two phosphorus or phosphorus and chlorine substituents is provided by the formation of a six-membered ring in the Diels–Alder reaction of ethynediylbisphosphonates or haloethynylphosphonates with donor open-chain alka-1,3-dienes. Ethynediylbisphosphonates are most active in these reactions. Therewith, the process proceeds readily at room temperature or under heating at 140–150°C [28].



Ia–Id **IIa–IId**

I, $R^1 = R^2 = R3 = H$ (**a**); R^1 = Me, $R^2 = R^3 = H$ (**b**); $R^1 = R^3 = H$, R^2 = Me (**c**); $R^1 = H$, $R^2 = R^3$ = Me (**d**).

As objects for study we used tetramethyl ethynediylbisphosphonate that forms products with lower boiling points. Carbocyclic bisphosphonates **Ia**–**Id** formed by the reaction of the bisphosphonate prepared from dibromoacetylene undergo partial spontaneous aromatization at room temperature to form aromatic bisphosphonates **IIa**–**IId**; the reaction is promoted by air oxygen and, probably, by bromine in catalytic amounts. With the bisphosphonates prepared from dichloroacetylene, such spontaneous aromatization did not occur. Chloroethynylphosphonates are less active as dienophiles, but they, too, form corresponding carbocyclic *o*-halophosphonates while at higher temperatures (~180–200°C) and longer time (8–12 h).

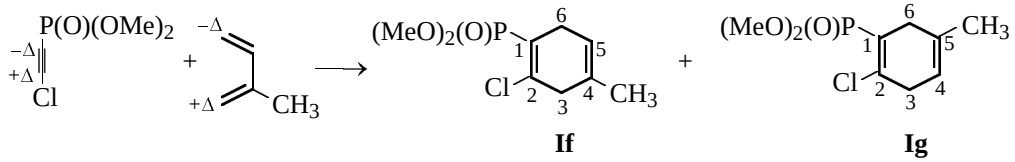


Ie–Ig

I, $R^1 = H$, $R^2 = R^3$ = Me (**e**); $R^1 = H$, $R^2 = H$, R^3 = Me (**f**); $R^1 = H$, R^2 = Me, R^3 =H (**g**); X = Cl (Br) [26].

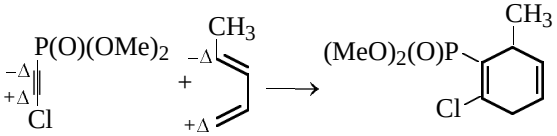
The synthesis proceeds better in ampules sealed under argon, in the presence of an inhibitor of polymerization (1,4-hydroquinone). Phosphonates **Ie**–**Ig** are high-boiling viscous stable liquids. Bromoethynylphosphonates can also be used in this reaction.

With chloroethynylphosphonate as example, we traced the reaction regioselectivity with unsymmetrical 2-substituted dienes. Isoprene forms a mixture of 4-methyl- and 5-methyl-substituted (2-chlorocyclohexa-1,4-dien-1-yl)phosphonates in a 3 : 1 ratio. The predominant formation of isomer **Ie** corresponds to polarization of the components and provides evidence for the electronic reaction control.

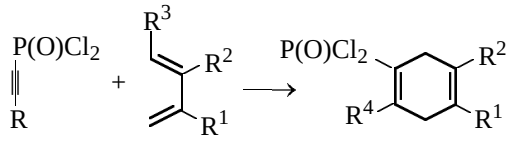


If **Ig**

The structure of isomers **If** and **Ig** is unambiguogly established by their ^{13}C NMR spectra. Ceratin reaction regioselectivity is observed with 1-substituted alka-1,3-dienes: With piperylene, only one isomer is formed, which corresponds to the electronic control of reaction regioselectivity [25]:

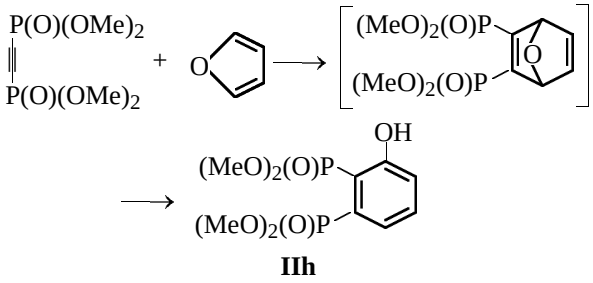


We failed to involve alkyl- and arylethynylphosphonic esters to the Diels–Alder reaction even by heating to 240°C. However, the more acceptor dichlorophosphinoyl group strongly enhances the polarity of the adjacent triple bond, and the condensation occurs successfully at 140–160°C and features a high regioselectivity. Noteworthy, the reactions of (3,3-dimethylbut-1-ynyl)phosphonic dichloride with alka-1,3-dienes involves cleavage of the phosphonate group to form corresponding benzene derivatives [27].



R^1, R^2, R^3 = H, CH_3; R = Ph, *t*-Bu, CH_3.

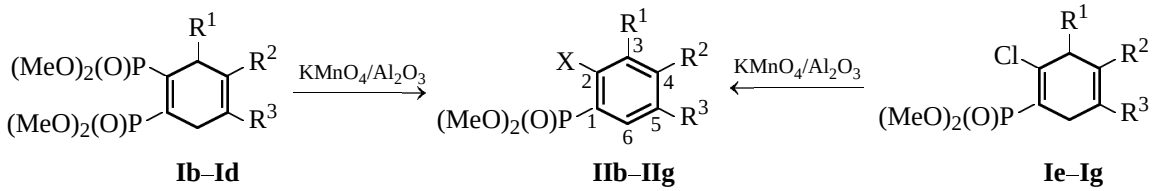
As known, ethyl (diethoxyphosphinoyl)ethynylcarboxylate $(EtO)_2P(O)C{\equiv}CCO_2Et$ enters the diene synthesis with furan to form the corresponding carbocyclic *o*-carboxyphosphonate [25]. Tetramethyl ethynediylbisphosphonate, too, reacts with furan but under more rigid conditions (200°C, 8 h). The initial condensation product was not registered, and the reaction resulted in exclusive formation of phenolic bisphosphonate **IIhe** via cleavage of the C–O bond.



IIh

The reaction involved profound polymerization of furan. Compound **IIh** was identified in the reaction mixtures by spectroscopy. With highly reactive electron-donor dienes, 1-dimethylamino- and 1-ethoxybuta-1,3-dienes, only traces of adducts (1–2%) and much polymerization products of the diene component were detected by ^{1}H NMR spectroscopy. At low temperatures, both competing reactions decelerated, but the product yields did not improved. Using Lewis acids ($FeCl_3$, $AlCl_3$, $SnCl_4$, $ZnCl_2$) and transition metal salts ($CuCl_2$, $NiCl_2$, $PdCl_2$) as catalysts and performing the reaction under conditions of high dilution, too, proved unsuccessful. Acceptor alka-1,3-dienes, such as 1,4-diphenylbuta-1,3-diene, 2,3-bis(dichlorophosphinoyl)buta-1,3-diene, and 2,3-bis(diphenylphosphanyl)buta-1,3-diene, do not undergo the diene synthesis even under rigid conditions: We failed to detect even traces of cyclocondensation products in the reactions in solvents (toluene, *o*-xylene, nitrobenzene) or in their absence, at temperatures ranging from 120°C to 250°C, or in the presence of the above-mentioned catalysts. Probably, the key factors responsible for the negative result here were both steric hindrances and insufficient reactivity of the ethynylbisphosphonate.

As known, 1,4-cyclohexadienes can be dehydrogenated to obtain substituted benzenes, using a wide range of reagents: Pd/C at 300°C [29], benzaldehyde or nitrobenzene [30], MnO_2 in boiling benzene [31], and $KMnO_4$ in the presence of dicyclohexyl-18-crown-6 [32]. 1,4-Dihydropyridine can be dehydrogenated by the reaction with the $KMnO_4$–Al_2O_3 system in aqueous benzene under reflux [33]. We found that 2-chlorocyclohexadienylphosphonates **Ie**–**Ig** and cyclohexadienediylbisphosphonates **Ib**–**Id** are also readily dehydrogenated affording chlorophenylphosphonates **IIe**–**IIg** and *o*-phenylenebisphosphonates **IIb**–**IId**. In our hands, the $KMnO_4$–Al_2O_3 system in acetone at 0°C proved the most convenient. Compounds **IIb**–**IIg** were obtained in good yields (50–70%) without admixtures of by-products.



Ib–**Id** **IIb**–**IIg** **Ie**–**Ig**

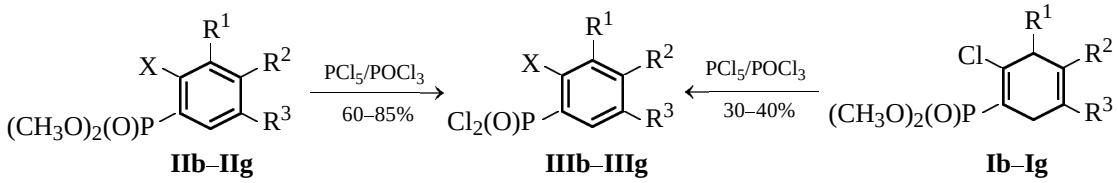
II, R^1 = Me, R^2 = R^3 = H, X = $P(O)(OMe)_2$ (**b**); R^1 = R^3 = H, R^2 = Me, X = $P(O)(OMe)_2$ (**c**); R^1 = H, R^2 = R^3 = Me, X = $P(O)(OMe)_2$ (**d**); R^1 = H, R^2 = R^3 = X = Cl (**e**); R^1 = H, R^2 = Me, R^3 = H, X = Cl (**g**).

With $KMnO_4$ without Al_2O_3, the yield is reduced (30–40%), and the consumption of $KMnO_4$ is increased. Other reagents (sulfur without solvent, SeO_2 in dioxane, benzoquinone in THF, or Pd/C in ethanol) can also be used for aromatization, but the expected phosphonates always formed in lower yields and were contaminated with hardly separable by-products (such as, respectively, phosphonothioaates, phosphonic acids, hydroquinone, or cyclohexylphosphonates). Phosphonates **IIb**–**IIg** are stable high-boiling viscous liquids, compounds **IIc**–**IIe** afford crystals on prolonged keeping.

Phosphonic halides are known to be more suitable

starting materials for preparing aromatic phosphines than corresponding dialkyl phosphonates [34, 35]. Moreover, the presence of mobile halide atoms at phosphorus allows functionalization and modification of the phosphorus-containing part of the molecule. Dimethyl alkylphosphonates are readily transformed into chlorides by treatment with PCl_5–$POCl_3$ [36].

We found that *o*-phenylenebisphosphonates **IIb**–**IId** and *o*-chlorophenylphosphonates **IIe**–**IIg**, too, react with PCl_5–$POCl_3$ to form *o*-phenylenebis(phosphonic dichlorides) **IIIb**–**IIId** and *o*-chlorophenylphosphonic dichlorides **IIIe**–**IIIg** [28] very readily and in high yields (60–85%).

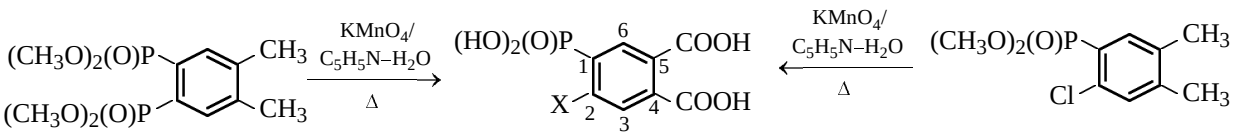


IIb–**IIg** **IIIb**–**IIIg** **Ib**–**Ig**

III, R^1 = Me, R^2 = R^3 = H, X = $P(O)Cl_2$ (**b**); R^2 = Me, R^1 = R^3 = H, X = $P(O)Cl_2$ (**c**); R^1 = H, R^2 = R^3 = Me, X = $P(O)Cl_2$ (**d**); R^1 = H, R^2 = R^3 = Me, X = Cl (**e**); R^1 = H, R^2 = H, R^3 = Me, X = Cl (**f**); R^1 = H, R^2 = Me, R^3 = H, X = Cl (**g**).

Phosphonic dichlorides **IIIb**–**IIIg** are also directly available by the reactions of (cyclohexa-1,4-diene-1,2-diyl)bisphosphonates **Ia**–**Id** and (2-chlorocyclohexa-1,4-dien-1-yl)phosphonates **Ie**–**Ig** with phosphorus pentachloride taken in a 1.5 molar excess, in the presence of phosphorus oxychloride. The reaction is accompanied by strong tarring, and the product yields are fairly low (30–40%). In general, this route proved to be less suitable, because the final chlorides were strongly contamined with isomeric cyclohexa-1,3- and cyclohexa-1,4-dienylphoshonic chlorides, which could not be removed by repeated high-vacuum distillation. Chlorides **IIIb**–**IIIg** are low-melting white crystalline substances with an unpleasant odor, easily hydrolyzed by air moisture.

For revealing pathways for further functionalization, we oxidized the methyl groups in *o*-phenylenebisphosphonate **IId** and *o*-chlorophenylphosphonate **IIe** with $KMnO_4$ into carboxy groups to obtain earlier unknown phosphorus-containing phthalic acids: 4,5-diphosphonophthalic (**IVd**) and 4-chloro-5-phosphonophthalic (**IVe**) acids.

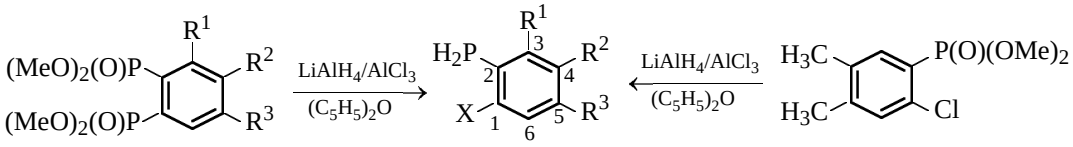


IId **IVd, IVe** **IIe**

X = $P(O)(OH)_2$ (**d**), Cl (**e**).

The oxidation requires rather rigid conditions. Therefore, attempted aromatization of **Id** and **Ie** and subsequent oxidation of the methyl groups without isolation of phosphonates **IId** and **IIe** resulted in polymerization of the starting carbocyclic compounds and tarring. By contrast, phosphonates **IId** and **IIe** could be easily and effectively oxidized in boiling pyridine. A significant excess of $KMnO_4$ is required, because it is also consumed to oxidize the methanol formed by hydrolysis of the ester. Acids **IVd** and **IVe** can also be prepared in aqueous medium but in a considerably lower yield. The phosphonophthalic acids obtained are high-melting white crystalline substances very well soluble in water and methanol.

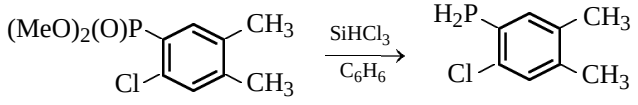
Compounds **IIb**–**IIg** can be reduced to the corresponding aromatic phosphines [37]. *o*-Phenylenebisphosphonates **IIc**, **IId** and 2-chlorophenylphosphonate **IIe** react with $LiALH_4$ in the presence of $AlCl_3$ in diethyl ether to form substituted *o*-phenylenebisdiphosphines **Vc**, **Vd** and 2-chlorophenylphosphine (**Ve**), respectively.



IIc, IId **Vc–Ve** **IIe**

V, R^2 = Me, R^1 = R^3 = H, X = PH_2 (**c**); R^1 = H, R^2 = R^3 = Me, X = PH_2 (**d**); R^1 = H, R^2 = R^3 = Me, X = Cl (**e**).

With $LiAlH_4$ in ether or THF and with $LiAlH_4$–$(CH_3)_3SiCl$ in THF, the reduction requires prolonged boiling, which results in formation of a great amount of polyphosphoric by-products and oxidation of the main product; the phosphines formed are difficult to isolate. We found that dimethyl (2-chloro-4,5-dimethylphenyl)phosphonate (**IIe**) is reduced with trichlorosilane in benzene to form phosphine **Ve** in higher yield and fairly pure.



IIe **Ve**

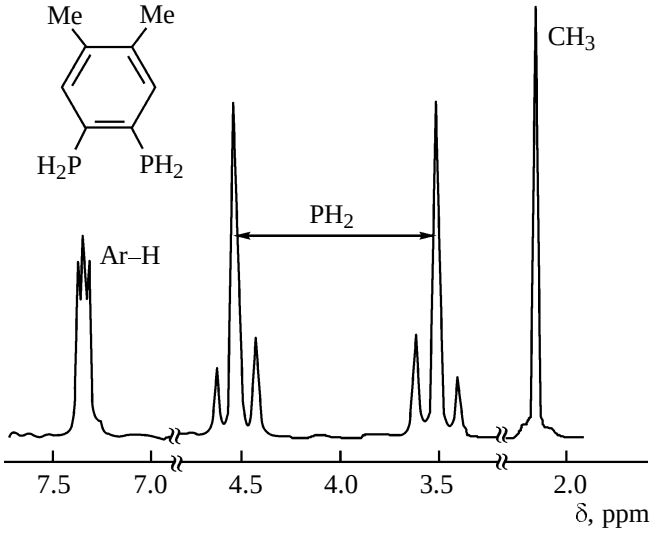
Phenylenebisphosphonates **IIc**, **IId** under the same conditions form with $SiHCl_3$ a hardly controlled mixture of polyphosphoryl compounds (δ_P –40 to –60 ppm).

Attempts to prepare phosphines **Vc**–**Ve** by reduction of phosphonic chlorides **IIIc**–**IIIe** were less successful, since the latter were extremely poorly soluble in diethyl ether, especially below zero. This wiped out the effect of the high reactivity of chlorides in this reaction and made them much less suitable synthons for preparing primary phosphines than dialkyl arylphospohnates **IIc**–**IId**.

Bisphosphine **Vc** is a colorless labile liquid with a very unpleasant odor, and compounds **Vd** and **Ve** are low-melting white crystalline substances. In the ^1H NMR spectrum, the phosphine proton signals appear in the high field as a multiplet assignable to an A_2X–XA_2 spin system [δ 4.0 ppm, $^1J_{HP}$ 200–210 Hz, $^3J_{HP}$ 23 Hz (see figure)] arising as a result of equal chemical shifts of two phosphorus and four proton signals at unequl J_{HP} constants.

The proton-decoupled ^{31}P NMR spectra of unsymmetrical bisphosphine **Vc**, like those of starting phosphonate **IIc** and chloride **IIIc** containing nonequivalent phosphorus nuclei, shows a typical *AB* system with $^3J_{PP}$ 38.9 Hz.

The proposed synthetic strategy (cyclohexa-1,4-dienylphosphonate → phenylphosphonate → phenylphosphine) allows preparation of ring-substituted *o*-phenylenebisphosphines and *o*-chlorophenylphosphines, earlier unavailable synthons for polydentate ligands.



^1H NMR spectrum of (4,5-dimethyl-*o*-phenylene)bisphosphine (**Vd**).

EXPERIMENTAL

All reagents and solvents were of chemical grade. Synthesis and all operations with phosphines were performed under oxygen-free argon of ultrapure grade. The ^1H, ^{13}C and ^{31}P NMR spectra were registered on a Bruker AC-200 instrument at 200.05 (^1H), 50.328 (^{13}C), and 81 MHz (^{31}P), solvents $CDCl_3$, CCl_4, C_6D_6, and D_2O. The ^1H and ^{13}C chemical shifts referred to TMS were measured using internal $CDCl_3$, and the ^{31}P chemical shifts, using external 85% H_3PO_4. The starting compounds: tetramethyl ethynediylbisphosphonate, dimethyl chloroethynylphosphonate, and 1,3-dienes were prepared by known procedures [38–46].

Tetramethyl (cyclohexa-1,4-diene-1,2-diyl)bisphosphonate (Ia). Tetramethyl ethynediylbisphosphonate, 12.1 g (0.05 mol), was placed in a cooled

50-ml ampule, after which 16.6 ml (0.2 mol) of freshly distilled and cooled (–30°C) buta-1,3-diene and 3–5 mg of hydroquinone were added. The ampule was sealed and heated at 120–125°C for 10 h. The reaction progress was monitored by ^{1}H NMR spectroscopy. After the reaction had been complete, excess buta-1,3-diene was distilled off at reduced pressure, and the residual oil was distilled in a vacuum. Yield 55%, bp 143–145°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 15.23 s. ^{13}C NMR spectrum, δ_C, ppm: 137.85 d.d ($C^{1,2}$, $^1J_{CP}$ 191.69 Hz, $^2J_{CP}$ 17.3 Hz), 121.69 d ($C^{4,5}$, $^3J_{CP}$ 4.5 Hz), 52.31 d (C_i, $^2J_{CP}$ 3.8 Hz), 29.43 d ($C^{3,6}$, $^2J_{CP}$ 12.7 Hz). ^{1}H NMR spectrum, δ, ppm: 5.20 m (2H), 3.34 d (12H, $^3J_{HP}$ 8.1 Hz), 2.54 (m, 4H).

Tetramethyl (3-methylcyclohexa-1,4-diene-1,2-diyl)bisphosphonate (Ib) was prepared similarly to **Ia** from 12.1 g (0.05 mol) of tetramethyl ethynediylbisphosphonate and 20 ml (0.2 mol) of piperylene. The reaction was performed at 165°C for 12 h. Yield 50%, bp 150–154°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 15.99 s. ^{13}C NMR spectrum, δ_C, ppm: 143.25 d (C^1, $^1J_{CP}$ 187.16 Hz), 138.03 d (C^2, $^1J_{CP}$ 190.6 Hz), 128.91 d (C^4, $^3J_{CP}$ 7.9 Hz), 120.46 d (C^5, $^3J_{CP}$ 8.7 Hz), 51.98 d (C_i, $^2J_{CP}$ 4.7 Hz), 33.25 d.d (C^3, $^2J_{CP}$ 16.05 Hz , $^3J_{CP}$ 10.07 Hz), 29.61 d.d, C^6, $^2J_{CP}$ 16.05 Hz, $^3J_{CP}$ 10.07 Hz), 20.70 s (C^7). ^{1}H NMR spectrum, δ, ppm: 5.37 m (2H), 3.42 d (12H, $^3J_{HP}$ 10.5 Hz), 2.69 m (4H), 0.81 d (3H, $^3J_{HH}$ 8.4 Hz).

Tetramethyl (4-methylcyclohexa-1,4-diene-1,2-diyl)bisphosphonate (Ic) was prepared similarly to **Ia** from 12.1 g (0.05 mol) of tetramethyl ethynediylbisphosphonate and 12.5 ml (0.13 mol) of isoprene. The reaction was performed at 140–160°C for 6 h. Yield 70%, bp 155–158°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 16.07 s. ^{13}C NMR spectrum, δ_C, ppm: 137.55 d.d ($C^{1,2}$, $^1J_{CP}$ 189.6 Hz, $^2J_{CP}$ 18.3 Hz), 127.97 d (C^5, $^3J_{CP}$ 3.9 Hz), 115.06 d (C^4, $^3J_{CP}$ 13.1 Hz), 51.39 d (C_i, $^2J_{CP}$ 5.8 Hz), 33.27 d.d (C^6, $^2J_{CP}$ 13.1 Hz , $^3J_{CP}$ 13.1 Hz), 29.97 d.d (C^3, $^2J_{CP}$ 13.1 Hz $^3J_{CP}$ 13.1 Hz), 20.88 s (C^7). ^{1}H NMR spectrum, δ, ppm: 5.10 m (1H), 3.55 d (12H, $^3J_{HP}$ 8.4 Hz), 2.80 m (2H), 2.75 m (2H), 1.20 s (3H).

Tetramethyl (4,5-dimethylcyclohexa-1,4-diene-1,2-diyl)bisphosphonate (Id) was prepared similarly to **Ia** from 12.1 g (0.05 mol) of tetramethyl ethynediylbisphosphonate and 9.0 ml (0.08 mol) of 2,3-dimethylbuta-1,3-diene. The reaction was performed at 120–140°C for 5 h. Yield 78%, bp 163–167°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 15.90 s. ^{13}C NMR spectrum, δ_C, ppm: 137.94 d.d ($C^{1,2}$, $^1J_{CP}$). 191.44 Hz , $^2J_{CP}$ 15.2 Hz), 120.81 d ($C^{4,5}$, $^3J_{CP}$ 4.2 Hz), 52.37 s (C_i), 36.10 d ($C^{3,6}$, $^2J_{CP}$ 12.9 Hz), 17.17 s ($C^{7,8}$). ^{1}H NMR spectrum, δ, ppm: 3.34 d (12H, $^3J_{HP}$ 8.8 Hz), 2.68 (m, 4H), 1.32 (s, 6H).

Dimethyl (2-chloro-4,5-dimethylcyclohexa-1,4-dien-1-yl)phosphonate (Ie) was prepared similarly to **Ia** from 8.4 g (0.05 mol) of dimethyl (chloroethynyl)phosphonate and 12.3 ml (0.15 mol) of 2,3-dimethylbuta-1,3-diene. The reaction was performed at 160–170°C for 8 h. Yield 60%, bp 98–100°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm (CCl_4): 16.20 s. ^{13}C NMR spectrum, δ_C, ppm: 139.80 s (C^2), 122.10 s (C^5), 120.40 s (C^4), 119.80 d (C^1, $^1J_{CP}$ 141.93 Hz), 51.13 d (C_i, $^2J_{CP}$ 6.5 Hz), 41.30 d (C^6, $^2J_{CP}$ 15.1 Hz), 36.0 d (C^3, $^3J_{CP}$ 10.0 Hz), 16.47 s (C^8), 16.36 s (C^7). ^{1}H NMR spectrum, δ, ppm: 3.35 d (6H, $^3J_{HP}$ 9.4 Hz), 2.56 (m, 4H), 1.22 (s, 6H).

Dimethyl (2-chloro-4-methylcyclohexa-1,4-dien-1-yl)phosphonate (If) was prepared similarly to **Ia** from 8.4 g (0.05 mol) of dimethyl (chloroethynyl)-phosphonate and 25.0 ml (0.25 mol) of isoprene. The reaction was performed at 180–200°C for 12 h. Yield 50% (together with isomer **Ig**), bp 90–94°C (1 mm Hg). Content in the mixture 65 mol %. ^{31}P NMR spectrum, δ_P, ppm (CCl_4:) 16.49 s. ^{13}C NMR spectrum, δ_C, ppm: 139.60 s (C^2), 128.10 s (C^4), 120.15 d (C_i, $^1J_{CP}$ 186.20 Hz), 116.34 d (C^5, $^3J_{CP}$ 11.1 Hz), 50.96 d (C_i, $^2J_{CP}$ 4.3 Hz), 39.36 d (C^6, $^2J_{CP}$ 12.0 Hz), 30.2 d (C^3, $^3J_{CP}$ 10.0 Hz), 20.69 s (C^7). ^{1}H NMR spectrum, δ, ppm: 4.87 m (1H), 3.23 d (6H, $^3J_{HP}$ 11.8 Hz), 2.23 (m, 4H), 1.15 (s, 3H).

Dimethyl (2-chloro-4-methylcyclohexa-1,4-dien-1-yl)phosphonate (Ig) formed together with **Ie** in the preceding experiment, content in the mixture 35 mol %. ^{31}P NMR spectrum, δ_P, ppm (CCl_4): 16.24 s. ^{13}C NMR spectrum, δ_C, ppm: 140.10 s (C^2), 129.23 d (C^5, $^3J_{CP}$ 11.1 Hz), 120.05 d (C_i, $^1J_{CP}$ 186.20 Hz), 115.50 s (C^4), 51.96 d (C_i, $^2J_{CP}$ 4.3 Hz), 35.80 d (C^6, $^2J_{CP}$ 12.0 Hz), 34.0 d (C^3, $^3J_{CP}$ 10.0 Hz), 20.96 s (C^7). ^{1}H NMR spectrum, δ, ppm: 4.64 m (1H), 3.23 d (6H, $^3J_{HP}$ 11.8 Hz), 2.23 (m, 4H), 1.15 (s, 3H).

Tetramethyl (3-methyl-*o*-phenylene)bisphosphonate (IIb). *a*. To 31.6 g (0.1 mol) of $KMnO_4$/Al_2O_3 (1 : 1) suspended in 100 ml of anhydrous acetone, a solution of 15.5 g (0.05 mol) of **Ib** in 80 ml of acetone was added under cooling and vigorous stirring. The reaction mixture was kept for 4 h at room temperature and 2 h under reflux. After cooling, the suspension was filtered, the solid was carefully washed with acetone, and the combined filtrate was evapo-

rated. The residue was fractionated in a vacuum (1.0 mm Hg).

b. A solution of 24.8 g (0.08 mol) of **Ib** in 100 ml of anhydrous acetone was slowly added under cooling and vigorous stirring to a solution of 38.4 g (0.24 mol) of $KMnO_4$ in 200 ml of acetone. The reaction mixture was kept at room temperature for 4 h and under reflux for 2 h. The product was isolated as described in procedure *a*. Yield 42% (*a*), 29% (*b*). bp 160–162°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 18.70 s. ^{13}C NMR spectrum, δ_C, ppm: 140.80 d.d (C^6, $^2J_{CP}$ 8.8 Hz, $^3J_{CP}$ 12.7 Hz), 134.12 d (C^4, $^3J_{CP}$ 13.1 Hz), 132.68 d.d (C^3, $^2J_{CP}$ 9.3 Hz, $^3J_{CP}$ 12.2 Hz), 131.26 d (C^5, $^3J_{CP}$ 12.9 Hz), 127.22 d.d (C^2, $^1J_{CP}$ 188.30 Hz, $^2J_{CP}$ 9.6 Hz), 121.13 d.d (C_i, $^1J_{CP}$ 192.4 Hz, $^2J_{CP}$ 10.3 Hz), 51.46 d (C_i, $^2J_{CP}$ 4.2 Hz), 19.30 s (C^7). ^1H NMR spectrum, δ, ppm: 7.53 d.d (1H, $^3J_{HP}$ 17.8 Hz, $^3J_{HH}$ 7.7 Hz), 7.21 m (1H), 6.79 d (1H, $^3J_{HH}$ 7.1 Hz), 3.46 d (12H, $^3J_{HP}$ 6.88 Hz), 1.90 s (3H).

Tetramethyl (4-methyl-*o*-phenylene)bisphosphonate (IIc) was prepared similarly to **IIb** from 15.5 g (0.05 mol) of **Ic** under the action of 28.4 g (0.09 mol) of $KMnO_4/Al_2O_3$ (1 : 1) (procedure *a*) or of 21.3 g (0.135 mol) of $KMnO_4$ (procedure *b*). Yield 62% (*a*), 37% (*b*). bp 163–166°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 18.01, 18.36 (*AB* system), J_{PP} 14.14 Hz. ^{13}C NMR spectrum, δ_C, ppm: 141.59 m (C^4, $^3J_{CP}$ 12.1 Hz), 135.16 d.d (C^6, $^2J_{CP}$ 8.5 Hz, $^3J_{CP}$ 13.6 Hz), 134.51 d.d (C^3, $^2J_{CP}$ 9.1 Hz, $^3J_{CP}$ 13.3 Hz), 131.36 d (C^5, $^3J_{CP}$ 13.4 Hz), 128.90 d.d (C^2, $^1J_{CP}$ 189.0 Hz, $^2J_{CP}$ 10.7 Hz), 125.74 d.d (C_i, $^1J_{CP}$ 191.7 Hz, $^2J_{CP}$ 9.7 Hz), 51.87 d (C_i, $^2J_{CP}$ 3.8 Hz), 51.79 d (C_i, $^2J_{CP}$ 4.6 Hz), 20.51 s (C^7). ^1H NMR spectrum, δ, ppm: 7.51 d.d (1H, $^3J_{HP}$ 14.0 Hz, $^3J_{HH}$ 7.6 Hz), 7.46 d (1H, $^3J_{HP}$ 20.0 Hz), 6.98 d (1H, $^3J_{HH}$ 7.8 Hz), 3.50 d (12H, $^3J_{HP}$ 7.41 Hz), 2.20 s (3H).

Tetramethyl (4,5-dimethyl-*o*-phenylene)bisphosphonate (IId) was prepared similarly to **IIb** from 16.2 g (0.05 mol) of **Id** under the action of 23.7 g (0.08 mol) of $KMnO_4/Al_2O_3$ (1 : 1) (procedure *a*) or 17.8 g (0.11 mol) of $KMnO_4$ (procedure *b*). bp 170–174°C (1 mm Hg). Yield 70% (*a*), 40% (*b*). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 18.95 s. ^{13}C NMR spectrum, δ_C, ppm: 140.06 d.d ($C^{4,5}$, $^3J_{CP}$ 10.9 Hz, $^4J_{CP}$ 4.2 Hz), 136.06 d.d ($C^{3,6}$, $^2J_{CP}$ 11.7 Hz, $^3J_{CP}$ 11.7 Hz), 126.12 d.d ($C^{1,2}$, $^1J_{CP}$ 190.1 Hz, $^2J_{CP}$ 8.1 Hz), 51.77 s (C_i), 18.5 s ($C^{7,8}$). ^1H NMR spectrum, δ, ppm: 7.50 m (2H, $^3J_{HP}$ 16.0 Hz), 3.37 d (12H, $^3J_{HP}$ 9.6 Hz), 1.90 (s, 6H).

Dimethyl (2-chloro-4,5-dimethylphenyl)phosphonate (IIe) was prepared similarly to **IIb** from 12.5 g (0.05 mol) of **Ie** under the action of 28.4 g (0.09 mol) of $KMnO_4/Al_2O_3$ (1 : 1) (procedure *a*), or 21.3 g (0.14 mol) of $KMnO_4$ (procedure *b*). Yield 64% (*a*), 42% (*b*). bp 105–108°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 18.14 s. ^{13}C NMR spectrum, δ_C, ppm: 142.38 d (C^4, $^4J_{CP}$ 2.2 Hz), 136.06 d (C6, $^2J_{CP}$ 8.2 Hz), 134.15 d (C^5, $^2J_{CP}$ 13.7 Hz), 132.73 d (C^2, $^2J_{CP}$ 3.0 Hz), 130.67 d (C^3, $^3J_{CP}$ 10.5 Hz), 122.35 d (C^1, $^1J_{CP}$ 193.5 Hz), 52.11 d (C_i, $^2J_{CP}$ 4.1 Hz), 18.97 s (C^7), 18.24 s (C^8). ^1H NMR spectrum, δ, ppm: 7.49 m (1H, $^3J_{HP}$ 15.0 Hz), 6.98 m (1H, $^4J_{HP}$ 6.2 Hz), 3.56 d (6H, $^3J_{HP}$ 13.0 Hz), 2.04 s (6H).

Dimethyl (2-chloro-4-methylphenyl)phosphonate (IIf) was prepared similarly to **IIb** from 18.2 g of the mixture of isomers **If** and **Ig** under the action of 60.8 g (0.192 mol) of $KMnO_4/Al_2O_3$ (1 : 1) (procedure *a*) or 45.6 g (0.29 mol) of $KMnO_4$ (procedure *b*). Yield (together with isomer **IIg**) 50% (procedure *a*) or 31% (procedure *b*). Content in the mixture 65 mol%. bp 85–92°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 18.48 s. ^{13}C NMR spectrum, δ_C, ppm: 139.80 d (C^2, $^2J_{CP}$ 2.1 Hz), 131.80 d (C^6, $^2J_{CP}$ 8.4 Hz), 128.70 d (C^3, $^3J_{CP}$ 2.9 Hz), 126.10 d (C^4, $^4J_{CP}$ 10.2 Hz), 125.20 d (C^5, $^3J_{CP}$ 14.4 Hz), 119.60 d (C^1, $^1J_{CP}$ 196.6 Hz), 52.60 d (C_i, $^2J_{CP}$ 6.3 Hz), 18.50 s (C^7). ^1H NMR spectrum, δ, ppm: 7.54 d.d (1H, $^3J_{HP}$ 15.79 Hz, $^3J_{HH}$ 5.2 Hz), 7.12 s (1H), 6.80 d (1H, $^3J_{HH}$ 7.7 Hz), 3.51 d (6H, $^3J_{HP}$ 12.1 Hz), 2.08 s (3H).

Dimethyl (2-chloro-5-methylphenyl)phosphonate (IIg) formed together with **If** in the preceding experiment, content in the mixture 35 mol%. bp 85–92°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 18.53 s. ^{13}C NMR spectrum, δ_C, ppm: 132.70 d (C^6, $^2J_{CP}$ 9.1 Hz), 131.30 d (C^5, $^3J_{CP}$ 13.7 Hz), 127.30 d (C^4, $^4J_{CP}$ 3.71 Hz), 126.79 d (C^2, $^2J_{CP}$ 4.7 Hz), 124.40 d (C^3, $^3J_{CP}$ 7.3 Hz), 122.35 d (C^1, $^1J_{CP}$ 187.7 Hz), 51.90 d (C_i, $^2J_{CP}$ 5.8 Hz), 18.70 s (C^7). ^1H NMR spectrum, δ, ppm: 7.47 d (1H, $^3J_{HP}$ 14.90 Hz), 7.02 d.d (1H, $^4J_{HP}$ 3.80 Hz, $^3J_{HH}$ 6.90 Hz), 6.91 d (1H, $^3J_{HH}$ 6.7 Hz), 3.62 d (6H, $^3J_{HP}$ 10.2 Hz), 2.20 s (3H).

(3-Methyl-*o*-phenylene)bis(phosphonic dichloride) (IIIb). To a solution of 15.4 g (0.05 mol) of **IIb** in 16.5 ml (0.18 mol) of $POCl_3$, 45.9 g (0.22 mol) of ground PCl_5 was added in small portions under cooling and stirring. The mixture was stirred under reflux for 4 h, phosphorus oxychloride was then distilled off, and the residue was distilled in an oil-pump vacuum.

Yield 69%, bp 146–150°C (0.05 mm Hg), ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 31.32 d, 31.14d, J_{PP} 12.60 Hz. ^{13}C NMR spectrum, δ_C, ppm: 146.30 d (C^6, $^2J_{CP}$ 9.9 Hz), 135.40 d.d (C^3, $^2J_{CP}$ 10.4 Hz, $^3J_{CP}$ 12.30 Hz), 135.20 d.d (C^2, $^1J_{CP}$ 185.5 Hz, $^2J_{CP}$ 7.9 Hz), 134.81 d (C^5, $^3J_{CP}$ 13.8 Hz), 134.34 d (C^4, $^3J_{CP}$ 13.80 Hz), 131.10 d.d (C^1, $^1J_{CP}$ 187.7 Hz, $^2J_{CP}$ 8.1 Hz), 20.40 s (C^7). ^{1}H NMR spectrum, δ, ppm: 7.86 d.d (1H, $^3J_{HP}$ 18.1 Hz, $^3J_{HH}$ 8.3 Hz), 7.74 m (1H), 7.12 d (1H, $^3J_{HH}$ 9.2 Hz), 2.38 (s, 3H).

(4-Methyl-*o*-phenylene)bis(phosphonic dichloride) (IIIc) was prepared similarly to **IIIb** from 15.4 g (0.05 mol) of **IIc** under the action of 45.9 g (0.22 mol) of PCl_5 in the presence of 16.5 ml (0.18 mol) of $POCl_3$ for 3 h. Yield 72%, bp 151–155°C (0.05 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 31.41 d, 31.11 d, J_{PP} 16.20 Hz. ^{13}C NMR spectrum, δ_C, ppm: 145.98 m (C^4, $^3J_{CP}$ 11.8 Hz), 135.70 d.d (C^2, $^1J_{CP}$ 185.1 Hz, $^2J_{CP}$ 8.3 Hz), 134.98 d.d (C^6, $^2J_{CP}$ 13.1 Hz, $^3J_{CP}$ 13.1 Hz), 134.79 d (C^5, $^3J_{CP}$ 19.1 Hz), 134.60 d (C^3, $^2J_{CP}$ 10.2 Hz), 132.15 d.d (C^1, $^1J_{CP}$ 188.4 Hz, $^2J_{CP}$ 7.5 Hz), 20.55 s (C^7). ^{1}H NMR spectrum, δ, ppm: 8.18 d.d (1H, $^3J_{HP}$ 29.02 Hz, $^3J_{HH}$ 7.8 Hz), 8.09 d (1H, $^3J_{HP}$ 29.21 Hz), 7.67 d (1H, $^3J_{HH}$ 7.8 Hz), 2.52 (s, 3H).

(4,5-Dimethyl-*o*-phenylene)bis(phosphonic dichloride) (IIId) was prepared similarly to **IIIb** from 16.1 g (0.05 mol) of **IId** under the action of 45.9 g (0.22 mol) of PCl_5 in the presence of 16.5 ml (0.18 mol) of $POCl_3$ for 3 h. Yield 75%, bp 164–169°C (0.05 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 31.08 s. ^{13}C NMR spectrum, δ_C, ppm: 144.23 d ($C^{4,5}$, $^3J_{CP}$ 12.3 Hz), 135.42 d ($C^{3,6}$, $^2J_{CP}$ 16.1 Hz, $^3J_{CP}$ 16.1 Hz), 132.48 d.d ($C^{1,2}$, $^1J_{CP}$ 187.88 Hz, $^2J_{CP}$ 11.2 Hz), 19.87 s ($C^{7,8}$). ^{1}H NMR spectrum, δ, ppm: 8.03 d (2H, $^3J_{HP}$ 16.01 Hz), 2.44 s (6H).

(2-Chloro-4,5-dimethylphenyl)phosphonic dichloride (IIIe) was prepared similarly to **IIIb** from 12.4 g (0.05 mol) of **IIe** under the action of 22.9 g (0.11 mol) PCl_5 in the presence of 8.3 ml (0.09 mol) $POCl_3$ for 3 h. Yield 85%, bp 88–93°C (0.05 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 29.12 s. ^{13}C NMR spectrum, δ_C, ppm: 145.83 d (C^4, $^4J_{CP}$ 4.6 Hz), 135.62 d (C^5, $^3J_{CP}$ 16.0 Hz), 134.34 d (C^6, $^2J_{CP}$ 12.4 Hz), 132.30 d (C^3, $^3J_{CP}$ 12.5 Hz), 132.03 s (C^2), 127.87 d (C^1, $^1J_{CP}$ 161.5 Hz), 19.45 s (C^8), 18.68 s (C^7). ^{1}H NMR spectrum, δ, ppm: 7.76 d (1H, $^3J_{HP}$ 17.8 Hz), 7.22 d (1H, $^4J_{HP}$ 8.8 Hz), 2.24 s (3H), 2.19 s (3H).

(2-Chloro-4-methylphenyl)phosphonic dichloride (IIIf) was prepared similarly to **IIIb** from 11.7 g of the mixture of isomers **IIf** and **IIg** under the action of 22.9 g (0.11 mol) of PCl_5 in the presence of 8.3 ml (0.09 mol) $POCl_3$ for 4 h. Yield 76% (together with isomer **IIg**) 65 mol%. bp 87–90°C (0.05 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 28.88 s. ^{13}C NMR spectrum, δ_C, ppm: 147.23 d (C^2, $^2J_{CP}$ 2.77 Hz), 136.20 d (C^4, $^4J_{CP}$ 2.61 Hz), 133.76 d (C^6, $^2J_{CP}$ 10.52 Hz), 132.15 d (C^3, $^3J_{CP}$ 15.4 Hz), 128.14 d (C_i, $^1J_{CP}$ 164.1 Hz), 127.39 d (C^5, $^3J_{CP}$ 15.80 Hz), 21.04 s (C^7). ^{1}H NMR spectrum, δ, ppm: 7.99 d.d (1H, $^3J_{HP}$ 17.21 Hz, $^3J_{HH}$ 7.81 Hz), 7.39 s (1H), 7.37 d (1H, $^3J_{HH}$ 10.0 Hz), 2.40 (s, 3H).

(2-Chloro-5-methylphenyl)phosphonic dichloride (IIIg) formed together with isomer **IIIf** in the proceding experiment, content in the mixture 35 mol%. bp 87–90°C (0.05 mm Hg). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 28.88 s. ^{13}C NMR spectrum, δ_C, ppm: 136.55 d (C^5, $^3J_{CP}$ 14.95 Hz), 135.21 d (C^4, $^4J_{CP}$ 4.83 Hz), 134.26 d (C^6, $^2J_{CP}$ 10.71 Hz), 132.23 d (C^2, $^2J_{CP}$ 5.99 Hz), 131.45 d (C^3, $^3J_{CP}$ 11.98 Hz), 130.68 d (C^1, $^1J_{CP}$ 159.49 Hz), 20.33 s (C^7). ^{1}H NMR spectrum, δ, ppm: 7.93 d (1H, $^3J_{HP}$ 16.61 Hz), 7.41 d (1H, $^3J_{HH}$ 7.00 Hz), 7.27 d.d (1H, $^4J_{HP}$ 4.6 Hz, $^3J_{HH}$ 8.2 Hz), 2.37 (s, 3H).

4,5-Diphosphonophthalic acid (IVd). To a solution of 9.7 g (0.03 mol) of **IId** in 50 ml of boiling 50% aqueous pyridine, $KMnO_4$ was added very slowly and carefully until the violet color no longer disappeared (a total of about 57 g). The reaction mixture was then refluxed for 2 h and then filtered. The precipitate of MnO_2 was washed with 50 ml of hot water. The filtrate was made strongly acidic with conc. HCl (by universal indicator), evaporated to dryness at reduced pressure, and dried. The dry residue was extracted with hot dioxane (3 × 30 ml), the solvent was distilled off, and the residue was dried for 8 h at 120–130 °C and recrystallized from dioxane–MeOH (3 : 1). mp 332–335 °C (decomp.). Yield 60%. ^{31}P NMR spectrum, δ_P, ppm (D_2O): 6.22 s. ^{13}C NMR spectrum, δ_C, ppm: 173.92 s ($C^{7,8}$), 140.60 d.d ($C^{1,2}$, $^1J_{CP}$ 172.34 Hz, $^2J_{CP}$ 10.4 Hz), 141.47 d ($C^{4,5}$, $^3J_{CP}$ 11.3 Hz), 135.04 d.d ($C^{3,6}$, $^2J_{CP}$ 9.3 Hz, $^3J_{CP}$ 9.3 Hz). ^{1}H NMR spectrum, δ, ppm: 8.64 m (2H, $^3J_{HP}$ 15.2 Hz), 4.60 (s, 6H, H_2O).

4-Chloro-5-phosphonophthalic acid (IVe) was

prepared similarly to **IVd** from 7.4 g (0.03 mol) of **IIe** under the action of 47.4 g (0.3 mol) $KMnO_4$. Yield 75%, mp 310–314°C (decomp.) from dioxane–MeOH (3 : 1). ^{31}P NMR spectrum, δ_P, ppm (D_2O): 5.97 s. ^{13}C NMR spectrum, δ_C, ppm: 171.92 s (C^8), 171.44 s (C^7), 140.77 d (C^5, $^3J_{CP}$ 4.9 Hz), 137.40 d (C_i, $^1J_{CP}$ 178.1 Hz), 137.08 s (C^4), 135.39 d (C^6, $^2J_{CP}$ 8.8 Hz), 131.66 d (C^3, $^3J_{CP}$ 8.7 Hz), 129.93 d (C^2, $^2J_{CP}$ 11.8 Hz). ^1H NMR spectrum, δ, ppm: 8.33 d (1H, $^3J_{HP}$ 14.04 Hz), 7.71 d (1H, $^4J_{HP}$ 4.9 Hz), 4.80 s (4H, H_2O).

(4-Methyl-*o*-phenylene)bisphosphine (Vc). To a vigorously stirred and cold (–70°C) suspension of 5.7 g (0.15 mol) of $LiALH_4$ in 100 ml of anhydrous ether, 8.0 g (0.06 mol) of $AlCl_3$ was quickly added and then a solution of **IIc** in 50 ml of ether was added dropwise at –60°C. After stirring for 4 h at room temperature and 1 h under reflux, the mixture was cooled to –30°C, and 2.8 ml (0.15 mol) of water preliminarily distilled under argon was added dropwis. The mixture was allowed to warm to room temperature, and then it was refluxed for 2 h and filtered. The filtrate was dried over Na_2SO_4 and evaporated. The residue was distilled in a vacuum. Yield 50%, bp 86–90°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm (C_6D_6): –125.47, –123.50 (*AB* system, $^3J_{PP}$ 38.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 139.07 d (C^5, $^3J_{CP}$ 4.07 Hz), 135.89 d.d (C^3, $^2J_{CP}$ 3.9 Hz, $^3J_{CP}$ 13.5 Hz), 135.40 d.d (C^6, $^2J_{CP}$ 3.9 Hz, $^3J_{CP}$ 13.6 Hz), 134.42 d.d (C_i, $^1J_{CP}$ 15.1 Hz, $^2J_{CP}$ 6.8 Hz), 130.29 d.d (C^2, $^1J_{CP}$ 14.9 Hz, $^2J_{CP}$ 6.9 Hz), 128.98 d (C^4, $^3J_{CP}$ 5.4 Hz), 20.70 s (C^7). ^1H NMR spectrum, δ, ppm: 7.44 d.d (1H, $^3J_{HP}$ 9.6 Hz, $^3J_{HH}$ 3.0 Hz), 7.38 d (1H, $^3J_{HH}$ 3.7 Hz), 7.02 d (1H, $^3J_{HP}$ 8.0 Hz), 4.04 d.d (4H, $^1J_{HP}$ 208.1 Hz, $^4J_{HP}$ 6.0 Hz), 2.31 s (3H).

(4,5-Dimethyl-*o*-phenylene)bisphosphine (Vd) was prepared similarly to **Vc** from 9.7 g (0.03 mol) of **IId** under the action of 5.7 g (0.15 mol) of $LiALH_4$ and 8.0 g (0.06 mol) of $AlCl_3$. Yield 55%, bp 103–106°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm (C_6D_6): –126.11 m. ^{13}C NMR spectrum, δ_C, ppm: 136.93 d ($C^{3,6}$, $^2J_{CP}$ 9.1 Hz), 136.73 d ($C^{4,5}$, $^3J_{CP}$ 10.2 Hz), 130.99 d.d ($C^{1,2}$, $^1J_{CP}$ 6.6 Hz, $^2J_{CP}$ 6.6 Hz), 19.07 s ($C^{7,8}$). ^1H NMR spectrum, δ, ppm : 7.34 d.d (2H, $^3J_{HP}$ 4.8 Hz, $^4J_{HP}$ 4.8 Hz), 4.01 d.d (4H, $^1J_{HP}$ 207.5 Hz, $^4J_{HP}$ 22.8 Hz), 2.21 s (6H).

(2-Chloro-4,5-dimethylphenyl)phosphine (Ve). *a*. Prepared similarly to **Vc** from 7.5 g (0.03 mol) of **IIe** under the action of 2.8 g (0.08 mol) of $LiAlH_4$ and 4.0 g (0.03 mol) of $AlCl_3$, followed by treatment with 1.5 ml (0.08 mol) of oxygen-free water. Yield 53%.

b. To a solution of 16.3 g (0.12 mol) of $SiHCl_3$ in 70 ml of anhydrous benzene cooled to 0°C, a solution of 7.5 g (0.03 mol) of **IIe** in 50 ml of benzene was quickly added. The solution was stirred under reflux for 12 h, cooled to 0°C, and a solution of 0.4 mol of NaOH in 100 ml of water distilled under argon was added. The mixture was kept heated at 60°C until the amorphous precipitate formed had dissolved completely. The organic layer was separated, and the aqueous layer was extracted with two portions of benzene. The combined organic extract was dried over Na_2SO_4, the solvent was distilled off, and the residue was distilled in a vacuum. Yield 60%, bp 80–83°C (1 mm Hg). ^{31}P NMR spectrum, δ_P, ppm (C_6D_6): –129.19 s. ^{13}C NMR spectrum, δ_C, ppm: 138.39 s (C^4), 136.25 d (C^3, $^3J_{CP}$ 10.8 Hz), 134.90 d (C^2, $^2J_{CP}$ 4.6 Hz), 134.77 d (C^5, $^3J_{CP}$ 7.9 Hz), 129.62 s (C^6), 126.64 d (C^1, $^1J_{CP}$ 9.6 Hz), 18.99 s (C^7), 18.60 s (C^8). ^1H NMR spectrum, δ, ppm: 7.29 d (1H, $^3J_{HP}$ 6.2 Hz), 7.13 d (1H, $^4J_{HP}$ 2.7 Hz), 3.98 d (2H, $^1J_{HP}$ 209.0 Hz), 2.23 (s, 6H).

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