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Effect of Electrolysis Conditions on the Process of Anodic Oxidation of Tertiary Phosphines in the Presence of Camphene

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Abstract—Anodic oxidation of tertiary phosphines (Et_3P, Pr_3P, Bu_3P, *i*-Bu_3P and Am_3P) in the presence of camphene and heterogenic base (trisodium phosphate) on platinum anode in acetonitrile solution of sodium perchlorate was studied. It is established that trialkylphosphine radical cations react with camphene to give two types of products: Camphenylphosphonium salts formed by elimination of proton, and phosphinimino-terpenylphosphonium salts which are obtained due to the rearrangement of terpenyl skeleton. Conditions of electrosynthesis are found where the summary yield of terpenylphosphonium products increases. The effect of length and degree of branching of alkyl substituents in trialkylphosphines on the rate of the reaction of phosphine radical cations with camphene and starting phosphine is found.

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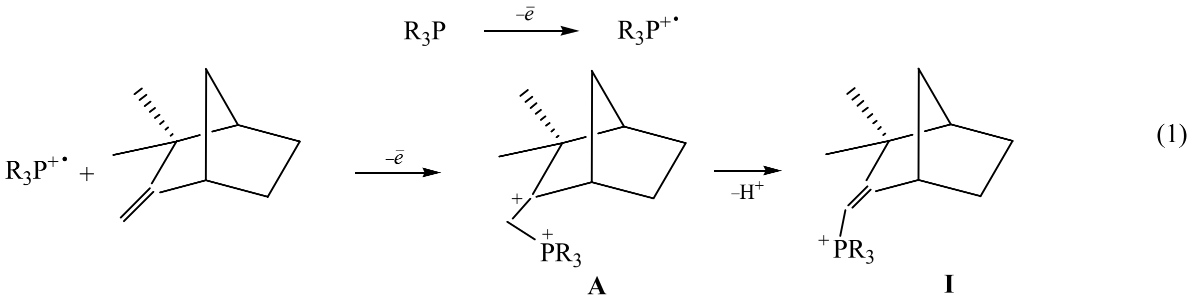
It was shown previously [1] that in the course of anodic oxidation of tertiary phosphines in the presence of camphene their addition to the terpene molecule resulting in the formation of camphenylphosphonium salts **I** [scheme (1)] takes place. It was found also that the process was complicated by the parallel reaction giving the protonated phosphines and phosphine oxides **II** [scheme (2)]. The protonation of starting phosphine by the protons eliminated from the carbocation A increases the yields of R_3PH^+.



(1)

$$R_3P \xrightarrow{-\bar{e}} R_3P^{+\bullet} \xrightarrow{+R_3P,\ -\bar{e}} R_3\overset{+}{P}\overset{+}{P}R_3$$

$$R_3\overset{+}{P}\overset{+}{P}R_3 + H_2O \longrightarrow R_3\overset{+}{P}H + \underset{\textbf{II}}{R_3PO} + H^+ \quad (2)$$

Note that in the course of electrosynthesis together with the compounds **I** (δ_P 23–24 ppm), the protonated phosphines (δ_P 10–15 ppm), the phosphine oxides **II** (δ_P 52–56 ppm), and the other products are also formed. They include quasiphosphonium salts R_3P^+OR **III** (δ_P 60–62 ppm) and the compounds with δ_P at 30–40 ppm, **IV**. The complete identification of the latter was not carried out due to the complications while isolation.

The aim of the present work was, firstly, to extend the series of phosphines involved with the purpose of

Results of preparative electrochemical oxidation of tertiary phosphines in the presence of camphene (platinum anode, trisodium phosphate as a base)[a]

Run no.	R_3P (M)	Camphene concentration, M	Parameters of electrolysis			Content of products in the reaction mixture (δ_P, ppm) by ^{31}P NMR data
			i, mA cm^{-2}	φ, V	F, F mol^{-1}	
1	Et (0.025)	0.030	0.2–3	0.6–1.0	0.95	**I** (29.4); 41%, **II** (54.5); 31%, **III** (60.5); 9%, **IV** (40.1 + 37.2); 19%
2	Et (0.0172)	0.029	0.4–5	0.6–1.0	0.93	**I** (29.7); 19%, **II** (56.4); 53%, **III** (62.2); 9%, **IV** (40.4 + 37.9); 19%
3	Pr (0.035)	0.037	0.4–3.5	0.6–1.0	1.12	**I** (22.5); 32%, **II** (55.0); 34%, **III** (60.8); 6%, **IV** (34.2 + 31.6); 28%
4	Pr (0.044)	0.040	0.04–0.6	0.8–1.4	0.4	**I** (22.6); 12%, **II** (53.9); 64%, **III** (59.1); 8%, **IV** (33.4 + 31.0); 16%
5[b]	Pr (0.034)	0.036	0.2–2	0.7–1.0	0.61	**I** (22.2); 15%, **II** (56.3); 18%, **III** (60.1); 4%, **IV** (31.1 + 34.0); 11%
6	Bu (0.0326)	0.032	0.4–2	0.6–1.0	0.96	**I** (23.7); 28%, **II** (52.1); 47%, **III** (59.3); 8%, **IV** (35.0 + 32.2); 17%
7[b]	Bu (0.0345)	0.037	0.1–2	0.7–0.9	0.63	**I** (23.8); 21%, **II** (56.0); 19%, **III** (60.7); 6%, **IV** (32.6 + 35.1); 11%
8	*i*-Bu (0.032)	0.037	0.2–2.8	0.7–1.0	1.1	**I** (19.6); 39%, **II** (47.5); 38%, **III** (56.0); 9%, **IV** (34.9 + 29.1); 14%
9	Am (0.035)	0.037	0.2–1.6	0.7–1.2	0.56	**I** (23.7); 12%, **II** (53.2); 65%, **III** (60.0); 10%, **IV** (34.9 + 32.1); 13%
10	Bu_2PPh (0.025)	0.030	0.1–0.2	0.8–1.6	0.63	**I** (18.9); 3%, **II** (42.8); 95%, **IV** (30.7 + 27.6); 2%

[a] Amount of electricity consumed for oxidation of phosphine, F mol^{-1}. [b] Data of [1].

establishing the effect of structure of substituents at phosphorus on the ratio of products of electrolysis. The second goal was to develop optimal conditions of performing electrolysis and isolation of the products for establishing their structure by physicochemical methods, for example, by NMR spectroscopy. Changes in the conditions of performing the electrolysis first of all included the addition of trisodium phosphate for neutralization of evolving protons. It should lead to an increase in the yield of the target products due to the prevention of protonation of phosphines.

The experiments were carried out on a platinum anode in a galvanostatic regime in a definite range of current density with the simultaneous control of the anode potential. As it was expected, the change in the conditions of electrolysis lead practically to complete absence of protonated phosphines in the reaction mixture. Besides, a complete absence of the products with chemical shifts about 40 ppm was observed. The upfield shift of signals of phosphine oxides was observed as well. The obtained results are generalized in the table.

As seen from the table, the addition of the base leads to an increase in the yield of all the products of electrosysis (save compound **III**). It is due to involving in further electrolysis of the additional amount of phosphine which is confirmed by the increase in the amount of consumed electricity from 0.6 to 1 F per mol because some part of phosphine was previously excluded from the anode process due to protonation [1].

For the evaluation of the effect of electrochemical parameters of electrolysis on the yield of the target products **I** and **IV** we carried out additional electrolyses. Hence, two experiments with triethylphosphine (see the table, exp. nos. 1 and 2) differed only in the value of the anode current density. As seen from the table it is necessary to maintain definite *i* values for obtaining camphenylphosphonium salts in high yield. It is found that it must not exceed 3 mA cm^{-2}. The increase in the current density value to 5 mA cm^{-2} leads to the twofold decrease in the content of the product **I** in the reaction mixture. At the same time amount of phosphine oxide **II** increases 1,5-fold. Yields of the other products do not change.

The value of the maintained anode potential is also important for the electrochemical processes under study. It is clearly seen that while performing electrolysis at the potentials above 1 V (see exp. nos. 4 and 9) the yields of camphenylphosphonium salts (about 30–40% in the reaction mixture under optimal conditions) decrease to 12% while the part of phosphine oxides increases from 30–45% to 64–64%. It is surprising that performing electrolysis at the anode potentials above 1.0 V proceeds at lower values of current density. For example, while at the electrolysis of tripropylphosphine (see exp. no. 3) under optimal conditions the current density value was maintained up to 3.5 mA cm^{-2}, during the oxidation at higher potentials (exp. no. 4) the initially set current density of 5 mA cm^{-2} could be maintained only for a small period of time, about several minutes, but then we were compelled to decrease *i* sharply to the value approximately 8 times lower due to the shift of the anode potential to more positive range up to the area of oxidation of camphene (1.4–1.5 V). Probably at higher anode potentials the adsorption of the solution components on electrode takes place causing the passivation of the latter and hence the current density decreases at the controlled anode potential. As seen from the results, the adsorption of the solution components favors the increase in the rate of electrooxidation of phosphines to phosphine oxides. Probably under these conditions the adsorbed trialkylphosphines are oxidized.

Hence, the analysis of the effect of electrochemical conditions of the experiment showed that for the increase in the yield of camphenylphosphonium salt it was desirable to carry out the process at current densities about 2–3 mA cm^{-2} and the anode potential excluding the adsorption of phosphines on electrode (up to 1.0 V). The importance of adsorption is confirmed by the experiments on the carbon-glass anode when the yields of phosphine oxides increased because of the passivation of anode [1]. Electrolyses with triphenylphosphine and dibutylphenylphosphine (see the table, no. 10) showed that these compounds passivate anode even at lower voltage of electrolysis which practically results in a quantitative electrosynthesis only of oxides of these compounds (90–95% in the reaction mixture).

The obtained data permit the evaluation of the effect of alkyl substituents in phosphines on the ratio of two main reactions [schemes (1) and (2)]. As seen from the table (exp. nos. 1, 3, 6, 8, 9) in the experiments performed under optimal conditions the increase in the amount of product **IV** in the reaction mixture is observed with the elongation of chain in the substituents of normal structure. It shows that at the increase in the length of the chain the ratio of the rates of the reactions of radical cations of trialkylphosphines with camphene and the starting phosphine [schemes (1) and (2)] changes to the side of the increase in the relative rate of diphosphonium salts formation. It may be ascribed to a higher stabilization of intermediates formed in the course of the synthesis of diphosphonium salts due to the increase in the electron-donating properties of hydrocarbon substituents on phosphorus. Triisobutylphosphine with the branched substituent showed the result the most close to tripropylphosphine which is evidently connected with definite sterical hindrances in the formation of diphosphonium salt.

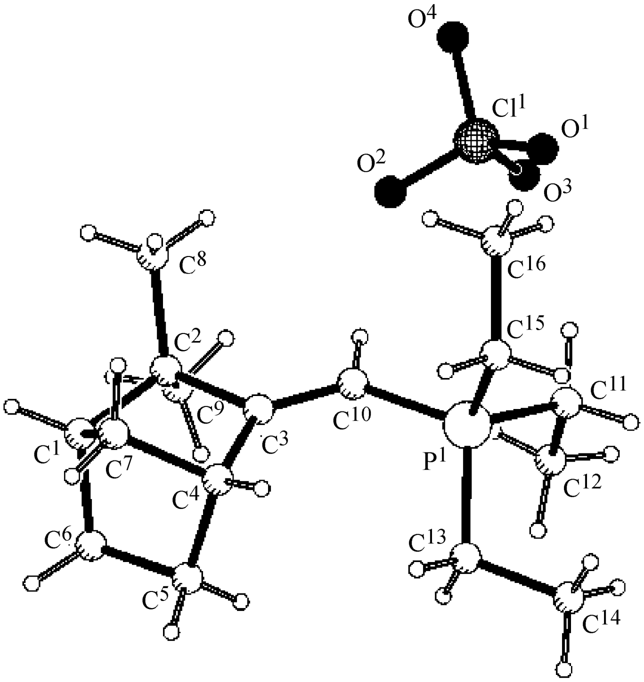
It follows from the obtained results that the change in the conditions of the experiment (addition of trisodium phosphate, choice of the optimal electrochemical parameters) besides the increase in the yield of the target products leads to the decrease in the number of the products formed in the course of the electrolysis. Therefore it became possible to isolate each product in the pure state that had been previously impossible [1]. The strategy of separation of compounds was as follows. In the first stage phosphorus-containing compounds **I** and **IV** potentially having terpene substituents were separated from phosphine oxides **II** and quasiphosphonium salts **III** by column chromatography**.** It was found that such chromatographic separation was possible in many polar organic solvents like acetone, acetonitrile, ethanol, chloroform or dichloromethane. In the next step attempts were made of separation of camphenylphosphonium salts **I** from the other products of electrolysis using different methods like extraction, column chromatography or precipitation of one of the components of the mixture with suitable solvent. The optimal conditions of separation are described in Experimental.

In [2] it was established that in the case of triethylphosphine the fraction with the increased content of product **I** could be obtained by column chromatography. We managed to isolate a fraction with 92% content of this compound (see Experimental). The crystallization of this fraction from methanol gave white needle-like precipitate. According to XRD analysis it was triethylcamphenylphosphonium perchlorate [3]. It is interesting to note that this compound crystallizes in the conglomerate form when each optical isomer forms its own crystals. It takes place despite the fact that racemic camphene was exposed to electrochemical phosphorylation (see the figure).

In the ^{1}H NMR spectrum of triethylcamphenylphosphonium salt alongside the intense signals of protons of triethylphosphino group (δ 1.09 and 2.36 ppm) a doublet signal of proton at the double bond with the geminal coupling constant with phosphorus (δ 5.12 ppm, $^2J_{PH}$ 18.6 Hz) is observed. Downfield shift of the signal as compared to the values in starting camphene (4.17 and 4.50 ppm) [4] is due to the effect of closely located phosphine group. Phosphine substituent which according to X-ray data [3] is trans-located in relation to the *gem*-dimethyl group also strongly affects tertiary protons on C^1 and C^4 carbon atoms (numbering of atoms corresponds to that shown in the figure). These protons give signals at 3.01 and 2.02 ppm instead of 2.65 and 1.89 ppm in camphene respectively. Probably due to the influence of phosphorus the signals of protons on C^5 carbon atom are observed at 1.13 and 1.91 ppm instead of 1.21–1.25 and 1.62–1.64 ppm as in the starting camphene [4].

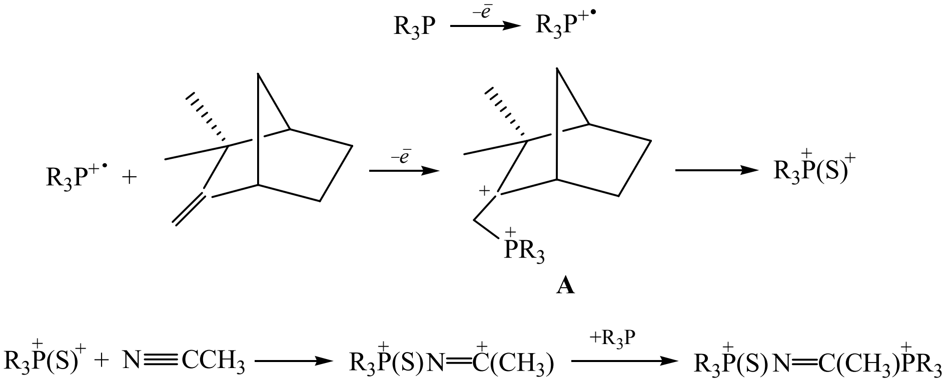
New procedure of separation of the products of electrosynthesis with the initial separation of phosphine oxides and quasiphosphonium salts permits not only to obtain the fractions with the increased content of camphenylphosphonium salts **I** but also the fractions containing the compounds with chemical shifts δ_P in the range 30–40 ppm. NMR spectra of these fractions show that their main components are probably the individual compounds containing two different phosphonium substituents. The compound with tripropylphosphine substituents (δ_P 34.2 and 31.6 ppm) we managed to isolate in a pure state. In the ^1H NMR spectrum of this product increased integral intensity of the methyl proton signals in phosphino groups is observed as compared to the intensity of *gem*-dimethyl protons (3:1 while in compound **I** it is equal to 3:2), the absence of signals of the double bond protons, the appearance of signal at d 3.82 ppm, and a quartet at δ ~2.63 ppm are observed. The signals at δ ~2.63 ppm most probably belong to PCH_2 protons (δ 2.61 ppm, $^2J_{PH}$ 16 Hz; d 2.64 ppm, $^2J_{PH}$ 13 Hz). The absence of signals of the double bond protons together with the simultaneous appearance of the PCH_2 group proves that compound **IV** is saturated. Unexpected appearance of a singlet at 3.8 ppm characteristic of the protons bound with nitrogen or the protons of NCH fragment permits a suggestion that the product contains the imine or acetamide group. It is quite possible because the electrosyntheses were carried out in acetonitrile. The reactions of electrochemical acetamidation by anodic generation of various carbocations in the presence of acetonitrile were reported [5]. The presence of the signal of the methyl group bound to acetamide or imino group confirms this hypothesis (a doublet at 2.35 ppm, $^3J_{PH}$ 9 Hz).

Hence, the analysis of ^1H NMR spectrum of compound **IV** permits a conclusion that it is a saturated salt with two phosphonium and one acetamide (or imino) group which could be formed only from acetonitrile used as a solvent. The absence of N–H bond vibrations in the IR spectrum supports the imine structure of this substituent. It is presumable that the synthesis of this product proceeds as the rearrangement of the terpene skeleton including the intermediate cycle opening in the carbocation **A** and the subsequent addition of acetonitrile molecule to the new cationic center. Further stabilization of this intermediate includes the reaction of iminocation with the second molecule of phosphine resulting in the formation of phosphiniminoterpenylphosphonium salt [scheme (3)]. The exact pathway of rearrangement of the carbocation **A** (cycle opening with the formation of monocyclic product as it was suggested in [1] or the Wagner rearrangement) is not clear nowadays. Though the nonequivalence of protons on C^{10} atom (numbering of atoms is shown in the figure) in the molecule **IV** (δ 2.61 and 2.64 ppm) may be explained by the presence of the adjacent asymmetric carbon atom (which indirectly confirms the hypothesis about the bornane structure of this compound and the occurrence of the camphene-bornane rearrangement) the refining of the structure of this compound requires further studies.



Crystalline structure of triethylcamphenylphosphonium perchlorate [3].

Hence, the obtained results show that in the course of the anodic addition of trialkylphosphine radical cations to the terpene molecule the initially formed



$$R_3\overset{+}{P}(S)^{+} + N{\equiv}CCH_3 \longrightarrow R_3\overset{+}{P}(S)N{=}\overset{+}{C}(CH_3) \xrightarrow{+R_3P} R_3\overset{+}{P}(S)N{=}C(CH_3)\overset{+}{P}R_3$$

(3)

S = terpene hydrocarbon skeleton.

carbocation **A** may be stabilized by two pathways. First one includes elimination of proton from the adjacent exocyclic carbon atom with the formation of camphenylphosphonium salts [scheme (1)]. Another one includes rearrangement of the terpene skeleton leading to new cationic center which adds an acetonitrile molecule. After that the addition of tertiary phosphine to the imino group takes place [scheme (3)]. For the evaluation of structural peculiarities of the products of electrosynthesis investigation of these compounds by NMR on different nuclei and two-dimensional spectroscopy is planned.

EXPERIMENTAL

NMR spectra were taken on a Varian Unity 300 spectrometer (300 MHz ^{1}H; 121 MHz ^{31}P against external 85% H_3PO_4). IR spectra were recorded on a UR-20 spectrometer.

Conditions of electrosynthesis. Preparative electrochemical oxidation was carried out in a glass cell with 100 ml anode and cathode volumes separated from one another with a porous diaphragm. It was performed in the galvanostatic regime with the constantly controlled anode potential. P-5827M potentiostate was used as a current source. Platinum cylinder with the working surface 50 cm^2 was used as anode. Nickel spiral with the surface area 20 cm^2 was used as an auxiliary electrode (cathode). Anode potential in the course of electrosynthesis was measured against Ag/Ag$^+$ (0.01M $AgNO_3$ in acetonitrile) reference electrode. The process was carried out under argon, and the electrolyte was constantly stirred.

Sodium perchlorate, 5–6 g, and trisodium phosphate, 5–7 g, were dissolved in a mixture of 60 ml of acetonitrile and 10 ml of THF. Camphene and trialkylphosphine were added to this electrolyte in small portions. Amounts of camphene and trialkylphosphite taken in each experiment and also the parameters of electrolysis such as operating values of current density, anode potentials, and the amount of consumed electricity are shown in the table. After the completion of electrolysis trisodium phosphate was filtered off, solvent was evaporated in a vacuum, and the residue was treated with 100 ml of dichloromethane to remove sodium perchlorate from the products of electrosynthesis. Dichloromethane solution was evaporated. Compositions of reaction mixtures according to ^{31}P NMR data are listed in the table. Reaction mixtures were chromatographed on a 50×15 cm column filled with silica gel (Acros Organics, 0.035–0.070 mm, pore diameter 6 nm).

Procedure for isolation of the products of electrosynthesis. *a. Experiments with triethylphosphine.* The composition of fractions obtained by chromatographic isolation (elution with chloroform) according to the ^{31}P NMR data was the following. **Fraction 1**: compound **I,** 92%; compound **IV,** 8%; 1.0 g of this fraction was dissolved in 10 ml of dry methanol. Under slow cooling 0.2 g of white crystalline precipitate identified as (2,2-dimethyl-3-methylidenenorbornane)triethylphosphonium perchlorate was isolated, mp 107–110°C. XRD analysis data for this substance are presented in [3], and its ^{13}C and ^{31}P NMR spectral data are reported in [2]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.18 d (1H, H^{10}, $^2J_{PH}$ 18.2 Hz), 3.01 s (1H, H^1), 2.28 d.q (6H, PCH_2CH_3, $^2J_{PH}$ 12.3Hz, $^3J_{HH}$ 7.7 Hz), 2.02 s (1H, H^4), 1.19 t (9H, PCH_2CH_3, $^3J_{HH}$ 7.7 Hz), 1.09 s [3H, $(CH_3)_2C$], 1.10 s [3H, $(CH_3)_2C$], protons of camphene ring: 1.11–1.15 m (1H), 1.38–1.52 m (2H), 1.68–1.80 m (1H), 1.85–1.93 m (1H). **Fraction 2**: compound **I,** 61%; **IV,** 27%;

unknown compound (δ_P 41.3 ppm), 12%. **Fraction 3**: compound **I,** 3%; **III,** 2%; **IV,** 82%; unknown compound (δ_P 41.3 ppm), 13%. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm (signals only of compound **IV**): 3.86 d.d (NCH), 2.60–2.66 d.d ($\mathrm{PCH_2}$, $^2J_\mathrm{PH}$ 13.0 Hz), 2.26 d [$\mathrm{CH_3C(PEt_3)}$=N, $^3J_\mathrm{PH}$ 9.0 Hz]. **Fraction 4**: compound **I,** 1%; **II**, 59%; **III,** 36%; **IV**, 4%.

b. Experiments with tripropylphosphine. Composition of fractions obtained by chromatography (elution with acetonitrile) on the basis of ^{31}P NMR data is as follows: **Fraction 1**: compound **I,** 56%; **IV,** 32%; unknown compound (δ_P 35.5 ppm), 12%. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm (signals only of compound **I**): 5.12 d (1H, H^{10}, $^2J_\mathrm{PH}$ 18.0 Hz), 3.11 s (1H, H^1), 1.10 s [3H, $\mathrm{(CH_3)_2C}$], 1.08 s [3H, $\mathrm{(CH_3)_2C}$]. **Fraction 2**: compound **I**, 43%; **II,** 27%; **IV**, 18%; unknown compound (δ_P 35.5 ppm), 12%. **Fraction 3**: compound **I**, 27%; **II**, 45%; **III**, 9%; **IV**, 19%. **Fraction 4**: compound **I,** 1%; compound **II**, 63%; **III**, 33%; **IV**, 3%. Fractions 1 and 2 were joined and dissolved in a mixture of methanol with diethyl ether (4:1 vol/vol). Cooling of the solution obtained yielded a precipitate containing 12% of compound **II** and 88% of compound **IV**. Repeated crystallization from methanol gave pure compound **IV** (δ_P 34.7 and 32.1 ppm). IR spectrum, (mull in mineral oil), ν, cm^{-1}: 1073 br ($\mathrm{ClO_4}$), 1606 w (C=N). ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm: 3.82 s (1H, H^1), 2.64 d [1H, $\mathrm{PCH_2}$(A), $^2J_\mathrm{PH}$ 13.0 Hz], 2.61 d [1H, $\mathrm{PCH_2}$(A1), $^2J_\mathrm{PH}$ 13.0 Hz], 2.30–2.42 m [6H, $\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_3(C{=}N)}$, $^3J_\mathrm{HH}$ 7.8 Hz], 2.28 d [3H, $\mathrm{CH_3C(PPr_3)}$=N, $^3J_\mathrm{PH}$ 9.0 Hz], 2.22–2.28 m (6H, $\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_3}$, $^1J_\mathrm{HH}$ 7.8 Hz), 1.50–1.64 m (12H, $\mathrm{PCH_2}\mathit{CH}_2\mathrm{CH_3}$), 1.05–1.12 m (18H, $\mathrm{PCH_2CH_2}\mathit{CH}_3$), 0.99 s [3H, $\mathrm{(CH_3)_2C}$], 0.96 s [3H, $\mathrm{(CH_3)_2C}$], protons of the hydrocarbon skeleton: 1.30–1.38 m (1H), 1.40–1.48 m (1H), 1.68–1.72 m (2H), 1.74–1.88 m (2H), 2.22 s (1H). ^{31}P NMR spectrum, δ_P, ppm: 34.7, 32.1.

c. Experiments with tributylphosphine. Composition of fractions obtained by chromatography (elution with dichloromethane) on the basis of ^{31}P NMR data: **Fraction 1**: compound **I**, 84%; **IV**, 12%; unknown compound (δ_P 34.8 ppm), 4%. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm: phosphine group protons 2.28 m ($\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_2CH_3}$), 1.42–1.45 m ($\mathrm{PCH_2}\cdot\mathit{CH}_2\mathit{CH}_2\mathrm{CH_3}$), 0.90–0.96 m ($\mathrm{PCH_2CH_2CH_2CH_3}$); clearly seen signals of compound **I**: 5.12 d (1H, H^{10}, $^2J_\mathrm{PH}$ 18.2 Hz), 3.00 s (1H, H^1), 2.02 s (1H, H^4), 1.12 s [3H, $\mathrm{(CH_3)_2C}$], 1.10 s [3H, $\mathrm{(CH_3)_2C}$]; clearly seen signals of compound **IV**: 3.82 d (1H, CHN), 2.56–2.60 d.d (2H, $\mathrm{PCH_2}$), 0.82 s [3H, $\mathrm{(CH_3)_2C}$]. **Fraction 2**: compound **I**, 26%; **II**, 36%; **III**, 13%; **IV**, 21%; unknown compound (δ_P 34.8 ppm), 4%. **Fraction 3**: compound **I**, 12%; compound **II,** 54%; **III**, 15%; **IV**, 19%.

d. Experiments with triisobutylphosphine. Composition of fractions obtained by chromatography (elution with 4:1 acetonitrile-diethyl ether) on the basis of ^{31}P NMR data: **Fraction 1**: compound **I,** 83%; **IV** – 10%, unknown compound (δ_P 36.2 ppm), 7%. ^{1}H NMR spectrum of the fraction ($\mathrm{CDCl_3}$), δ, ppm: 5.10 d (H^{10}, $^2J_\mathrm{PH}$ 18.4 Hz), 2.99 s (H^1), 2.28 m [$\mathrm{P}\mathit{CH}_2\mathrm{CH}\cdot\mathrm{(CH_3)_2}$], 2.01 s (H^4), 1.88 m [$\mathrm{PCH_2}\mathit{CH}\mathrm{(CH_3)_2}$], 1.01 d [$\mathrm{PCH_2CH(}\mathit{CH}_3)_2$, $^3J_\mathrm{HH}$ 7.8 Hz]. **Fraction 2**: compound **I,** 68%; **II**, 26%; unknown compound (δ_P 36.2 ppm), 6%. **Fraction 3**: compound **II**, 92%; **III**, 8%. While dissolution of fraction 2 in 4:1 methanol-diethyl ether and cooling the crystals of pure compound **I** are formed. ^{1}H NMR spectrum was identical to the above-presented data.

e. Experiments with tripentylphosphine. Composition of fractions obtained by chromatography (elution with 4:1 acetonitrile-diethyl ether) on the basis of ^{31}P NMR data: **Fraction 1**: compound **I**, 54%; **II**, 5%; **III**, 10%; **IV,** 26%. **Fraction 2**: compound **I**, 15%; **II**, 65%; **III,** 15%; **IV**, 5%. **Fraction 3**: compound **II**, 76%; **III**, 11%; **IV,** 3%; unknown compound (δ_P 40.5 ppm), 10%.

f. Experiments with dibutylphenylphosphine. By column chromatography (elution with acetone) the following fraction was isolated: compound **I**, 35%, **II**, 59%, **IV**, 6%. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm: 7.0–8.0 (phenyl ring protons), 1.90–2.22 m ($\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_2CH_3}$), 1.62–1.68 m ($\mathrm{PCH_2}\mathit{CH}_2\mathrm{CH_2CH_3}$), 1.40–1.46 m ($\mathrm{PCH_2CH_2}\mathit{CH}_2\mathrm{CH_3}$), 0.88–0.92 t ($\mathrm{PCH_2}\cdot\mathrm{CH_2CH_2}\mathit{CH}_3$), clearly seen minor signal 5.51 d ($^2J_\mathrm{PH}$ 20.4 Hz).

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