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Electrochemical Oxidation of Tertiary Phosphines in the Presence of Camphene

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Abstract—Anodic oxidation of tertiary phosphines (tripropyl-, tributyl-, and triphenylphosphine) in the presence of a bicyclic alkene (camphene) on a platinum and a glassy carbon electrodes was studied. For the first time the voltammetric characteristics of the process of camphene anodic oxidation were obtained. The electrochemical reactions with alkyl and aromatic phosphine were found to be dissimilar. The results of preparative electrooxidation of trialkylphosphines showed that in the course of electrolysis the tertiary phosphine cation-radicals generated on the anode enter into two concurrent reactions: (1) with the parent phosphine to form eventually trialkylphosphonium salts and trialkylphosphine oxides presumably as complex compounds and (2) with camphene to form trialkylcamphenylphosphonium salts and probably phosphonium salts with a monocyclic substituent. Preparative electrochemical oxidation of triphenylphosphine in the presence of camphene affords almost exclusively either triphenylphosphine oxide (in the experiment with platinum anode) or the triphenylphosphine oxide complex with perchloric acid (at the electrolysis on a glassy carbon anode).

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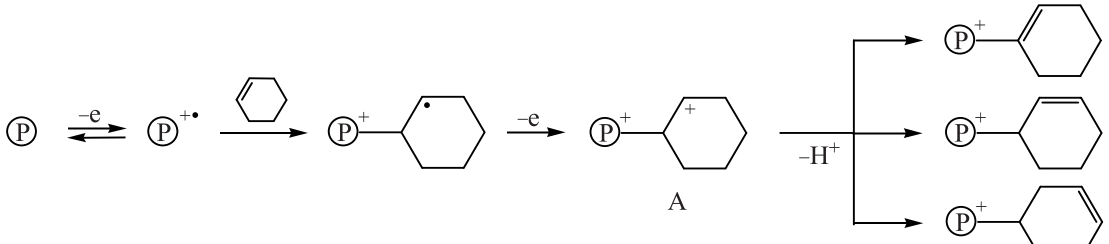
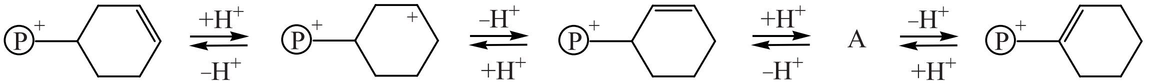
The anode-initiated addition of organophosphorus cation-radicals to alkenes was shown formerly [1–3] to give phosphorylated olefins [scheme (1)]. In the course of electrolysis are commonly formed regioisomeric alkenyl (cycloalkenyl) phosphoric compounds originating from the prototropic isomerization reactions [scheme (2)]. These features of the electrochemical phosphorylation of alkenes stimulate further studies.



(1)

Ⓟ = R_3P, $(RO)_3P$, $(RO)_2POSiMe_3$, $(RO)_2PNR_2$
$ROP(NR_2)_2$, $(RO)_2POC(O)CH_3$, Ph_3P



(2)

It was interesting to continue the study of the same electrochemical processes on sterically overloaded alkenes and bicyclic monoterpenes. In particular, camphene is useful for this purpose. The camphene molecule is attractive first of all by the relative accessibility of the double bond for the attack by organophosphorus cation-radical owing to its exocyclic position, and secondly, due to the presence contiguous to the multiple bond of quaternary and tertiary nodal carbon atoms. The last event will inhibit

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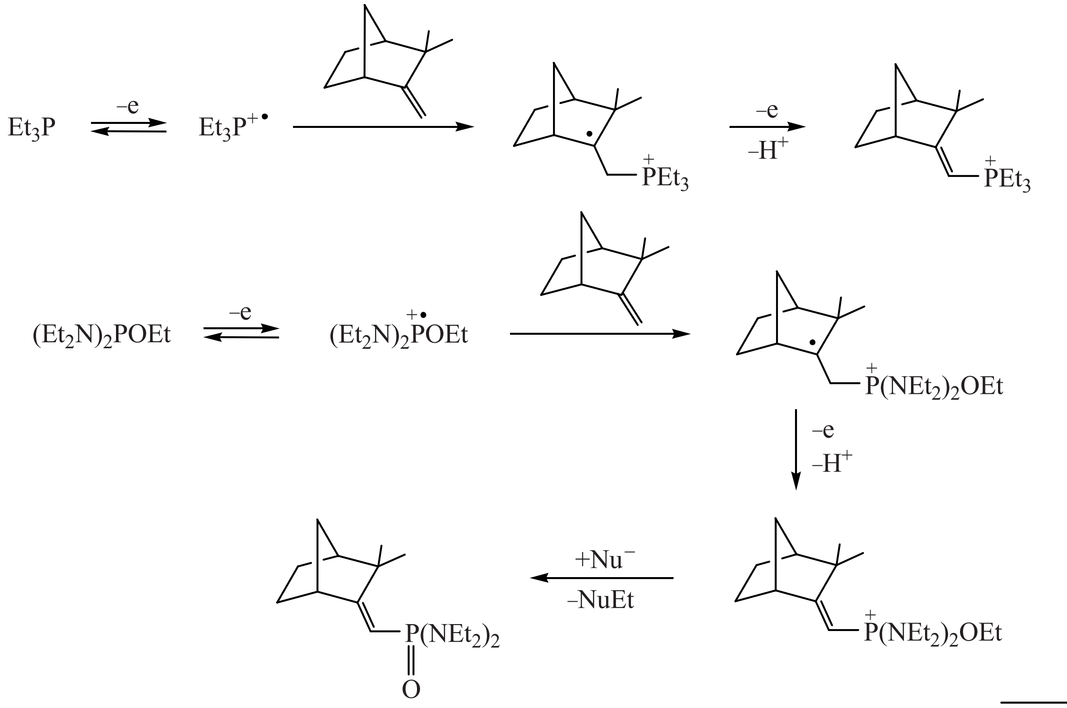
† Deceased.

the migration of the double bond by the mechanism of prototropic isomerization [scheme (2)]. Under such conditions the only possible pathway of migration of the double bond remains the opening of one of the rings. The study of the trends in the electrochemical and chemical reactions of this type (with the camphene ring cleavage) is also of scientific interest.

It is noteworthy that the study of the processes of the terpene electrochemical phosphorylation is important also from the practical viewpoint: phosphorylated terpenes can be biologically active compounds and are promising catalysts for the enantioselective synthesis [4, 5].

Preliminary investigations of the electrochemical phosphorylation of camphene [6, 7], showed that in the course of anodic oxidation of some organophosphorus compounds (triethylphosphine, *N,N,N',N'*-tetraethyl-*O*-ethyldiamidophosphite) in the presence of camphene camphenylphosphonium salts were formed, the substitution products of one of the hydrogen atoms at the camphene double bond [scheme (3)].



(3)

Despite a low yield of camphenylphosphonium salts, the study of the camphene electrochemical phosphorylation is still promising enough because the reactions with complete retention of initial structure are not typical for the camphene (and terpene as a whole) chemistry. In this paper we report on the results of our experiments on the anodic oxidation of tertiary phosphines with either aliphatic (tripropylphosphine and tributylphosphine) or aromatic (triphenylphosphine) substituent in the presence of camphene (**I**).

Voltammetric measurements showed that camphene gives only one oxidation wave on platinum electrode (Fig. 1, curve *1*). The observed linear dependence of the limit current height on the square root of the rate of potential sweep indicates that this current is of diffusion character. The value of the half-wave potential found from the dependence of the potential

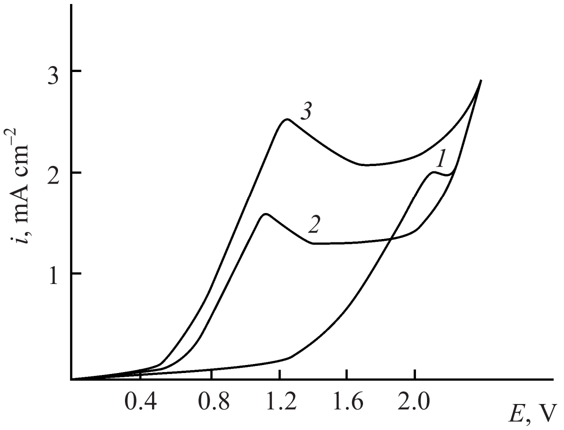


Fig. 1. Voltammetric curves of oxidation of camphene and tributylphosphine. Solvent CH_3CN, background electrolyte 0.01 M $NaClO_4$, reference electrode Ag/Ag$^+$. Potential sweep 1 V s^{-1}. (*1*) camphene, C = 0.005 M; (*2*) tributylphosphine, C = 0.005 M; and (*3*) tributylphosphine, C = 0.005 M + camphene, C = 0.0005 M.

Results of thermochemical oxidation of tertiary phosphines in the presence of camphene

Run no.	Phosphine (mol)	Anode	Electric current amount Q mol^{-1}	Composition of reaction mixture (δ_P, ppm), by the data of ^{31}P NMR spectroscopy
1	Ph_3P (0.01)	Pt	0.36	**IIIa** (30.7) – 93%, 13.2 – 4%, 22.1 – 3%
2	Ph_3P (0.025)	Glassy carbon	0.42	**IIa** (32.7) – 94%, 13.0 – 4%, 22.1 – 2%
3	Pr_3P (0.033)	Pt	0.62	**IIb** (56.3) – 18%, **IVb** (11.6) – 38%, **Vb** (31.1) – 5%, **VIb** (34.0) – 6%, **VIIb** (22.2) – 15%, **VIIIb** (60.1) – 4%, 37.1 – 7%, 40.9 – 7%
4	Pr_3P (0.01)	Glassy carbon	0.18	**IIb** (54.5) – 21%, **IIIb** (53.2) – 45%, **IVb** (11.4) – 4%, **Vb** (30.6) – 6%, **VIb** (33.4) – 3%, **VIIb** (22.4) – 1%, **VIIIb** (59.1) – 5%, 35.5 – 8%, 39.3 – 7%
5	Bu_3P (0.0345)	Pt	0.63	**IIc** (56.0) – 19%, **IVc** (14.4) – 30%, **Vc** (32.6) – 6%, **VIc** (35.1) – 5%, **VIIc** (23.8) – 21%, **VIIIc** (60.7) – 6%, 38.4 – 6%, 42.1 – 7%
6	Bu_3P (0.058)	Glassy carbon	0.32	**IIc** (56.4) – 3%, **IIIc** (52.4) – 47%, **IVc** (14.0) – 8%, **Vc** (32.6) – 4%, **VIc** (35.1) – 9%, **VIIc** (23.8) – 7%, **VIIIc** (58.9) – 10%, 35.2 – 8%, 38.9 – 4%

on log $(i/i_d - i)$ equals 1.82 V. The absence of a reverse wave indicates the general irreversibility of the process of camphene anodic oxidation. Comparison of the heights of the waves of camphene and commonly used reference compound (phenothiazine) registered under the same conditions shows that the electrochemical oxidation of **I** is a one-electron process. Repeating the potential sweep gives well reproducible oxidation wave of **I** indicating the absence of a substantial adsorption process on the platinum electrode involving the camphene molecule. It should be noted that at the cathodic sweep of potential no reduction wave is observed.

Adding camphene to the electrolyte containing tributylphosphine ($E_{1/2} = 0.84$ V, $n = 0.66$ e [8]) leads to the increase in the height of the oxidation wave to one-electron level (Fig. 1, curve *3*). Note that this effect is observed even at adding camphene in amount of 10% to the initial tributylphosphine content. Further increase in the relative content of camphene in solution does not induce any changes in the morphology of the phosphine wave. When camphene concentration reaches approximately the initial concentration of tributylphosphine, the camphene wave at the potentials 1.6–1.9 V begins to appear. These observations show that adding of camphene leads to a change in the nature of electrochemical oxidation of tertiary phosphines it the near-electrode layer. However an unequivocal conclusion on the character of the processes from only the data of voltammetry cannot be drawn. The principal information concerning the mechanism of anodic oxidation of tertiary phosphines in the presence of camphene was obtained using the method of preparative electrolysis.

Preparative electrochemical experiments were carried out on platinum and glassy carbon (GC) electrodes in galvanostatic regime at the change of anodic potential from 0.7 to 1.2 V (the area of oxidation of only tertiary phosphines). To increase the solubility of camphene in electrolyte (solution of sodium perchlorate in acetonitrile) a small amount of tetrahydrofuran was added. The conditions of the electrolysis and the composition of the reaction mixtures (by the data of ^{31}P NMR spectroscopy) are listed in the table.

As seen from the data in the table, the results of electrosynthesis depend substantially on the nature of substituent at the phosphorus atom. In the experiments with triphenylphosphine (the table, nos. 1 and 2) in the ^{31}P NMR spectrum appeared a signal of practically only one phosphorus-containing compound (Fig. 2a), while after electrooxidation of aliphatic phosphines the formation was registered of a series of compounds (Fig. 2b). Further investigations showed that triphenylphosphine cation-radical practically did not react with camphene and the process of electrolysis on platinum electrode (the table, no. 1) led to the synthesis of triphenylphosphine oxide as had been found earlier at the electrooxidation of triphenylphosphine in the absence of any substrate (both on the glassy carbon [9] and platinum [10] anodes). However, the ^{1}H NMR data for the product of electrosynthesis with triphenylphosphine on the glassy carbon anode (the table, no. 2) showed that this compound had another structure. Its IR spectrum differs from that of triphenylphosphine oxide by a small shift of the phosphorus–oxygen band (1188 cm^{-1} in triphenylphosphine oxide and 1181 cm^{-1} in this product). Its melting point (192–202ºC) differs from that of triphenylphosphine oxide (mp 159ºC [11]). By the data of elemental analysis the composition of this product corresponds to the complex $(Ph_3PO)_4\cdot HClO_4$ (**IIa**). The treatment of the complex with sodium ethoxide (in ethanol) or boiling with distilled water affords pure triphenylphosphine oxide Ph_3PO with δ_P 28 ppm (**IIIa**). Content of other products of electrosynthesis (δ_P 13 ppm and 22 ppm) in the reaction mixture that might include camphenyltriphenylphosphine derivatives is insignificant (5% or less).

Other results were obtained in experiments with tripropylphosphine and tributylphosphine (see the table, nos. 3–6). From the ^{31}P NMR spectrum of the reaction mixture after electrolysis with tributylphosphine on the platinum anode (Fig. 2b) follows that the electrochemical oxidation of trialkylphosphine in the

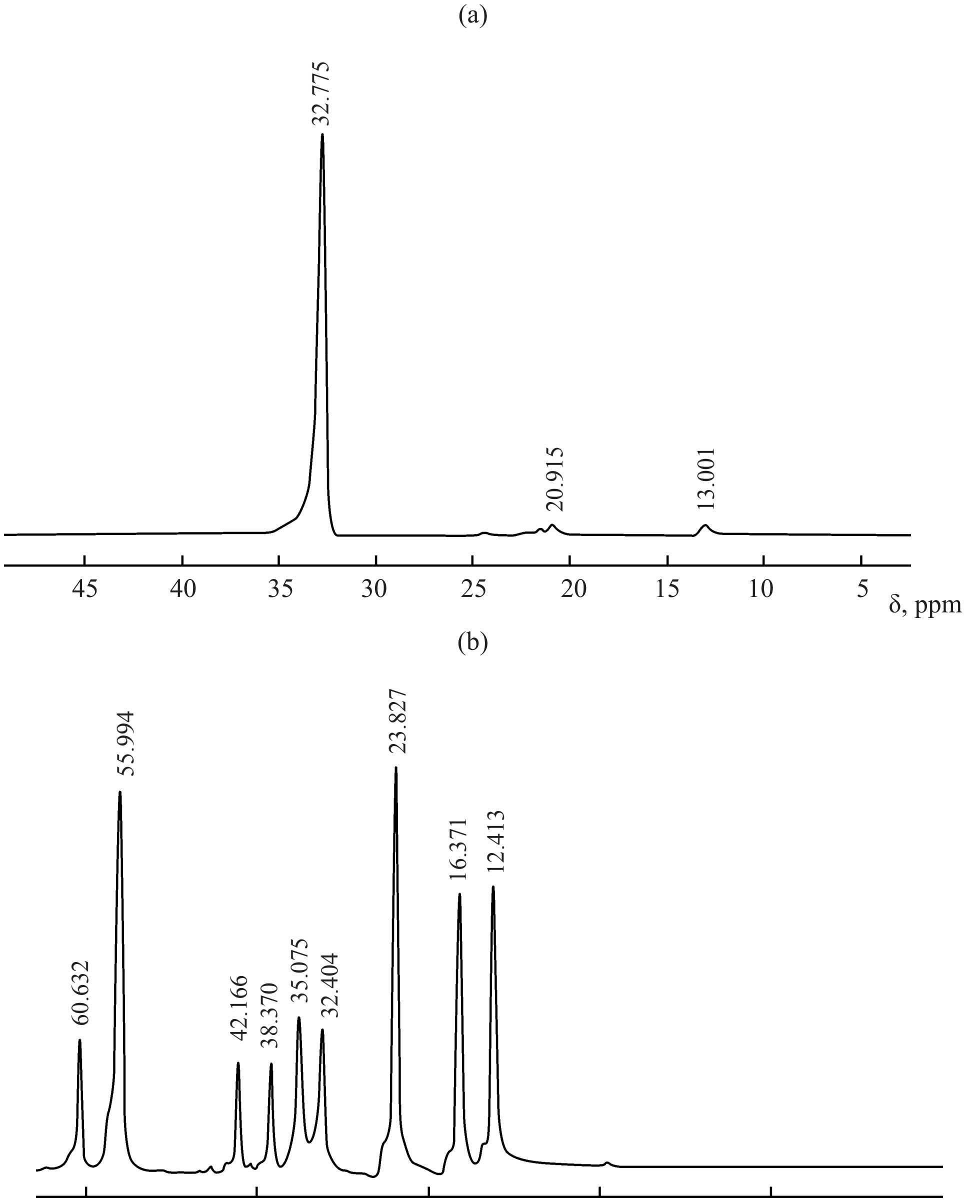


Fig. 2. $^{31}P-\{^1H\}$ NMR spectra of the products of phosphine electrochemical oxidation in the presence of camphene. (a) electrooxidation of triphenylphosphine on glassy carbon anode, reaction mixture; (b) electrooxidation of tributylphosphine on the platinum anode, reaction mixture; (c) electrooxidation of tributylphosphine on the platinum anode, reaction mixture after adding NaOH; (d) electrooxidation of tributylphosphine on the platinum anode, hexane extract from the reaction mixture.

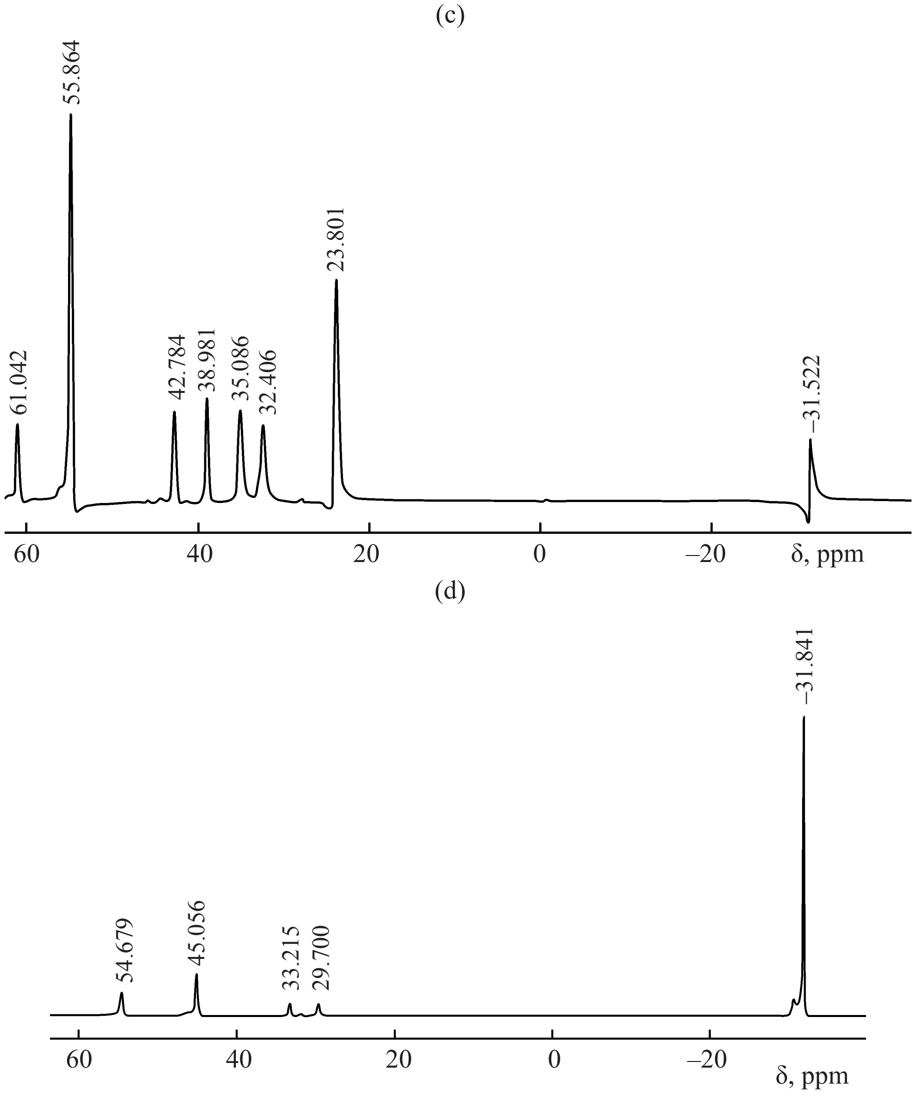
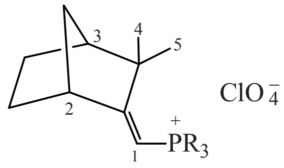


Fig. 2. (Contd.)

presence of camphene leads to the formation of a series of phosphorus-containing compounds that probably includes compounds with a P–H bond (doublet signals in the region of 15 ppm) which were decomposed at the action of NaOH (Fig. 2c). Obviously, the doublets near 15 ppm belong to the protonated phosphine R_3PH^+ [**VI**, R = Pr (**b**), Bu (**c**)] transformed into Bu_3P (δ_P –31.4 ppm) at the action of alkali. Addition of base led also to small shift (~2 ppm upfield) of the signals in the region of 56–58 ppm characteristic of trialkylphosphine oxides. It can be assumed that like in the electrolysis of triphenylphosphine the complex $(Bu_3PO)_x{\cdot}HClO_4$ (**IIc,** δ_P 56 ppm) is formed that after adding alkali transforms into Bu_3PO (**IIIc**). In the experiments with tripropyl-phosphine (see the table, nos. 3, 4) similarly at the action of a base on the products of electrosynthesis appears the parent phosphine (δ_P –32.8 ppm) and small upfield shift occurs due to the transformation of $(Pr_3PO)_x{\cdot}HClO_4$ (**IIb**, δ_P 56 ppm) into Pr_3PO (**IIIb**, δ_P 53 ppm).

The treatment of the mixture of the electrosynthesis products with bases (triethylamine, sodium ethoxide) followed by extraction with a non-polar solvent (hexane, diethyl ether) leads to the isolation mainly of parent tripropylphosphine or tributylphosphine and of related phosphine oxides. It is noteworthy that unlike the tertiary phosphines the complete extraction of phosphine oxides from the reaction mixtures failed even at multiple extractions. Probably phosphine oxides form in part some complexes with other products of electrosynthesis. An indirect evidence for this assumption is the appearance of R_3PO signals in our experiments at lower field (δ_P 52–54 ppm) than the signal of pure Pr_3PO and Bu_3PO whose chemical shifts fall to the range 43–48 ppm [12]. It is interesting to note that after extraction with hexane (Fig. 2d) the spectrum contains both signals of pure R_3PO (δ_P 43.6 ppm) and a peak at 54.1 ppm that probably corresponds to a complex of **III** with some product of electrosynthesis that is partially also extracted with the non-polar solvent.

For the isolation of other products of electrosynthesis we used a method of column chromatography. We succeeded in isolation of relatively pure product of the electrosynthesis that shows in ^{31}P NMR spectrum a signal in the region of 22–24 ppm. Structure of this compound was established by ^1H NMR spectroscopy on the example of tributylphosphine oxidation in the presence of camphene on the platinum anode that has a signal δ_P 23.8 ppm (Fig. 3). In its ^1H NMR spectrum besides the strong signals of tributylphosphine groups of protons (δ_H 0.92 ppm, 1.44 ppm, 1.48 ppm and 2.27 ppm) a doublet signal of the proton at a double bond (δ_H 5.2 ppm) is clearly seen. The value of spin-spin coupling constant is 17.8 Hz, that is characteristic of geminal phosphorus–proton coupling ($^2J_{PH}$). The downfield shift of the signals as compared with the parent camphene (4.8 ppm) is also understandable by the effect of closely located phosphine group. The presence of signals of gem-dimethyl group (1.04 and 1.07 ppm) and patterns location characteristic of the protons at secondary and tertiary aliphatic carbon atoms in the region of 1–3 ppm allows a conclusion that the camphene structure is preserved. As compared with camphene, the nodal tertiary protons of the obtained compound resonate at lower field (δ_H 3.0 and 2.0 ppm instead of δ_H 2.7 and 1.9 ppm respectively in camphene), that probably is a result of the influence of phosphine group. Therefore we conclude that the products with δ_P 22–24 ppm are camphenylphosphoniun salts of the following structure:



R = Pr (**VIIb**), Bu (**VIIc**).

In the ^1H NMR spectra of the fractions with enhanced content of camphenylphosphonium salts **VIIb** and **VIIc** there are also the signals of other phosphorus-containing products (the table, compounds **Vb**, **VIb** and **Vc**, **VIc**). The occurrence of the signals of protons at a double bond in the region of 4.5–4.8 ppm (minor peaks in Fig. 3) is characteristic of one of these compounds. The distance between the peaks is over 40 Hz, hence this is not due to the spin–spin coupling with phosphorus nucleus. It can be suggested

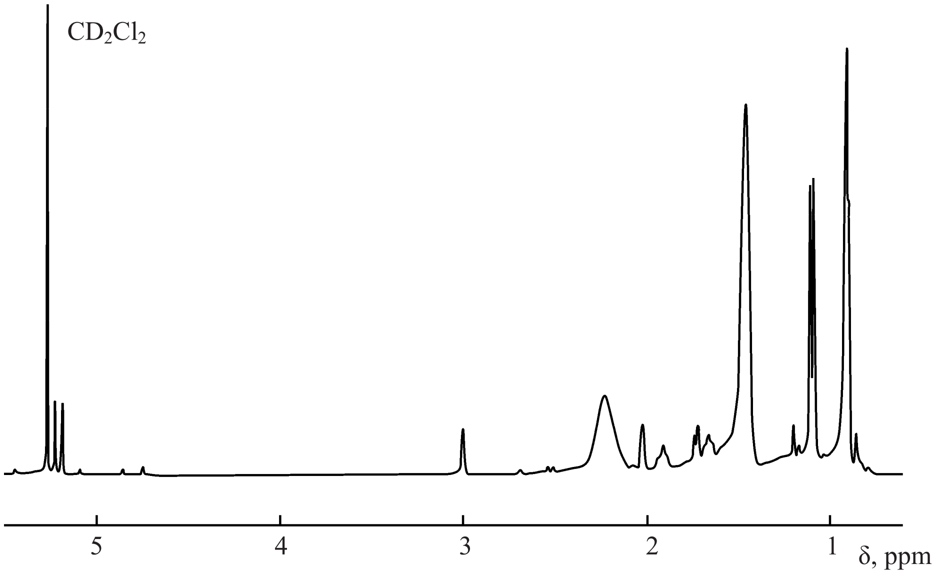


Fig. 3. Electrooxidation of tributylphosphine in the presence of camphene on the platinum anode. ^1H NMR spectrum of first chromatographic fraction (eluent dichloromethane).

that these signals belong to unsymmetrical protons at the double bond in the cyclic substituent that are remote from the phosphine group (the absence of coupling with phosphorus). But we failed to isolate the compounds pure and establish exactly their structures.

By column chromatography of the reaction mixture after electrooxidation of tributylphosphine in the presence of camphene on the platinum anode we succeeded to isolate also a fraction containing together with tributylphosphine oxide a relatively significant amount of a product with δ_P 60 ppm (see Experimental, fraction 3). The ^{1}H NMR spectrum of this fraction contains mainly the signals of butyl group but also a multiplet (of less intensity than the signals of butyl group) in the region characteristic of the protons of alkoxy groups (δ_H 3.9 ppm) which probably belongs to the product with δ_P 60 ppm. The compounds with δ_P 60 ppm probably are quasiphosphonium salts R_3P^+OR'[**VIII**, R = Pr (**b**), Bu (**c**)] that are formed presumably at the dealkylation with trialkylphosphine oxide of one of the products of electrolysis.

At the electrochemical oxidation of trialkylphosphines in the presence of camphene besides the camphenylphosphoric compounds the protonated phosphines and phosphine oxides (as complexes) are formed arising in the reaction of organophosphorus cation–radicals with the parent molecules [13]. We found that protonated trialkylphosphine oxides (δ_P 75 ppm [13]) were transformed further into compounds **IIb** and **IIc**.

Thus, at the electrochemical oxidation of trialkylphosphines in the presence of camphene proceed several concurrent reactions. The following scheme of the process of anodic oxidation of trialkylphosphines in the presence of camphene may be constructed. The organophosphorus compound cation-radicals formed on the anode enter into two concurrent reactions. By the first pathway the cation-radicals react with camphene at its double bond. Then the dicationic intermediate formed either enters into the reactions of additional oxidation and deprotonation to afford camphenylphosphonium salts **VII** where the terpene structure remains intact, or suffers a process of cleavage of one camphene ring followed by migration of double bong in the ring to form monocyclic phosphonium salt, as attested indirectly by the structures of compounds **Vc** or **VI** (the minor signals in the ^{1}H NMR spectra of the fractions where camphenylphosphonium salts dominate). The second pathway is the reaction with the parent phosphine that after oxidation affords diphosphonium salt that is hydrolyzed to form trialkylphosphonium derivative **IV** and protonated phoshine oxide **II**.

The experiments with tripropylphosphine and tributylphosphine on the glassy carbon electrode led to the reaction mixtures with enhanced content of trialkylphosphine oxide complex compounds **III** that were registered in the reaction mixture at the experiments on platinum electrode (Fig. 2b). Obviously owing to the anode passivation the complete transformation of the parent tripropyl- and tributylphosphines at the chosen potentials does not occur (see the value of the passed electric current in the table), and residues then are oxidized at the isolation.

Thus, we established that at the electrochemical oxidation of tertiary phosphines in the presence of camphene proceed several concurrent reactions. This feature is different in the studied reactions from the earlier described reactions of anodic phosphorylation of alkenes with simpler structure [1–3] where were detected the products of phosphine addition to the alkene. This is understandable because of a lower accessibility of the camphene double bond due to its steric overloading to the attack of the tertiary phosphine cation-radical generated on anode. This leads to lower reaction rate of phosphine cation-radicals with camphene as compared with simple alkenes, and competition of the parent phosphine for the cation-radical becomes significant.

EXPERIMENTAL

The voltammetric measurements were carried out with the use of special cell of 10 ml volume. As a source of polarizing voltage was used a potentiostat PI50-1 coupled with a PR-9 programmer and a digital oscillograph with the memory C9–8. The working electrode was platinum disk with the surface area 0.196 cm^2, the cathode was bottom mercury. The silver electrode Ag/Ag$^+$ (0.01 M $AgNO_3$ in acetonitrile) was taken as a reference electrode. Oxygen was removed from the studied solutions by dry argon.

The preparative electrochemical oxidation was carried out in a 100-ml glass cell with the anode and cathode spaces separated by a porous diaphragm, in galvanostatic regime with continuously controlled anode potential. As a source of direct current was used a P-5827M potentiostat. As anode was taken platinum (working area 50 cm^2) or glassy carbon cylinders (working area 24 cm^2, type SU-2000). As an auxiliary electrode (cathode) was used nickel coil with the surface area 20 cm^2. In the process of electrolysis the potential was measured relatively to the reference electrode Ag/Ag$^+$ (0.01 M $AgNO_3$ in acetonitrile). The process was carried out under argon atmosphere, the electrolyte was continuously stirred.

The NMR spectra were registered on a Varian Unity instrument with operating frequency 300 MHz (^{1}H) or 121 MHz (^{31}P, external reference 85% solution of H_3PO_4). The IR spectra were taken on a UR-20 spectrophotometer.

Preparative electrochemical oxidation of triphenylphosphine in the presence of camphene on a platinum electrode. In a mixture of acetonitrile (60 ml) and tetrahydrofuran (10 ml) was dissolved 6.43 g (0.05 mol) of sodium perchlorate, 4.07 g (0.03 mol) of camphene, and 2.60 g (0.01 mol) of triphenylphosphine (by adding by portions). The electrolysis was carried out at the anode current density 0.02–0.2 μA cm^{-2}, the electrode potential varied from 0.7 to 1.2 V. At the electrolysis to avoid the anode passivation a procedure of intermittent change of the electrode polarity was applied. During the electrolysis the platinum anode was periodically renewed. Through the electrolyte was passed 350 Q of electric current. After the end of electrolysis the solution was evaporated in a vacuum. The residue was treated with methylene chloride (100 ml) for separation of the electrosynthesis products from the sodium perchlorate. The methylene chloride extract was evaporated. The reaction mixture composition (by the data of ^{31}P NMR spectroscopy) is shown in the table. Soon in the reaction mixture separated a white precipitate of triphenylphosphine oxide **IIIa**. Yield 1.72 g (62%); mp 156–159ºC; ^{31}P NMR spectroscopy, δ, ppm: 26 (DMSO). IR spectrum , ν, cm^{-1} 1681 (P=O).

Preparative electrochemical oxidation of triphenylphosphine in the presence of camphene on a glassy carbon electrode. In a mixture of acetonitrile (70 ml) and tetrahydrofuran (10 ml) was dissolved 5.21 g (0.04 mol) of sodium perchlorate, 3.33 g (0.025 mol) of camphene, and 6.48 g (0.025 mol) of triphenylphosphine (by adding by portions). The electrolysis was carried out at the anode current density 0.04–1.25 μA cm^{-2} , the electrode potential varied from 0.8 to 1.2 V. At the electrolysis to avoid the anode passivation a procedure of intermittent change of the electrode polarity was applied. Through the electrolyte was passed 1010 Q of electric current. After the end of electrolysis the solution was evaporated in a vacuum. The residue was treated with methylene chloride (100 ml) for separation of the electrosynthesis products from the sodium perchlorate. The methylene chloride extract was evaporated. The reaction mixture composition (by the data of ^{31}P NMR spectroscopy) is shown in the table. Soon at cooling (~ –10ºC) from the reaction mixture separated a white crystalline precipitate $(Ph_3PO)_4 \cdot HClO_4$ (**IIa**). Yield 6.63 g (71 %); mp 192–202ºC ; ^{31}P NMR spectrum, δ, ppm: 28.8 (CH_3CN). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.21 (s, ^{1}H), 7.42 m (24H, meta protons of phenyl ring), 7.49 m (12H, para protons of phenyl ring), 7.63 m (24H, ortho protons of phenyl ring). IR spectrum , ν, cm^{-1} 1688 (P=O). Found, %: C 71.07, H 4.81. $C_{54}H_{46}ClO_8P_4$. Calculated, %: C 71.25, H 5.03.

Preparative electrochemical oxidation of tripropylphosphine in the presence of camphene on a platinum electrode. In a mixture of acetonitrile (40 ml) and tetrahydrofuran (10 ml) was dissolved 4.68 g (0.038 mol) of sodium perchlorate, 4.93 g (0.036 mol) of camphene, and 5.40 g (0.034 mol) of tripropylphosphine (by adding portionwise). The electrolysis was carried out at the anode current density 0.2–2 μA cm^{-2}, the electrode potential varied from 0.7 to 1.0 V. Through the electrolyte was passed 2020 Q of electric current. After the end of electrolysis the solution was evaporated in a vacuum. The residue was treated with methylene chloride (100 ml) for separation of the electrosynthesis products from the sodium perchlorate. The methylene chloride extract was evaporated. The reaction mixture composition (by the data of ^{31}P NMR spectroscopy) is shown in the table. The reaction mixture was treated with a solution of triethylamine (3.53 g, 0.034 mol) in diethyl ether (10 ml) and stored for a half hour. Then tripropylphosphine (δ_P –32 ppm) and tripropylphosphine oxide (δ_P 44 ppm) were extracted with hexane. The residue was chromatographed on a glas column 30 cm in height and 15 mm in diameter, adsorbent silica gel Acros Organics (0.035–0.070 μ, pore diameter 6 nm), eluent acetonitrile, developing in iodine vapor. The chromatographic fractions composition was determined on the basis of the data of ^{31}P NMR spectroscopy:

Fraction 1: compound **Vb** – 6, **VIb** – 31, **VIIb** – 63%.

Fraction 2: compound **IIIb** – 16, **Vb** – 16, **VIb** – 22, **VIIb** – 36, **VIIIb** – 10%.

Fraction 3: compound **IIIb** – 59, **Vb** – 9, **VIb** – 15, **VIIb** – 17%.

The ^{1}H NMR spectrum of compound **VIIb** (first chromatographic fraction), δ, ppm (CDCl$_3$): 0.91 t ($^3J_{HH}$ 6.0 Hz, CH_3CH$_2$CH$_2$P), 1.60 m (CH$_3$CH_2CH$_2$P), 2.18 m (CH$_3$CH$_2$CH_2P), 1.18 and 1.23 (s, H^4 and H^5), 2.11 (s, H^3), 3.06 (s, H^2), 5.18 d ($^2J_{PH}$ 17.8 Hz, H^1). The ^{1}H NMR spectra of the third chromatographic fraction, δ, ppm (CDCl$_3$): the strongest peaks (compound **IIIb**): 0.92 t ($^3J_{HH}$ 6.0 Hz, CH_3CH$_2$CH$_2$P), 1.60 m (CH$_3$CH_2CH$_2$P), 2.18 m (CH$_3$CH$_2$CH_2P).

Preparative electrochemical oxidation of tripropylphosphine in the presence of camphene on a glassy carbon electrode. In a mixture of acetonitrile (70 ml) and tetrahydrofuran (10 ml) was dissolved 5.0 g (0.04 mol) of sodium perchlorate, 1.4 g (0.0103 mol) of camphene, and 1.2 g (0,0075 mol) of tripropylphosphine. The electrolysis was carried out at the anode current density 0.04–2 μA cm^{-2}, the electrode potential varied from 0.7 to 1.2 V. Through the electrolyte was passed 180 Q of electric current. After the end of electrolysis the solution was evaporated in a vacuum. The residue was treated with methylene chloride (100 ml) for separation of the electrosynthesis products from the sodium perchlorate. The methylene chloride extract was evaporated. The reaction mixture composition (by the data of ^{31}P NMR spectroscopy) is shown in the table.

Preparative electrochemical oxidation of tributylphosphine in the presence of camphene on a platinum electrode. In a mixture of acetonitrile (40 ml) and tetrahydrofuran (10 ml) was dissolved 5.434 g (0,044 mol) of sodium perchlorate, 5.012 g (0.0369 mol) of camphene, and 6.983 g (0.034 mol) of tributylphosphine a (by adding by portions). The electrolysis was carried out at the anode current density 0.1–2 μA cm^{-2}, the electrode potential varied from 0.7 to 0.9 V. Through the electrolyte was passed 2105 Q of electric current. After the end of electrolysis the solution was evaporated in a vacuum. The residue was treated with methylene chloride (100 ml) for separation of the electrosynthesis products from the sodium perchlorate. The methylene chloride extract was evaporated. The reaction mixture composition (by the data of ^{31}P NMR spectroscopy) is shown in the table. The reaction mixture was treated with a solution of triethylamine (3.78 g, 0.036 mol) in diethyl ether (10 ml) and stirred for half an hour. Ethereal layer was removed: it contained only parent tributylphosphine (δ$_P$ –32 ppm). To the reaction mixture was added hexane. The ^{31}P NMR spectrum of the hexane extract is depicted in Fig. 2d. The residue after extraction was chromatographed on a glass column 30 cm in height and 15 mm in diameter, adsorbent silica gel Acros Organics (0.035–0.070μ, pore diameter 6 nm), eluent dichloromethane, developing in iodine vapor.

The chromatographic fractions composition is based on the data of ^{31}P NMR spectroscopy:

Fraction 1: compound **Vc** – 11, **VIc** – 14, **VIIc** – 75%.

Fraction 2: compound **IIIc** – 30, **Vc** – 17, **VIc** – 21, **VIIc** – 22, **VIIIc** – 10%.

Fraction 3: compound **IIIc** – 63, **Vc** – 13, **VIc** – 13, **VIIc** – 8, **VIIIc** – 3%.

The ^{1}H NMR spectrum of compound **VIIc** (first chromatographic fraction) δ, ppm (CDCl$_3$): 0.92 t ($^3J_{HH}$ 6.0 Hz, CH_3CH$_2$CH$_2$CH$_2$P), 1.44 m (CH$_3$CH_2·CH$_2$CH$_2$P), 1.48 m (CH$_3$CH$_2$CH_2CH$_2$P), 2.27 m (CH$_3$CH$_2$CH$_2$CH_2P), 1.05 and 1.07 s (H^4 and H^5), 2.02 s (H^3), 3.01 s (H^2), 5.20 t ($^2J_{PH}$ 17.8 Hz, H^1).

The second fraction (Table 3) was chromatographed further with ethanol as eluent. Compositon of the obtained is based on the data of ^{31}P NMR spectra:

Fraction 1: compound **Vc** – 28, **VIc** – 25, **VIIc** – 42, **VIIIc** – 5%.

Fraction 2: compound **IIIc** – 35, **Vc** – 14, **VIc** – 18, **VIIc** – 24, **VIIIc** – 9%.

Fraction 3: compound **IIIc** – 48, **Vc** – 5, **VIc** – 5, **VIIc** – 14, **VIIIc** – 28%.

The ^{1}H NMR spectum of the third chromatographic fraction, δ, ppm (CDCl$_3$): 0.92 m (CH_3CH$_2$CH$_2$CH$_2$P), 1.44 m (CH$_3$CH_2CH$_2$CH$_2$P), 1.48 m (CH$_3$CH$_2$CH_2·CH$_2$P), 2.25 m (CH$_3$CH$_2$CH$_2$CH_2P), 3.90 (d.t, $^3J_{HH}$ 6.0 Hz, $^3J_{PH}$ 2.0 Hz, POCH_2).

Preparative electrochemical oxidation of tributylphosphine in the presence of camphene on a glassy carbon electrode. In a mixture of acetonitrile (65 ml) and tetrahydrofuran (15 ml) was dissolved 7.57 g (0.06 mol) of sodium perchlorate, 4.97 g (0.036 mol) of camphene, and 11.88 g (0.059 mol) of tributylphosphine a (by adding portionwise). The electrolysis was carried out at the anode current density 0.1–1 μA cm^{-2}, the electrode potential varied from 0.7 to 1.2 V. Through the electrolyte was passed 2268 Q of electric current. After the end of electrolysis the solution was evaporated in a vacuum. The residue was treated with methylene chloride (100 ml) for separation of the electrosynthesis products from the sodium perchlorate. The methylene chloride extract was evaporated. The reaction mixture composition (by the data of ^{31}P NMR spectroscopy) is shown in the table.

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