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ELECTROCHEMICAL SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS

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The electrolysis of tertiary phosphines in the presence of aromatic or heteroaromatic compounds made it possible to carry out the electrochemical synthesis of the respective aryl(heteroaryl)phosphonium salts with good yield. The anodic oxidation of the esters of phosphorous acids in the presence of aromatic compounds led to the formation of respective esters of arylphosphonic acid.

INTRODUCTION

The ability of aromatic phosphines and apparently other phosphorus compounds to be anodically oxidised,¹ i.e. to the removal of an electron, and the formation of intermediate radical cations is of interest from various points of view and especially for the electrochemical synthesis of organophosphorus compounds. In the anodic oxidation of triphenylphosphine in the presence of halogenide ions we showed² that instead of the expected anodic substitution reaction with the formation of the ring-substitution products, by analogy with the electrochemical oxidation of aromatic amines, the anodic addition reaction occurred at the phosphorus atom with the formation of triphenyldihalogenphosphorane. Obviously, at the removal of an electron from a molecule of phosphine the positive charge becomes localized mainly on the phosphorus atom. Therefore, it is suggested that the radical cations have a rather strong electrophilic ability and it can be expected that the electrochemical oxidation of the organophosphorus compounds, in the presence of the suitable substrates, will lead to the products with the new phosphorus-carbon bond.

In the present investigation we have studied the electrochemical oxidation of the tertiary phosphines, Ph_3P , Bu_3P , phosphites, $(\text{EtO})_3\text{P}$, $(\text{BuO})_3\text{P}$,

and O,O-diethylphenylphosphonite, $(\text{EtO})_2\text{PPh}$, in acetonitrile on a platinum electrode with 0.1 M NaClO_4 or 0.02 M NaBF_4 as supporting electrolyte in the presence of aromatic (benzene, toluene, naphthalene) and heteroaromatic (thiophene, furan) compounds.

EXPERIMENTAL

The methods of voltamperography on stationary and rotating electrodes were used. The details of the methods have been described in a previous paper.¹ The preparative electrolysis was performed in a divided cell in galvanostatic conditions with a current density between 1.6 and 3.3 mA/cm^2 . The working volume of anolyte was equal to 40 ml. A platinum anode had an electrode surface of 30 cm^2 . The area of a platinum cathode was equal to 5 cm^2 . The potential of the working electrode was referred to a silver-0.01M silver nitrate electrode in acetonitrile medium. The extraction and the identification of the products from the reaction mixture were performed by ordinary ways and methods.

RESULTS AND DISCUSSION

As follows from Table I all the investigated organophosphorus compounds were oxidized on a platinum electrode in the accessible potential region, moreover the esters of phosphorous acids are oxidized less readily as compared to phosphines. From the data of the cyclic voltamperography and

TABLE I

Characteristics of oxidation waves of the organophosphorus compounds in absence or presence of ArH.

Compound ^a	$E_{1/2}$, V	n	ArH ^b
Bu ₃ P	0.90	0.7	—
	0.90	1.0	C ₄ H ₄ S
	0.90	1.0	C ₄ H ₄ O
	0.90	0.8	C ₆ H ₆
Ph ₃ P	0.95	0.7	—
	0.95	1.0	C ₄ H ₄ S
	0.95	0.9	C ₁₀ H ₈
	0.95	1.0	C ₄ H ₄ O
(EtO) ₂ PPh	1.20	0.66	—
	1.22	0.98	C ₆ H ₆
	1.24	1.00	C ₆ H ₅ CH ₃
(EtO) ₃ P	1.60	0.66	—
	1.60	0.96	C ₆ H ₆
	1.62	1.00	C ₆ H ₅ CH ₃
(BuO) ₃ P	1.56	0.66	—
	1.60	1.00	C ₆ H ₆
	1.60	1.00	C ₆ H ₅ CH ₃

^a C = 5.10⁻³M;

^b Concentration of benzene, toluene, naphthalene, thiophene and furan are equal to 2.10⁻¹, 2.10⁻², 1.10⁻¹, 1.10⁻¹, 1.10⁻¹M respectively.

the method of rotating disk electrode with a ring it follows that the oxidation process is irreversible. The number of the electrons passing from a molecule to the electrode was estimated by correlation with the standard (phenothiazine and *p*-anisylidiphenylamine) and amounted to about 0.7 in all cases. Such a decrease of the limiting oxidation current of the organophosphorus compounds could be due to the following chemical and electrochemical reactions of the supposed radical cations with the participation of the initial molecules.¹

Figure 1 shows the potentiodynamic polarization curves of the oxidation of triphenylphosphine, furan and their mixture. The anodic oxidation of furan proceeds with an appreciable rate at potentials above 1.5 V ($E_{1/2}$ = 1.6 V). Therefore, at the oxidation potentials of Ph₃P the anodic oxidation current of furan may be neglected. At the same time as may be seen from Figure 1 the height of the oxidation wave of triphenylphosphine increases appreciably in the presence of furan. Similar results were obtained for triphenylphosphine in the presence of thiophene and naphthalene, for tributylphosphine in the presence of thiophene and furan and also for esters of phosphorous acids in the presence of benzene and toluene. In all these cases as well as the case described above aromatic and

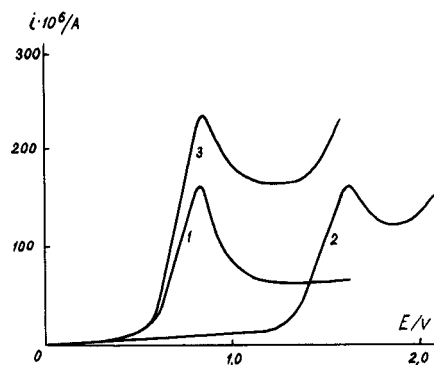


FIGURE 1 Polarization curves of oxidation at Pt stationary electrode: (1) triphenylphosphine ($C = 5.10^{-3}$ M); (2) furan ($C = 1.10^{-3}$ M); (3) triphenylphosphine ($C = 5.10^{-3}$ M) + furan ($C = 1.2.10^{-2}$ M). Scan rate 1.2V m⁻¹.

heteroaromatic compounds (HAr) were anodically oxidized less readily than the investigated organophosphorus compounds. The increase in the limiting oxidation current of the organophosphorus compounds in the presence of the less readily oxidized compounds (HAr) may indicate the interaction of the primary radical cations with HAr near the electrode surface. In Figure 2 a typical dependence of the height of the oxidation wave of phosphine Ph₃P on the concentration of HAr (furan) is given which clearly shows that as the concentration of furan is increased, the height of the wave reaches a limiting value which conforms to the transfer of one electron on the average. A similar picture was obtained for the investigated systems (Table I).

The preparative electrolysis of acetonitrile solutions of triphenyl- and tributylphosphine in the presence of an excess of HAr made it possible to establish the nature of the products of interaction between radical cations and HAr. In Table II the results of some selected preparative electrolysis are

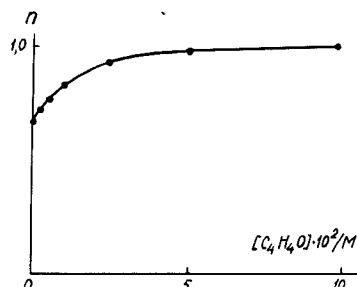


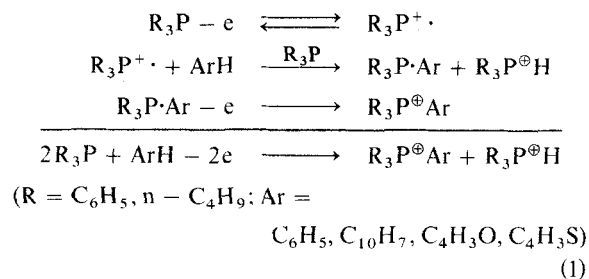
FIGURE 2 Dependence of oxidation wave height of triphenylphosphine (in units of number of electrons) on concentration of furan [C₄H₄O]. Concentration of triphenylphosphine is equal to $C = 5.10^{-3}$ M.

TABLE II
Results of some selected preparation electrolysis of tertiary phosphines.

R	ArH	Product	Analysis		m.p., °C	P ^a , ppm
			found, %	calcd., %		
C ₄ H ₉	C ₄ H ₄ O	[(C ₄ H ₉) ₃ P ⁺ (C ₄ H ₃ O)]ClO ₄ ⁻	C 52.00	51.95	230	- 34
			H 8.50	8.45		
			P 8.20	8.38		
			Cl 9.70	9.58		
C ₄ H ₉	C ₆ H ₆	[(C ₄ H ₉) ₃ P ⁺ (C ₆ H ₅)]ClO ₄ ⁻	C 57.40	57.24	122	- 30
			H 8.60	8.48		
			P 8.20	8.15		
			Cl 10.08	9.32		
C ₆ H ₅	C ₁₀ H ₈	[(C ₆ H ₅) ₃ P ⁺ (C ₁₀ H ₇)]ClO ₄ ⁻	C 68.36	68.78	209	- 23
			H 4.34	4.50		
			P 6.11	6.35		
			C 61.41	61.14	227	- 16
C ₆ H ₅	C ₄ H ₄ S	[(C ₆ H ₅) ₃ P ⁺ (C ₄ H ₃ S)]BF ₄ ⁻	H 4.63	4.17		
			S 7.12	7.41		
			C 59.70	59.38	235	- 16
			H 4.10	4.05		
C ₆ H ₅	C ₄ H ₄ S	[(C ₆ H ₅) ₃ P ⁺ (C ₅ H ₃ S)]ClO ₄ ⁻	S 7.22	7.20		
			P 7.03	6.97		

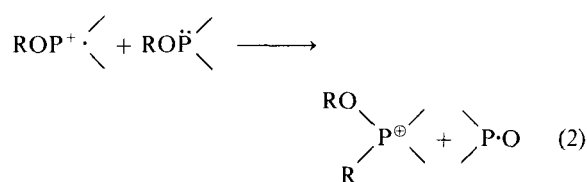
^a Phosphorus chemical shifts were measured relative to 85% H₃PO₄ as external standard, the negative sign indicates the reference resonates to high-frequency of the sample.

given which show that it has been possible to carry out a synthesis of arylphosphonium cations R₃P⁺Ar. It has been noticed that during an electrolysis the solution was becoming more acid and that in the presence of nitrogen bases (pyridine) the electrolysis made it possible to increase the yield of a phosphonium salt from 15–20% to 60–70% by phosphine. Apparently in the formation of P—Ar bond a proton is cleaved and a part of the initial phosphine is removed from the area of the electrode reaction owing to its protonation. The scheme of electrochemical synthesis of arylphosphonium cations neglecting the side reactions may be represented as the following sequence of steps (1)



It can be supposed that esters of phosphorous acids which much like tertiary phosphines are oxidized anodically will give unstable radical cations as a result of the removal of an electron

from a molecule. One of the probable ways of the transformation of the primary radical cations can be an electrophilic attack of a radical cation on a molecule of the initial ester with the formation of the corresponding quasi-phosphonium cation and the products of the following transformation of the intermediate free radical $\text{P} \cdot \text{O}$.



If the electrophilicity of the intermediate radical cation $ROP^+ \cdot$, the cation $\text{P}^+ \text{O}$ (the product of following oxidation of the free radical $\text{P} \cdot \text{O}$) is rather strong, their electrophilic attack on an aromatic ring and the formation of a new P—C_{sp}² bond can be expected.

In Table III the results of preparative oxidation of the investigated esters in the presence of benzene and toluene are given which show that in all cases

TABLE III

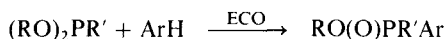
Results of some selected preparation electrolysis of esters of phosphorus acids.

Ester	ArH	Product	Analysis		b.p., °C	n _D ²⁰	P ^a , ppm
			found, %	calcd., %			
(EtO) ₃ P	C ₆ H ₆	(EtO) ₂ P(O)C ₆ H ₅	P13.65	13.25	37/0.02 Torr	1.4870	— 17
(BuO) ₃ P	C ₆ H ₆	(BuO) ₂ P(O)C ₆ H ₅	P11.88	11.51	115/0.1 Torr	1.4689	— 18
(EtO) ₂ PPh	C ₆ H ₆	(EtO)P(O)Ph ₂	P12.61	12.60	127/0.07 Torr	1.5677	— 31
(EtO) ₃ P	C ₆ H ₅ CH ₃	(EtO) ₂ P(O)C ₆ H ₄ CH ₃ ^b	P13.43	13.60	92/0.04 Torr	1.4942	— 17

^a Phosphorus chemical shifts were measured relative to 85% H₃PO₄ as external standard, the negative sign indicates the reference resonates to high-frequency of the sample.

^b The mixture of *p*- and *o*-tolylphosphonates in the ratio of 2 to 1.

the corresponding esters of the tetracoordinative phosphorus with a new P—Ar bond were formed. This means that the process of the electrosynthesis proceeded in the direction of Arbuzov's reaction under the described conditions.



(R = Et, Bu; R' = OR, Ph; ArH = C₆H₆, C₆H₅CH₃)
(3)

It should be noted that according to the NMR data the oxidation of triethylphosphite in the presence of toluene led to the formation of two isomers: *p*- and *o*-tolylphosphonates as the final products in the ratio of 2 to 1.

REFERENCES

1. Yu. M. Kargin, E. V. Nikitin, G. V. Romanov, O. V. Parakin, B. S. Mironov, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, **226**, 1101 (1976).
2. Yu. M. Kargin, E. V. Nikitin, G. V. Romanov, O. V. Parakin, T. G. Levshina, and A. N. Pudovik, *Zh. Obshch. Khim.*, **48**, 743 (1978).
3. E. V. Nikitin, O. V. Parakin, Yu. M. Kargin, G. V. Romanov, and A. N. Pudovik, U.S.S.R., No. 652186 (01.03.1977), *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* No. 10, 1979.
4. E. V. Nikitin, O. V. Parakin, Yu. M. Kargin, G. V. Romanov, and A. N. Pudovik, U.S.S.R., No. 655702 (01.03.1977), *Otkrytiya, Izobret., Obraztsy, Tovarnye Znaki* No. 13, 1979.