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ARTICLE

External Oxidant-Free Cross-Coupling: Electrochemically Induced Aromatic C–H Phosphonation of Azoles with Dialkyl-*H*-Phosphonates Under Silver Catalysis

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A convenient external oxidant-free method of phosphorylation of azole derivatives (benzo-1,3-azoles, 3-methylindole, 4-methyl-2-acetylthiazole) by dialkyl-H-phosphonates through catalytic oxidation of their mixture under electrochemical mild conditions (room temperature, normal pressure) in the presence of silver salts or oxide (1%) is proposed. This method allows to obtain the desired azole dialkylphosphonates with good yield (up to 75%). The transformations of silver and phosphorous precursors and intermediates using cyclic voltammetry, ESR, NMR spectroscopy were investigated, and a radical process mechanism was proposed. It has been found that the $AgP(O)(OEt)_2$ is oxidized earlier than other components of the reaction mixture with elimination of a radical. ESR spectrum of this radical's adduct was obtained in the presence of radical trap PBN. Ag^{2+} is out of the catalytic cycle.

Introduction

Benzo-1,3-azoles and their derivatives have unique biological properties. Therefore, benzoxazoles possess antitumor activity [1,2], and also are non-nucleoside topoisomerase I inhibitors [3]. They can be seen as a structural bioisomers of natural nucleotides, such as adenine and guanine, allowing them to easily interact with polymers in living systems [4]. Substituted benzoxazoles possess high biological activity. The derivatives of benzoxazole have become bases for plant protection products (for example, insectoacaricide with contact-intestinal action – "Zolon", S-2,3-dihydro-(6-chloro-2-oxibenzoxazole-3-ilmetyl)-O,O-diethyltiophosphate[5]), herbicides [6], antidiabetics, neuroleptics, etc.[7] It has been recently found that 3-phosphoindoles are good inhibitors of HIV-1 [8]. Search for new low-waste ways to obtain phosphorus-containing derivatives of heterocycles including azoles through direct phosphorylation of C-H bonds is a relevant topic.

Phosphorylated derivatives of benzoxazoles were obtained first in 60s of the last century by Razumov A.I. through heating of *ortho*-aminophenol and diethyl diethoxymethylphosphonate with alcohol flashing off [9,10] (Scheme 1, *1*).

The method of obtaining of 2-diethyl-indol-2-ylphosphonate according to cross-coupling of dibromvinyl-*ortho*-aminobenzole with diethylphosphite in the presence of palladium salts was described (Scheme 1, *2*) [11]. Li proposed the method of direct catalytic oxidative phosphorylation of aromatic azoles in the absence of bases and acids with palladium salts as catalysts and excess of oxidant $K_2S_2O_8$ (Scheme 1, *3*). The reaction proceeds slowly at 100 °C, yields of C-2 phosphorylated derivatives of azoles comprise 40-70% [12]. In 2012, Wang suggested the cross-coupling of 1*H*-indole and diethylphosphite with C(sp^2)-P bond formation with yield of 18-71% [13] (Scheme 1, *4*). Huang has realized phosphorylation of furans, thiophens, thioazoles, pyrrols and pyridines in the presence of catalytic amounts (0.2 equivalent) of $AgNO_3$ using 3 equivalents of $K_2S_2O_8$ as an oxidant (Scheme 1, *5*) [14]. Kim described dehydrocoupling of substituted pyrrols and dialkylphosphites under similar reaction conditions (Scheme 1, *6*) [15]. Yu-Fen Zhao has found that depending on the nature of oxidant – peroxide one can obtain a variety of products in the reaction of benzothiazoles and *H*-phosphonates, derivatives of benzothiazole, 2-acylbenzothiazoles and dialkyl benzothiazole-2-ylphosphonates, respectively, under mild conditions and without participation of metals [16] (Scheme 1, *7*). The regioselective cross-coupling between N-substituted indoles and dialkylphosphites was studied in 2016 (Scheme 1, *8*) [17]. The reaction was carried out in the presence of photo-oxidative catalyst $Ru(bpy)_3(PF_6)_2$ in combination with oxygen as a pure oxidant under exposure to visible light. The products were 2-indolephosphonates with yields 70-82% [17]. Zou suggested usage of Ag-catalyst in the presence of 1.5 equivalent of $Mg(NO_3)_2$ as an oxidant for the phosphorylation of indoles substituted into second and third position. Yield of 3-indolephosphonate is bigger in case of using 2-substituted indoles rather than 3-substituted indoles (Scheme 1, *9*) [18].

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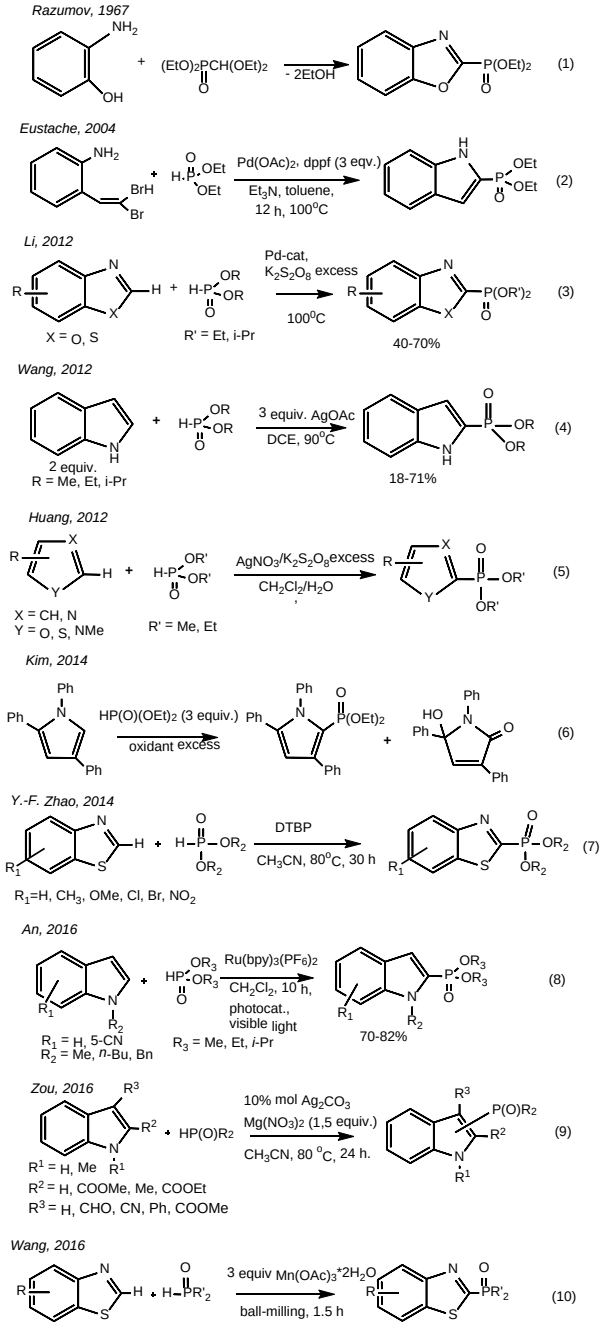
Electronic Supplementary Information (ESI) available: [General considerations, electrochemical synthesis details, products spectra]. See DOI: 10.1039/x0xx00000x



Scheme 1 Known approaches towards azole phosphonates.

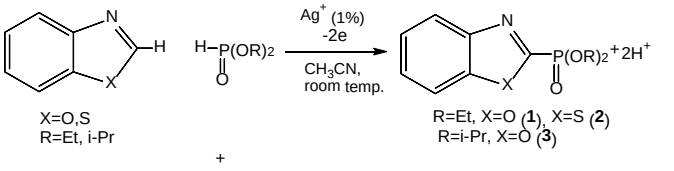
Wang has developed in 2016 method for constructing C(sp^2)-P bonds based on the coupling of benzoazoles or azoles derivatives with organophosphorus compounds in the presence of triple excess of $Mn(OAc)_3$ under "ball-milling" (Scheme 1, *10*) [19].

The disadvantages of the above reactions usually include the need for large excess of oxidant, elevated temperatures and duration of reaction. Of course, the most attractive methods are atom-economical direct C-H/P-H coupling reactions of azoles with dialkyl-H-phosphonates. The development of such environmentally safe and simple catalytic techniques is especially relevant. In this regard, the electrochemical methods that meet criteria of "green chemistry", characterized by mild conditions (low temperature, normal pressure), regeneration of catalyst on electrode, as well as environmental safety and low-waste processes are very promising. Electrochemically induced catalytic C–H bond functionalization has become highly attractive strategic approach to green, clean and efficient transformations in organic synthesis. Thus, the new electrochemical reactions of the C(sp2)-H phosphorylation[20-27] have been proposed in recent years. The progress of electroorganic synthesis in this field is described in numerous reviews[22,23,28-32] and papers, concerning some recent advances in C-H functionalization, such as fluoroalkylation[33-38], amination[39-42], aziridination[43], oxygenation[44-46], arylation[47], alkylation[48], amino-oxygenation[49], etc. The first electrochemical oxidative phosphorylation of benzoxazole in the presence of a 3d metal catalyst was reported in 2016. [50]

The purpose of this work is to create a new method for phosphorylation of benzo-1,3-azoles derivatives with dialkylphosphites through electrocatalytic activation of C-H bonds in aromatic substrates in the presence of silver salts-catalysts and in the absence of specially added oxidizers at room temperature, as well as to clarify mechanism of the reaction.

Electrosynthesis

Joint electrolysis of mixture of benzo(oxa)zole and dialkyl-*H*-phosphonates (1:1) in CH_3CN under oxidizing conditions in the presence of catalytic amounts of silver salts at room temperature leads to 2-phosphorylated benzo(oxa)zoles (dialkyl-benzothia(oxa)zole-2-yl-phosphonates (Scheme 2):

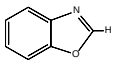
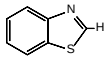
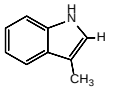
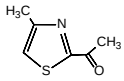
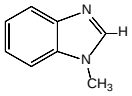
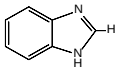


Scheme 2 Electrochemically induced coupling reactions of heteroarenes (benzoxazole or benzothiazole) with phosphites under silver catalysis

Silver salts (nitrate, acetate and carbonate) and silver (I) oxide were tested as catalysts. Electrolysis process was controlled by ^{31}P-NMR. The results of electrolysis are presented in Table 1.

The usage of $AgNO_3$ as a catalyst resulted in low yields of phosphorylated benzothia(oxa)azoles. Increase of the electricity amount has no effect on the final product yield, the ^{31}P signal of source dialkylphosphite has always been present in the reaction mixture. Diisopropyl phosphite turned out to be less reactive under these conditions than diethyl phosphite. Catalytic activity of silver acetate AgOAc was higher than $AgNO_3$. It can be assumed that OAc^- assists in P-H metallation, as it was described for OAc^- assisted C-H activation[51-53] previously. We found that the rate of key intermediate $AgP(O)(OEt)_2$ formation from AgOAc is higher than that from $AgNO_3$ one in other similar conditions.. Thus, when AgOAc is being mixed with $H(O)P(OEt)_2$ in acetonitrile, a gel-like mass immediately forms after being stirred for an hour, and the

Table 1. Results of azoles phosphorylation. Anode potential is 1.2-1.4 V ref.Ag/AgCl

N	Catalyst	Base	Product yield,%
			
1	$AgNO_3$	-	41
2	*$AgNO_3$	-	30
3	AgOAc	processing of t-BuOK after electrolysis	61
4	AgOAc	t-BuOK	62
5	*AgOAc	processing of t-BuOK after electrolysis	60
6	AgOAc	K_2CO_3	63
7	AgOAc	Na_3PO_4	75
8	*AgOAc	Na_3PO_4	74
9	AgOAc	NaH_2PO_3	63
10	Ag_2CO_3	-	8
11	Ag_2O	-	35
			
12	$AgNO_3$	-	42
13	*$AgNO_3$	-	45
14	AgOAc	Na_3PO_4	51
15	AgOAc	NaH_2PO_3	54
			
16	$AgNO_3$	Na_3PO_4	41
17	AgOAc	Na_3PO_4	50
18	Ag_2O	Na_3PO_4	31
			
20	AgOAc	Na_3PO_4	74
21	*AgOAc	Na_3PO_4	71
			
22	AgOAc	*t*-BuOK	traces
			
23	AgOAc	*t*-BuOK	traces

* Results when using diisopropyl-H-phosphonate

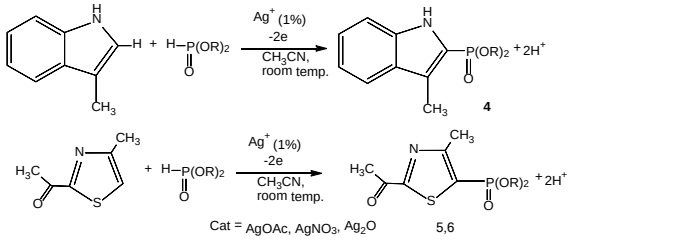
conversion is 100%. The yield of $Ag(O)P(OEt)_2$ is quantitative (white powder), a single singlet signal with δ 107 ppm in the ^{31}P NMR spectrum in pyridine is fixed, the signal of the initial $H(O)P(OEt)_2$ is absent. But the interaction of $AgNO_3$ and $H(O)P(OEt)_2$ in acetonitrile is slower at room temperature.

Prior to electrolysis, no products in the reaction mixture including arene, diethyl phosphite and silver salt after stirring for 24 hours are observed. The single signal for $(EtO)_2P(O)H$ preserves constant intensity. During the electrolysis, the transformation of the initial substrates into the products and possible intermediates was monitored. Only after passing more than 2F of electricity through the reaction mixture the signal of source $(EtO)_2P(O)H$ disappears, the ^{31}P NMR spectrum contains signals of the products (**1-3**) – phosphorylated arene in nitrogen-protonated and non-protonated forms. In order to produce a clean reaction product the mixture was processed with a base. *t*-BuOK, Na_3PO_4 and Et_3N were tested as bases. Only after processing with *t*-BuOK the protonated product form fully converts into target arene phosphonate. Holding of electrolysis in the presence of base (K_2CO_3, Na_3PO_4 and NaH_2PO_3 were used) allowed to obtain the final product at the end of the electrolysis, leaving out the protonated form. Benzothiazole is phosphorylated under these conditions forming 2-substituted derivative **2**.

Optimization of synthesis conditions (**1-3**) through variation of the nature of silver catalyst and base showed that the best yields are achieved with silver acetate as a catalyst and Na_3PO_4 as a base (75%) (Table 1).

3-Methylindole, 4-methyl-2-acetylthiazole and benzimidazoles were also tested as the substrates in electrochemical phosphorylation of heterocyclic compounds. It turned out that 2-phosphonated methylindole or 5-phosphonated 4-methyl-2-acetylthiazole are formed under electrocatalytical conditions with yields of 31-50% for indole and 71-74% for thiazole (Scheme 3, Table 1). As in case of benzo-1,3-azoles, the best catalyst is silver acetate (Table 1). The benzimidazoles do not react with $(RO)_2P(O)H$.

Thus, a convenient preparative electrochemical protocol for synthesis of phosphonated azoles using silver catalysts with low loading (1%) has been developed. Electrolysis takes place in one stage, in the absence of specifically added oxidants at room temperature with good yields.



Scheme 3 Electrochemically induced coupling reactions of 3-methylindole and 4-methyl-2-acetylthiazole with phosphites under silver catalysis.

Cyclic voltammetry and ESR spectroelectrochemistry for mechanistic considerations

In order to investigate details of the process, we have studied electrochemical properties of the participants of the aromatic C-H phosphorylation (Table 2).

It should be noted that there are virtually no literature data about oxidation potentials of $Ag^0/Ag^+/Ag^{2+}$ in organic media,

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Table.2 Electrochemical data for participants of Ag-catalyzed reaction. CH_3CN, Pt w.e., 0.1 M Bu_4NBF_4, 100 mV/s, Ag/AgCl reference electrode.

N	Compound	E_p^{ox}, V
1	AgOAc	1.89
2	$AgNO_3$	2.10
3	Ag_2O	1.90
4	Benzoxazole	2.26
5	Benzothiazole	2.13
6	3-Methylindole	2.10
7	4-Methyl-2-acetylthiazol	1.99
8	Diethyl-*H*-phosphonate	-
9	Diisopropyl-*H*-phosphonate	-
10	$AgP(O)(OEt)_2$	1.10

authors often mention silver(II) high standard potential in acidic water (E^0 = 1.98 V vs. normal hydrogen electrode, NHE) [54,55]. Rare works mention potential of Ag^+/Ag^0 (it strongly depends on the nature of the solvent, 0.61 V in acetone and 1.08 V in CH_2Cl_2 (ref. Ag/AgCl) [56], but due to the lack of data on silver salt anions and exact experimental conditions it is difficult to discuss these data. $AgNO_3$ in a solution of HNO_3 is oxidized according to [57] at 1.5 V (ref. SSE) or 2.15 V (ref. Ag/AgCl) on boron-doped diamond electrodes, while water is oxidized at almost the same potentials under these conditions, as shown by the authors. At that nitrate ion is being decomposed and brown NO gas is being formed. However, under conditions of our electrolysis in the presence of arenes there is no formation of NO.

So, the redox properties of all silver catalysts under electrosynthesis conditions have been studied. The voltammograms of Ag^+ (AgOAc or $AgNO_3$) in oxidative region always have adsorption peak of oxidation of impurities Ag(0) at relatively low potentials (~0.3 V), whose height is poorly reproduced and depends on the luminance of samples and electrolyte mixing time until registration of the curves (Figure 1, top). The oxidation peak of Ag^+ in Ag^{2+} is in the region of high positive potentials for AgOAc, $AgNO_3$ and Ag_2O (1.89-2.10 V) (Table 2), voltammograms for all silver catalysts are similar (Fig. 1, top).

Aromatic substrates (benzoxazole, benzothiazole and others) are oxidized at high anode potentials (1.99÷2.26 V) (Table 1). Oxidation of silver acetate, the best catalyst, was also investigated by ESR spectroscopy. Solution of silver acetate AgOAc in acetonitrile is ESR silent, but its oxidation at potential of about +2.8 V in ESR-electrochemistry cell at room temperature the intense ESR spectrum appears. It represents a single homogeneous widened band with the following parameters: g = 2.155, ΔH_{p-p} = 72 G. This signal appears as a result of oxidation of solvated ion Ag (I) to the Ag (II). After reaching the maximum intensity the temperature dependence of this spectrum was registered (Fig. 2, left).

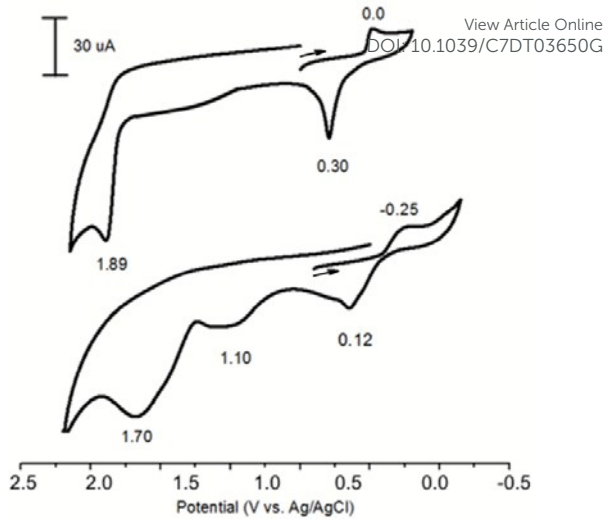


Figure 1 CVs of AgOAc in CH_3CN (top), and $AgP(O)(OEt)_2$ in Py+CH_3CN (1:10) (bottom). Conditions: 0.1 M Bu_4NBF_4. Working electrode – GC, reference electrode – Ag/AgCl, scan rate 100 mV/s.

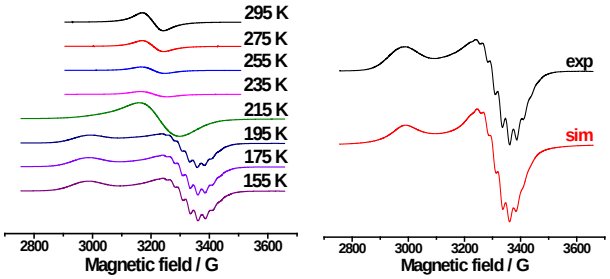


Figure 2 ESR spectrum of solution AgOAc in acetonitrile at +2.8 V. Temperature dependence (left); spectrum of frozen solution (155 K) and its simulation (right).

Spectrum of frozen solution matches the case of stretched axial symmetry of environment of Ag (II) ion (Fig. 2, right). Splitting on the environment nuclei manifests itself on the perpendicular component of the ESR spectrum. As can be seen from the simulation that these are splitting on 4 nitrogen nuclei of, apparently, acetonitrile molecules surrounding the ion. The spin-Hamiltonian parameters – $g_\parallel$ = 2.315, $g_\perp$ = 2.075 4:a_N = 25 G, close to the literature data for the Ag^{2+} obtained under other conditions and other surroundings of metal ion [58-60]. However, because the potentials of preparative electrochemical synthesis do not reach the oxidation potentials of Ag^+/Ag^{2+}, Ag^{2+} is not involved in the catalytic cycle under investigation.

Despite the many works on silver catalysis, the mechanisms of these reactions are investigated very superficially and are usually postulated. It can be assumed that Ag^+ reacts at the first stage with $(RO)_2P(O)H$, as suggested in the silver-catalyzed reaction of phosphonation [13]. However, nobody has researched properties of $(RO)_2P(O)Ag$. H.Wang suggested that the reaction of Ag^+ with $(RO)_2P(O)H$ immediately leads to the formation of radical $(RO)_2P(O)^\bullet$ [13], and the radical nature of the reaction was based on indirect data – blocking of reaction in the presence of radical inhibitor butylated hydroxytoluene [13]. Huang [14], Cheng[61] and A.Wang [62] assumed that Ag^+ is oxidized

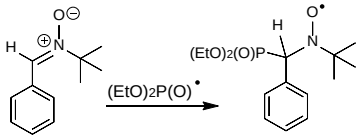
to Ag^{2+} under the action of oxidant $K_2S_2O_8$, which further oxidizes $(EtO)_2P(O)H$ to radical-cation interacting with arene. If 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), a radical scavenger, was added to the reaction system, the dehydrogenative cross-coupling reaction of arene with diethyl phosphite was quenched, so, this result suggests that the reaction may undergo a radical mechanism [14]. This plausible mechanism of the dehydrogenative cross-coupling reaction is similar to that proposed by Effenberger et al.[63]. Zou[18] and others[14,15] also postulated a radical mechanism of oxidative phosphorylation in the presence of Ag-catalyst only basing on absence of products in the presence of two equivalents of TEMPO. However, no intermediates were obtained and their reactivity was not proven. However, the failure of the reaction in the presence of TEMPO can be explained by the fact that the latter is easily oxidized by the applied oxidant $K_2S_2O_8$, for example. Moreover, if TEMPO was taken in two-fold excess over the oxidant, the entire oxidant was consumed by the side reaction of TEMPO oxidation, which is easily oxidized to about 0 V ref Fc^+/Fc or +0.42 V ref.Ag/AgCl [64, 65], but not by oxidation of more difficultly oxidized H-phosphonate, arenes or Ag^+.

In order to explore the mechanism of phosphorylation of azoles, we synthesized $AgP(O)(OEt)_2$ and investigated its reactivity. Voltammogram of $AgP(O)(OEt)_2$ has three distinct anodic peaks at 0.12, 1.10 and 1.70 V (Figure 1, bottom), the first and the third of which can be attributed to oxidation of Ag^0/Ag^{+1} and Ag^{+1}/Ag^{+2} (they are observed also for AgOAc at similar potentials), and the second, 1.10V, to oxidation of anion $(EtO)_2P(O)^-$ (similar to oxidation of $(EtO)_2P(O)Na$ [66]).

In order to establish the character of the catalytic cycle and the character of the intermediate P(O)-Ag bond scission (ionic or radical type), we have carried out a number of ESR experiments under anaerobic conditions. Joint oxidation of $(EtO)_2P(O)Ag$ and spin trap PBN (PBN = N-tert-butyl-α-phenylnitrone) mixture at +0.9 V in ESR-spectroelectrochemical cell is characterized by appearance and increase in intensity of ESR signal of the PBN bound radical species of $(EtO)_2P(O)$ adduct (Figure 3 and Scheme 4).

The spin-adduct spectrum was simulated and the following spin-Hamiltonian parameters were obtained: g = 2.0060, a_N = 14.71 G, a_P = 24.17 G, a_H = 3.36 G. These parameters almost completely coincide with the parameters of the adduct $(EtO)_2P(O)$-PBN, known from the literature : a_N = 14.65 G, a_P = 24.33 G, a_H = 3.06 G [67].

We can thus conclude that $(EtO)_2P(O)^\bullet$ reacts readily with the spin trap and the spin adduct is quite stable. At potential of +1.5 V, a new non-basic signal appears and grows, apparently, due to the oxidation of the spin-trap itself.



Scheme 4 Trapping of phosphorus-centered radical by PBN.

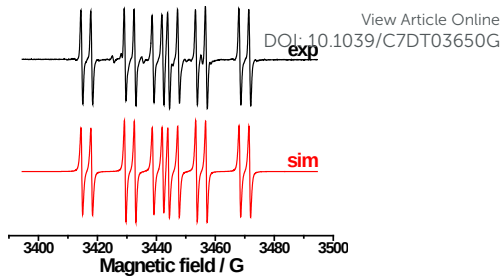
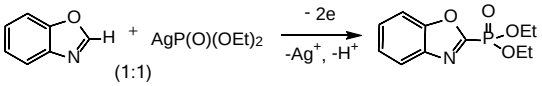


Figure 3 ESR spectra obtained during anodic joint electrolysis of $(EtO)_2P(O)Ag$ and spin trap PBN solution at +0.9 V in CH_3CN, recorded at 293 K with simulations.

Oxidation of solution AgOAc and benzoxazole in acetonitrile in ESR-cell leads to a result similar to the oxidation of solution of pure AgOAc in acetonitrile – the emergence of a single band in the spectrum at +2.8 V with the same magnetic resonance parameters. Ag^{2+} participation in electrochemically induced coupling reactions of heteroarenes with phosphites under silver catalysis can be excluded.

We performed a counter electrosynthesis involving $Ag(O)P(OEt)_2$ as a phosphorylation reagent and benzoxazole in a ratio of 1: 1.

Oxidation of $Ag(O)P(OEt)_2$ during the joint electrolysis leads to the formation of phosphorylated benzoxazole and its protonated form (Scheme 5).

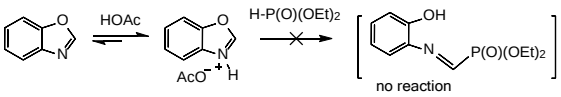


Scheme 5 Joint electrolysis of $(EtO)_2P(O)Ag$ and benzoxazole

The latter, after treatment with base, passes to the final product.

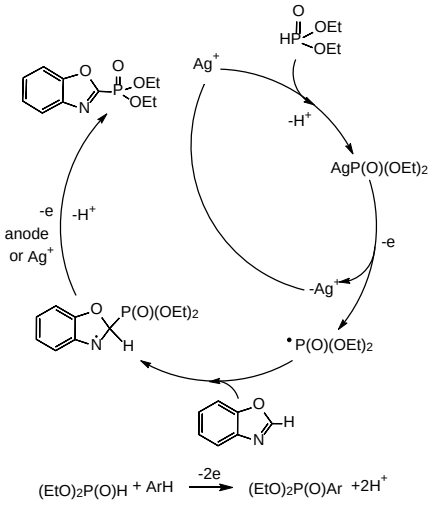
The formation of Ag^{2+}under the investigated conditions is impossible, since the electrolysis potential is comparatively low. ESR study of reaction mixtures confirms the absence of Ag^{2+} at all stages of synthesis.

Since in some works on the amination of benzoxazole in the presence of iodide ions (mediators) under oxidizing conditions, including electrochemical conditions, the assumptions about the formation of structures with an open cycle were made previously [68-69], we analyzed the ^{31}P and ^1H NMR spectra of the reaction mixtures before and after passing 1F, 2F and 2.5F electricity (see SI). It was found that no ring opening of the oxazole was observed, at all stages only initial and final target products were present. Apparently, this is due to the fact that $(EtO)_2P(O)$-H phosphite does not react with protonated benzoxazole in contrast to dialkylamine (Scheme 6 and SI).



Scheme 6 No ring opening reaction in the conditions under study

The analysis of literature data and conducted research allowed us to propose the following scheme of electrocatalytic phosphorylation of azoles (Scheme 7), using benzoxazole reaction as an example. Initially, silver(I) cation react with dialkyl-H-phosphonate, $(EtO)_2P(O)Ag$ is oxidized and yields to



Scheme 7 Proposed mechanism of the dehydrogenative cross-coupling reaction (benzoxazole case).

$(EtO)_2P(O)^{\bullet}$ radical. Its addition to heteroarene leads to the radical intermediate, which may lose a hydrogen cation, an electron (at the anode or under Ag^+ action), successively giving desired benzoxazole phosphonate.

Conclusions

In conclusion, we have developed a silver-catalyzed dehydrogenative cross-coupling reaction of azole derivatives with dialkyl phosphites under mild conditions without traditional external oxidant excess, affording the corresponding phosphonated products with up to 75% yield and have investigated the catalytic mechanism. The key stage of this electrochemical process is silver dialkyl phosphonate oxidation yielding to phosphorus-centered radical.

Conflicts of interest

There are no conflicts to declare.

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