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Electrochemical phosphorylation of arenes catalyzed by cobalt under oxidative and reductive conditions

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ABSTRACT

Catalyst capable to operate in cathode and anode spaces simultaneously was found. Electrochemical regeneration of active form of catalyst Co^{2+} bpy (1%) under oxidative as well as reductive conditions allows the C–H/P–H coupling of dialkyl-H-phosphonate and various aromatic or heteroaromatic compounds.

GRAPHICAL ABSTRACT



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Phosphorylation; cobalt; electrocatalysis; CH-substitution

1. Introduction

Organophosphorus compounds are important class of substances which are widely used in various areas of human activity. Typical methods for the preparation of arylphosphonates are multi-stage and long-term processes requiring high temperature and the use of additional expensive reagents.^[1-5]

Organic electrosynthesis is considered as a methodology for the environmentally friendly preparation of organic compounds, since dangerous and toxic redox agents, which may be necessary and commonly used in classical reactions, are replaced by a reaction at the electrode under an influence of electric current.^[6–8] Traditional electrochemical methods in organic synthesis have been considered in many monographs and reviews.^[5, 9] In recent years new strategies and applications of the implementation of organic electrooxidative^[10-13] and electroreduction^[14-18] reactions have been developed. In comparison with direct electrolysis, indirect processes in which redox mediators (catalysts) are used have more opportunities and advantages both in terms for synthesis and research of the mechanisms of processes.^[19] For example, indirect organic electrosynthesis often demonstrates a higher selectivity of the reaction, since electrolysis is carried out at lower potentials than the oxidationreduction potentials of the initial reagents.

2. Results and discussion

C-H bond activation reactions catalyzed by transition metals are considered as a powerful tool for the functionalization and production of organic molecules possessing huge

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Scheme 1. Phosphorylation of arenes catalyzed by Co. Conditions: rt, Q = 2F per mol of diethyl-H-phosphonate, $[Co^{2+}bpy]$ (1%), CH₃CN.

importance for the pharmaceutical industry and material science.^[20, 21] Methods of direct functionalization of C–H bonds can be considered as atom-economical approaches. Over the past decades, the strategy for activating of C–H bonds has been successfully implemented mainly using 4d- and 5d-transition metals (Pd, Pt, Ag, etc.). The use of more cost-effective alternative systems based on more common metals such as cobalt to activate C–H bonds seemed impossible until recently, despite the predominance of such metals in the active center of different enzymes, and as a rule harsh reaction conditions were often required to achieve their reactivity.

We assumed that the phosphorylation of aromatic compounds can be realized in one stage and at room temperature taking advantage of the electrochemical metal complex catalysis.^[22-28]

We carried out a series of experiments to obtain phosphorylated aromatic compounds (benzene and its derivatives, coumarins) using $CoCl_2bpy$ as a catalyst and commercially available inexpensive and stable diethyl-*H*-phosphonate as phosphorylating reagent. The distinctive feature of the process is an equimolar ratio of arene:phosphorylation reagent (1:1) and the room temperature. It was found that Co is capable to catalyze the phosphorylation reaction of arenes under both the electrooxidation and electroreduction conditions (Scheme 1).

The maximum yields of the products are achievable after keeping the reaction mixture prior to electrolysis for some time necessary for the formation of cobalt phosphonate.^[6] 100% conversion of diethyl-*H*-phosphonate was achieved during the synthesis; it did not remain in the reaction mixture after passing 2 F of electricity. The phosphorylation product was not formed in the absence of the catalyst.

3. Conclusions

Thus, a cobalt catalyst which is able to work in cathode and anode spaces simultaneously was found. It has been established that the electrochemical regeneration of active form of catalyst (1%) based on unsaturated complex Co^{2+} bpy under oxidative as well as reductive conditions allows the C–H/P–H coupling of dialkyl-*H*-phosphonate and various aromatic or heteroaromatic compounds with yields up to 80% in reductive conditions and up to 68% in oxidative conditions. The use of a cobalt complex in electroreductive conditions leads to a better yield of arylphosphonates as the reaction proceeds without overpotential (–0.3 V vs Fc⁺/Fc). Electrochemical reactions are easily scaled, which also applies to their advantages and can be realized in the future.

4. Experimental

4.1. NMR experiments

NMR spectras were recorded with multi-nuclear spectrometer Bruker AVANCE-400 (400.1 MHz (¹H), 100.6 MHz (¹³C) and 162.0 MHz (³¹P)). Chemical shifts are given in parts per million relative to SiMe₄ (1H, internal solvent) and 85% H₃PO₄ (³¹P, external). The spectroscopic data for 1-7 matched that reported in the literature.^[6]

4.1.1. Diethyl phenylphosphonate (1)

Colorless oil. ³¹P NMR (162 MHz, CDCl₃) 18.3. ¹H NMR (400 MHz, CDCl₃) 7.82–7.73 (m, 2H), 7.55–7.47 (m, 1H), 7.43–7.38 (m, 2H), 4.16–3.87 (m, 4H), 1.31 (t, $J_{H-H} = 7.0$ Hz, 6H).

4.1.2. Diethyl 4-cyanophenylphosphonate (2)

White solid; mp =31-33 °C. ³¹P NMR (162 MHz, CDCl₃) 15.5. ¹H NMR (400 MHz, CDCl₃) 7.92 (dd, J_{P-H} =13.4 Hz, 2H), 7.78-7.72 (m, 2H), 4.23-4.07 (m, 4H), 1.34 (t, J_{H-H} =7.3 Hz, 6H).

4.1.3. Diethyl 3-(dimethylamino)phenylphosphonate (3)

Yellow solid; mp =55–58 °C. ³¹P NMR (162 MHz, CDCl₃) 19.2. ¹H NMR (400 MHz, CDCl₃) 7.59–7.50 (m, 2H), 7.35–7.29 (m, 3H), 4.21–4.01 (m, 4H), 2.98 (s, 6H), 1.27 (t, $J_{H-H} = 7.1$ Hz, 6H).

4.1.4. Diethyl 4-nitrophenylphosphonate (4)

Colorless viscous oil. ³¹P NMR (162 MHz, CDCl₃) 13.2. 1H NMR (400 MHz, CDCl₃) 8.33 (dd, J = 6.9 Hz, 2H), 7.97 (dd, J = 12.7 Hz, 2H), 4.21–4.11 (m, 4H), 1.71–1.66 (m, 4H), 1.37 (t, J = 7.2 Hz, 6H).

4.1.5. Diethyl 2-oxo-2H-chromen-3-ylphosphonate (5)

White solid; mp =65–66 °C. ³¹P NMR (162 MHz, CDCl₃) 10.37. ¹H NMR (400 MHz, CDCl₃): 8.53 (d, ³J_{PH} = 17.2 Hz, 1H, C₄-H), 7.66–7.60 (m, 2H, ArH), 7.37–7.33 (m, 2H,

Table 1. Electrochemical phosphorylation of arenes by diethyl-*H*-phosphonates (ratio 1:1). Conditions: room temperature, Q = 2F per mol of diethyl-*H*-phosphonate, galvanostatic mode, (1%) [Co²⁺bpy], isolated yields.

V:-L-L (0/)*

		field (%)	
Number	Product	Reduction condition	Oxidation condition
1	P(O)(OEt)2	56	31
2	NC-P(O)(OEt) ₂	80	48
3	P(O)(OEt) ₂	78	44
4	Me ₂ N O ₂ N-P(O)(OEt) ₂	76	50
5	P(O)(OEt) ₂	59	52
6	P(O)(OEt) ₂	70	68
7		73	65

*The yield of the main product.

ArH), 4.34–4.22 (m, 4H, 2CH₂), 1.37 (t, J = 7.1 Hz, 6H, 2CH₃).

4.1.6. Diethyl 7-methyl-2-oxo-2H-chromen-3-ylphosphonate (6)

Yellow solid; mp =62-64 °C. ³¹P NMR(162 MHz, CDCl₃) 10.9. ¹H NMR (400 MHz, CDCl₃): 8.40 (s, 1H, C₄-H), 7.39 (d, J=7.5 Hz, 1H, ArH), 7.06 (d, J=7.4 Hz, 2H, ArH), 4.19 (m, 4H, 2CH₂), 2.40 (s, 3H, 7-CH₃), 1.30 (s, 6H, 2CH₃).

4.1.7. Diethyl 6-methyl-2-oxo-2H-chromen-3-ylphosphonate (7)

Yellow solid; mp =74–76 °C. ³¹P NMR (162 MHz, CDCl₃) 11.4. ¹H NMR (400 MHz, CDCl₃): 8.40 (d, J = 17.1 Hz, 1H, 4-H), 7.38 (d, J = 8.5 Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.17 (d, J = 8.5 Hz, 1H, ArH), 4.23–4.17 (m, 4H, 2CH₂), 2.35 (s, 3H, 6-CH₃), 1.31 (t, J = 7.4 Hz, 6H, 2CH₃).

4.2. Preparative electrochemical syntheses

All reactions were carried out under dry argon atmosphere. The preparative electrolysis was performed using a direct current source B5-49 in a three-electrode cell of 40 mL with a separation of the anode and cathode compartments. The potential value of the working electrode was recorded using a direct current voltmeter V7-27 in relation to the Ag/AgCl

(0.01 M, NaCl) reference electrode that had two sections separated with Vycor, the second one containing a saturated solution of the background salt in CH₃CN. The surface area of the working platinum (Pt) U-shaped electrode amounted to 48.00 cm^2 . A ceramic plate with a pore size of $10 \,\mu\text{m}$ was used as a membrane. During the preparative synthesis, the electrolyte was continuously stirred using a magnetic stirrer with a continuous inflow of an inert gas that was run through a purification system to remove oxygen and other impurity gases. A platinum grid served as a cathode, and the catholyte was a saturated solution of Et₄NBF₄ supporting electrolyte in the corresponding solvent.

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