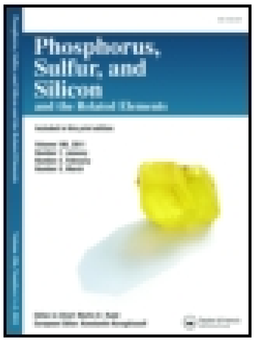

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Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: https://www.tandfonline.com/loi/gpss20

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To cite this article: M. N. Khrizanforov, S. O. Strekalova, V. V. Grinenko, A. I. Kononov, E. L. Dolengovski & Y. H. Budnikova (2019): C-P bond formation via selective electrocatalytic C-H phosphorylation, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2018.1555538

To link to this article: https://doi.org/10.1080/10426507.2018.1555538

PHOSPHORUS, SULFUR, AND SILICON AND THE RELATED ELEMENTS
https://doi.org/10.1080/10426507.2018.1555538

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SHORT COMMUNICATION

C-P bond formation via selective electrocatalytic C-H phosphorylation

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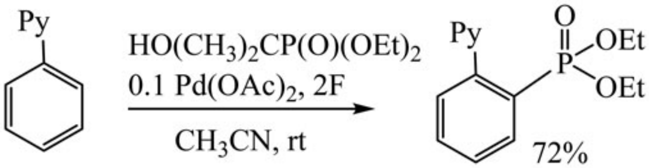
ABSTRACT
A new approach to phosphorylation of 2-phenylpyridine was proposed. It is possible to obtain the product of diethyl (2-(pyridin-2-yl)phenyl)phosphonate product in good yield (72%) by this method.

ARTICLE HISTORY
Received 28 September 2018
Accepted 29 November 2018

KEYWORDS
Phosphorylation; electrosynthesis; electrocatalysis; CH-substitution

GRAPHICAL ABSTRACT



Introduction

C-P bond containing organophosphorus compounds are widely used in medical chemistry, biochemistry, materials, phosphine-containing ligands for catalysis, and organic synthesis.[1–5] There are only few electrochemical approach for the C-H substitution with phosphorus-containing nucleophiles.[1] Successful examples of electrochemical reactions have been mainly known so far only for functionalization of nitroaromatic substrates.[5]

Results and discussion

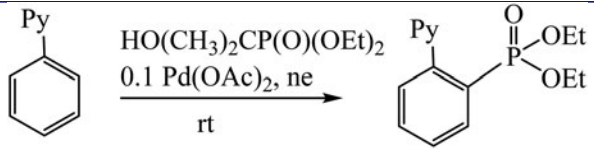
We used our accumulated experience in electrochemical C–H-substitution[6–9] to develop a ligand-directed C-H-phosphorylation method by electrochemical oxidation under mild conditions involving $Pd(OAc)_2$ as the catalyst and $(CH_3)_2C(OH)P(O)(OC_2H_5)_2$ as the accessible phosphorus precursor. The use of the electrochemical method allowed the conduction of the reaction at room temperature without the addition of the oxidant with a controlled potential it was possible to analyze the reaction steps particularly.

The electrochemical oxidation of 2-phenylpyridine and $(CH_3)_2C(OH)P(O)(OC_2H_5)_2$ (ratio 1:1.1, dropwise addition of phosphorus agent during the whole electrolysis) in the presence of 10 mol% of palladium acetate gives the ortho-phosphorylation product in a yield of 72% in optimal process conditions (Table 1).

Conclusions

The interaction of 2-phenylpyridine with $(CH_3)_2C(OH)P(O)(OC_2H_5)_2$ in the presence of $Pd(OAc)_2$ at 1.5 V (vs. Ag/AgCl) leads to the formation of diethyl-(2-pyridin-2-yl)phenyl)phosphonate.

Table 1. Electrochemical phosphorylation of 2-phenylpyridine by $(CH_3)_2C(OH)P(O)(OC_2H_5)_2$ (1:1.1 ratio).



Solvent:	E of anode, V vs. Ag/AgCl	Amount of electricity	Product yield (%)
DMF	1.0	2F	0
CH_3CN	1.0	1F	0
CH_3CN	1.0	2F	20
DMF	1.5	2F	0
CH_3CN	1.5	1F	8
CH_3CN	1.5	2F	72

Conditions: Room temperature, $Pd(OAc)_2$ catalyst (10% based on 2-Ph-Py). Isolated yields of diethyl-(2-pyridin-2-yl)phenyl)phosphonate.

Experimental

The solution for electrolysis was prepared by mixing of 2-phenylpyridine (1.4 mmol, 0.22g,), $(CH_3)_2C(OH)P(O)(OC_2H_5)_2$ (1.6 mmol, 0.31g) and $Pd(OAc)_2$ (0.14 mmol, 0.03g) in CH_3CN (30 mL). Electrolysis was carried out in undivided electro-chemical cell at ambient temperature under argon atmosphere at the potential of working electrode corresponding to oxidation potential of the $Pd(OAc)_2$ (1.5 V vs. Ag/AgCl). The amount of electricity passed through the electrolyte were 2 F per one mole of $(CH_3)_2C(OH)P(O)(OC_2H_5)_2$ ($75\,mA \times h^{-1}$). After completing the electrolysis, the solution

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was washed with distilled water (100 ml) and extracted with $CHCl_3$ (3 × 100 mL). The organic layer was dried over magnesium sulfate and filtered. The residual solution was concentrated. The reaction mixture was filtered through a plug of silica (eluated with 5% EtOAc: 95% hexane). The filtrate was concentrated, and the diethyl-(2-pyridin-2-yl)phenyl)phosphonate was isolated (0.29 g, 72%, colorless oil). ^{1}H NMR (400 MHz, C_6D_6) δ: 8.83 (d,J = 5.93 Hz, 1H); 8.13 (dt, J = 7.99; 1.25 Hz, 1H); 7.88 (d,J = 7.29 Hz, 2H); 7.66 (d, J = 7.54 Hz, 1H); 7.42 (t, J = 7.89 Hz,2H); 7.34 (m, 1H); 4.05 (dq, J = 7.09; 7.95 Hz, 4H); 1.22 (t,J = 7.01 Hz, 6H). ^{31}pNMR (162 MHz, C_6D_6): δ 16.6. ESI-HRMS (+*ve*): $[C_{15}H_{18}NO_3P]^+$: found 293.66. Anal Calcd: C, 61.85; H, 6.23; N, 4.81; O, 16.48; P, 10.63 for $C_{15}H_{18}NO_3P$. Found: C, 61.57; H, 6.17; P, 10.55.

Acknowledgments

The authors gratefully acknowledge the Russian Science Foundation No 14-23-00016 for financial support and CSF-SAC FRC KSC RAS for the registration of spectra (NMR, ESI, Raman, etc.).

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