



Novel approach to metal-induced oxidative phosphorylation of aromatic compounds



M.N. Khrizanforov*, S.O. Strekalova, K.V. Kholin, V.V. Khrizanforova, M.K. Kadirov, T.V. Gryaznova, Y.H. Budnikova

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, 8 Arbuzov Str., Kazan 420088, Russian Federation

ARTICLE INFO

Article history:

Received 30 December 2015
Received in revised form 23 May 2016
Accepted 1 June 2016
Available online 22 June 2016

Keywords:

Phosphorylation
Oxidation
Electrosynthesis
catalyst
Metal
Complex
C–H functionalization

ABSTRACT

We propose a new approach to the phosphorylation of benzenes bearing both electron withdrawing and electron donating substituents on the ring and some coumarins (coumarin, 6-methylcoumarin, 7-methylcoumarin) under the action of dialkyl *H*-phosphonate (RO)₂P(O)H (R = Et, *n*-Bu, *i*-Pr), based on catalytic oxidation of arene and *H*-phosphonate (1:1) mixture in electrochemically mild conditions (room temperature, normal pressure) using the bimetallic catalyst system Mn^{II}bpy/Ni^{II}bpy (1%). This method produces a dialkyl aryl phosphate with high yield (up to 70%) and 100% conversion of *H*-phosphonate.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Dialkyl aryl phosphonates are important as intermediates in the synthesis of pesticides and bioactive compounds [1–4]. Several methods are recognized as being traditional for the synthesis of dialkyl aryl phosphonates. The most common of them involve the phosphorylation reaction of aryl halides [5–13]. It has been described some examples of the radical phosphorylation of aromatic compounds by dialkyl *H*-phosphonate, including naphthalene in the presence of *tert*-butyl peroxide [14], various arenes in the presence of oxidants (NH₄)₂[Ce(NO₃)₆] [15] or Na₂S₂O₈ and AgNO₃ [16], and Mn(II)/Co(II)/O₂ [17], but the most successful example is the Ishii phosphorylation of benzene by dialkyl *H*-phosphonate [17]. However, it has a number of disadvantages, including an elevated reaction temperature but not very high substrate conversion to monophosphorylation product, being specifically 6% (25 °C) to 69% (60 °C) for benzene. The possibility of obtaining aryl phosphonates with yields of up to 59% through the electrochemical oxidation of trialkyl phosphites in the presence of benzene and its derivatives was first described

by Masui [18] in 1979 and was later repeated by Kargin [19] at a ratio (benzene: dialkyl *H*-phosphonate 5:1) in acetonitrile in the presence of background salt NaClO₄. Gallardo proposed the electrochemical phosphorylation of benzene nitro derivatives with phosphorus(III) compounds, including dialkyl *H*-phosphonate under oxidizing conditions [20]; however, his approach does not work for non-substituted benzene because the key step of the process is nucleophilic addition of *H*-phosphonate to the aromatic ring (S_NAr mechanism) followed by σ-H adduct oxidation. More recently in 2013 Cheng et al. [21] developed a phosphorylation method of aromatic substrates, benzene derivatives containing electron-deficient directing groups catalyzed by system Ag^I/K₂S₂O₈, but the method did not prove suitable for benzene. A novel efficient Pd-catalyzed cross-coupling of triarylbismuths with a variety of P(O)–H compounds has been developed by Yufen Zhao and coll. [22]. This method provides a general tool for the preparation of various valuable arylphosphonates, arylphosphinates, and arylphosphine oxides, but is unsuitable for direct aromatic C–H phosphonation. Copper-catalyzed phosphorylation of terminal alkynes in the presence of diphenylphosphine oxide added dropwise to the reaction mixture is one of new examples of P-C cross-coupling reactions [23].

The preparation of aryl phosphonate through the direct phosphorylation of C–H bond of aromatic substrates remains one of the

* Corresponding author.

E-mail address: khrizanforov@gmail.com (M.N. Khrizanforov).

most important approaches because it corresponds to the principles of green chemistry, namely atom economy, single-step, low in waste, etc. The desired catalytic conditions in this context are particularly attractive, given the fact that the catalytic reactions of aromatic compounds phosphorylation are limited. Perhaps benzene in this row is one of the most difficult substrates, given that its structure has no favorable C–H substitution factors, i.e., functional groups, activating bonds or directing functionalization. Typically, if it is possible to select conditions for the phosphorylation of benzene, its derivatives give even higher yields [17–19].

3-Phosphonated coumarins have been shown to exhibit their cytotoxicity on some human leukemia cell lines as well as high alkylating activity [24–26] as was heretofore usually obtained through Arbuzov [27–30] or Knoevenagel [31–33] reactions. Generally these methods give byproducts, are often based on the multi-stage consecutive reactions and do not correspond to the principles of atom economy, and hence have a low efficiency. As far as is known, until recently only a few reports from the Zhang [34], Wu [35] and Qu [36] research groups described the phosphorylation of coumarins through radical reaction, which required excessive amounts of $\text{Mn}(\text{OAc})_3$ (3 eqv.) and an aliphatic acid as a solvent [34] or salts of expensive metals such as silver [36] and palladium [35].

None of the known methods described above allows one to obtain an arene phosphorylation product with high yield and conversion at room temperature in a single stage. In that regard, electrochemical catalytic reactions of aromatic compounds direct phosphorylation [37–42] are particularly attractive. We assume that it would be possible to realize the phosphorylation of benzene and coumarin by taking advantage of electrochemical metal complex catalysis [43–47].

2. Materials and methods

2.1. Cyclic voltammetry

Cyclic voltammograms were recorded with a BASi Epsilon E2P (USA) potentiostat. The device comprises a measuring unit, PC Delloptplex 320 with the Epsilon-EC-USB-V200 software. As background electrolytes, tetrabutylammonium tetrafluoroborate (C_4H_8)₄NBF₄ was used. The working electrode was a stationary disc glassy-carbon electrode (the surface area of 6 mm²). Ag/AgCl (0.01 M KCl) was used as a reference electrode and a Pt wire as counter electrode. The reference electrode was connected with the cell solution by a modified Luggin capillary filled with the supporting electrolyte solution (0.1 M Bu₄NBF₄ in CH₃CN). Thus, the reference electrode assembly had two compartments, each terminated with an ultra-fine glass frit to separate the AgCl from the analyte.

A platinum wire was used as an auxiliary electrode. The scan rate was 100 mV s⁻¹. The measurements were performed in a temperature-controlled electrochemical cell (volume from 1 mL to 5 mL) in an inert gas atmosphere (N₂). Between measurements or prior to a registration of a voltammetry wave, the solution was actively stirred with a magnetic stirrer in the atmosphere of constant inflow of an inert gas that was run through a dehydrating system, and then through a nickel-based purification system B1-GAScleaner (manufactured by OOO Modern Laboratory Equipment, Novosibirsk) to remove trace quantities of oxygen.

2.2. ESR experiments

Oxygen was removed from liquid samples by three cycles of “freezing in liquid nitrogen – evacuation – thawing” and after the last cycle the electrolysis cell was filled with gaseous helium. The

Table 1

Electrochemical phosphorylation of arenes by dialkyl *H*-phosphonates (at the ratio of 1:1). Conditions: room temperature, Q = 2 F per mol dialkyl *H*-phosphonate, galvanostatic mode when using (1%) [MnCl₂bpy/Ni(BF₄)₂bpy], with isolated yields. bpy: 2,2'-bipyridine.

Product	Yield (%)	
	Electrosynthesis immediately after the mixing of substrates	Electrosynthesis 1 day after mixing of substrates
1	30	50
2	29	46
3	30	48
4	30	55
5	37	70
6	31	61
7	30	54
8	36	68
9	35	58
10	25	50
11	37	71
12	29	60
[13:14] = [1:2]	25	68
[15:16] = [1:1]	30	56
[17:18] = [1:4]	30	71

Table 2

Potentials and currents of the first oxidation peaks of catalysts used for the arenes phosphorylation reaction at room temperature.

Complex	E _p (V)
Ni(BF ₄) ₂ bpy	1.90 (35 μA)
MnCl ₂ bpy	1.14 (32 μA)

material of the auxiliary electrode was platinum, the reference electrode was Ag/AgCl equipped with a bridge of a carbon slate-pencil, and a gold wire 0.5 mm in diameter served as a working electrode. The measurements were carried out on an apparatus program complex including an analog electrochemical system with a potentiostat and a PWR-3 programmer, an ELEXSYS E500 ESR spectrometer of the X-range, and an E14-440 analog-to-digital and digital-to-analog modulus (L-Card), a fourth-generation computer, and a unique three-electrode helical cell [48,49]. ESR spectra were simulated using the WinSim 0.96 program (developed by NIEHS).

2.3. Preparative electrochemical syntheses

All reactions were carried out under dry argon atmosphere. The preparative electrolyses were performed using a direct current source B5-49 in a three-electrode cell with 40 mL volume 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 of them 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 cm². A ceramic plate with a pore size of 10 μm 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 and PyHBF₄ supporting electrolyte in the corresponding solvent.

2.4. NMR experiments

NMR spectra were recorded with multi-nuclear spectrometer Bruker AVANCE-400 (400.1 MHz (¹H), 100.6 MHz (¹³C)) and

Download English Version:

<https://daneshyari.com/en/article/4757305>

Download Persian Version:

<https://daneshyari.com/article/4757305>

[Daneshyari.com](https://daneshyari.com)