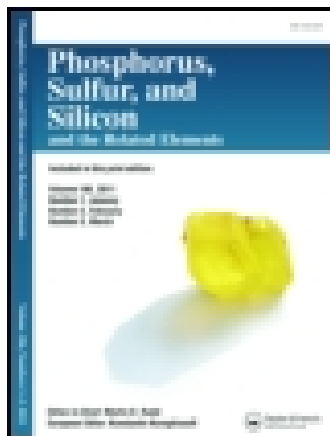


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Cu-Catalyzed Oxidative Phosphorylation of Alkanols with White Phosphorus and H₂O₂

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Cu-CATALYZED OXIDATIVE PHOSPHORYLATION OF ALKANOLS WITH WHITE PHOSPHORUS AND H₂O₂

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Oxidative phosphorylation of alkanols with white phosphorus in the presence of catalytic amounts of CuCl₂ has been effected. The reaction proceeds in the aqueous H₂O₂–HCl system exothermically to form dialkylphosphites and trialkylphosphates in a total yield of up to 35%. Conditions for selective synthesis of dialkylphosphites in moderate yield have been found.

Keywords: Alkanols; catalytic system CuCl₂–H₂O₂; dialkylphosphites; phosphorylation; trialkylphosphates; white phosphorus

INTRODUCTION

The traditional synthetic methods for the preparation of esters of three- and four-coordinate phosphorus acids are based on the reactions of phosphorus chlorides with oxygen-centered nucleophiles.¹ However, despite the simplicity and efficiency, this way has significant disadvantages. Preparation of the initial phosphorus chlorides involves handling of elemental chlorine, which is not only highly toxic, but also causes noticeable wearing of the equipment. On this background, the use of white phosphorus looks as an attractive alternative for the preparation of phosphorus acids, employing the so called “chlorine-free technologies.”

The formation of trialkylphosphites upon phosphorylation of alkanol solutions (MeOH or EtOH) of alkali metal alcoholates with white phosphorus was reported in a dissertation by G. Kahl.² The reaction

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is accompanied by the evolution of an equimolar amount of PH_3 . Introduction of carbon tetrachloride in this system inhibits the formation of PH_3 .^{3,4} The interaction of white phosphorus with CCl_4 and alcohols in polar aprotic solvents also results in formation of trialkylphosphites.^{5,6}

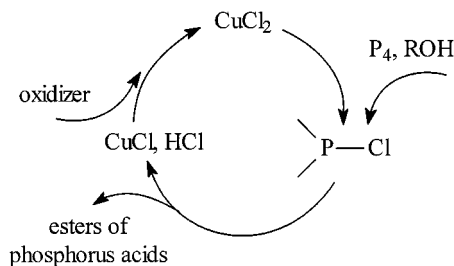
In Dorfman et al.,⁷⁻⁹ reaction of white phosphorus with alcohols in the presence of a 20-fold molar excess (in relation to phosphorus) of copper(II) salts was reported to afford the esters of three- and four-coordinate phosphorus acids in a high yield, although no experimental details were given. The necessity of using substantial amounts of copper salts renders this method almost useless in the preparative aspect.

The aim of the present investigation is the search for new approaches to the synthesis of three- and four-coordinate phosphorus acid esters, starting from white phosphorus and alkanols.

White phosphorus is known to be readily oxidized by salts of metals possessing low redox potentials.¹⁰ Additionally, the possibility of three-coordinate phosphorus atom halogenation with copper(II) chloride, was shown earlier.¹¹

Thus, one may assume that in the system $\text{P}_4\text{-CuCl}_2\text{-ROH}$ at the initial reaction step, the reduction of divalent copper ion to Cu(I) would occur, with simultaneous formation of phosphorus chloride which, in turn, can react in situ with alkanol.

Therefore, one should expect that introduction of a reagent capable of oxidizing Cu(I) to Cu(II) to the reaction mixture would secure the below catalytic cycle of the alkanols phosphorylation with white phosphorus (Scheme 1).



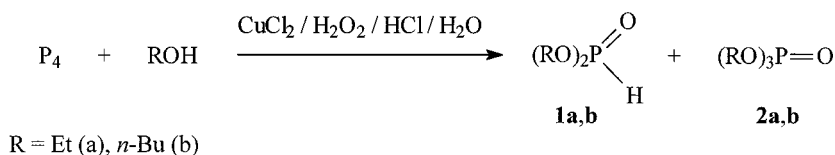
SCHEME 1

RESULTS AND DISCUSSION

In order to check the above assumption, we have studied the phosphorylation of alkanols with white phosphorus in the presence of catalytic

amounts (5–20 mas% of phosphorus mass) of copper(II) chloride and a cooxidant.

Ethanol and *n*-butanol exothermically react with white phosphorus in the system $\text{CuCl}_2\text{--H}_2\text{O}_2\text{--HCl--H}_2\text{O}$ to produce dialkylphosphites **1a,b** and trialkylphosphates **2a,b** at complete phosphorus conversion (Scheme 2, Table I).



SCHEME 2

The aggregate state of white phosphorus was found to affect the result of the reaction studied. The use of fine-dispersed phosphorus or the so-called “phosphorus snow” prepared by rapid cooling of intensively stirred emulsions of white phosphorus in benzene—*n*-butanol mixture (1:1 volume ratio) is more efficient for the synthesis of products **1b,2b**,

TABLE I Phosphorylation of Alkanols with White Phosphorus in the $\text{CuCl}_2\text{--H}_2\text{O}_2\text{--HCl--H}_2\text{O}$ System^a

Run	CuCl ₂ , mol per 1 P atom	HCl, ^c mol per 1 P atom	Product yield, % ^b	
			(RO) ₂ P(O)H	(RO) ₃ P=O
1	0.045	2.00	14	11
2	0.090	4.00	11	24
3	0.023	1.00	21	2
4	0.045	Not used	15	Not found
5	0.045	0.09	15	7
6	0.045	2.00	18	12
7 ^d			25	2
8	0.250	4.00	10	25
9 ^d			24	5

^aEthanol (run 1) or *n*-butanol (runs 2–9) were used in the reaction. In all runs, the volume ratio alkanol:benzene was 1:1; the molar ratio P:H₂O₂ (30% aqueous solution was used) was 1:2 and the reaction temperature was in the range 15–22°C.

^bThe yields of dialkylphosphite and trialkylphosphate were determined based on their relative content in the reaction mixture calculated from the ratio of integral intensities of the peaks in the ³¹P NMR spectrum; in all runs the phosphorus conversion was 100%.

^cA concentrated aqueous solution of HCl was used.

^dCopper(II) chloride and HCl were not added to the reaction mixture. Instead, aqueous phases obtained in runs 3 and 5, respectively, were used.

rather than using solutions of phosphorus in benzene or suspension of phosphorus in *n*-butanol.

Under best conditions, the total yield of ethyl esters **1a,2a** is 25% (Table I, run 1) and that of *n*-butyl esters **1b,2b** is 35% (Table I, run 2).

According to the ^{31}P NMR data, along with the above mentioned products, the reaction mixture contains also mono- and dialkylphosphates.

The use of hydrogen peroxide complexes with urea or with sodium carbonate, as well as ammonium persulfate as oxidants in this reaction results in lowering (by $\sim 2\text{--}3$ times) of the yield of the products **1b,2b**.

It is known that oxidation of Cu(I) to Cu(II) can be performed by passing oxygen into hydrochloric aqueous solutions of copper(I) chloride at a temperature of $\sim 95^\circ\text{C}$.¹² However, on heating ($85\text{--}95^\circ\text{C}$) *n*-butanol with white phosphorus and the system $\text{CuCl}_2\text{--HCl--H}_2\text{O}$ with oxygen flow, the products **1b** and **2b** are practically not formed.

The efficiency and chemoselectivity of *n*-butanol phosphorylation in the system $\text{CuCl}_2\text{--H}_2\text{O}_2\text{--HCl--H}_2\text{O}$ significantly depend on the amount of copper salt used (Table I). Thus, increasing the content of the latter results in a higher yield of trialkylphosphate **2b** (Table I, compare runs 3 and 8).

The aqueous phase formed under the above conditions can be used instead of CuCl_2 for repeated phosphorylation of *n*-butanol with white phosphorus. The reaction is thus directed toward predominant formation of dibutylphosphite **1b** (Table I, runs 7 and 9). When the reaction is carried out with 20-fold molar excess of copper(II) chloride relative to P_4 in the absence of hydrogen peroxide, such as under the conditions used in Dorfman et al.⁹ and Van Wazer,¹⁰ only phosphate **2b** in 60% yield is formed.

In the example with *n*-butanol, it was shown that the reaction can be carried out in the absence of HCl. Moreover, it leads to a drastic increase of the process chemoselectivity: Exclusive formation of dibutylphosphite **1b** in a yield of up to 15% is observed (Table I, run 4).

Copper(II) sulfate and acetate can be employed in this reaction to give similar results.

EXPERIMENTAL

^{31}P NMR spectra were taken on the following spectrometers: Varian VXR-500S (202 MHz operating frequency) and Bruker DPX 400 (400 and 162 MHz). The ^{31}P chemical shifts were measured relative to 85% phosphoric acid.

Phosphorylation of ethanol (Table I, run 1). To a suspension of 2.5 g (20.1 mmol) of white phosphorus in 100 ml of benzene-ethanol mixture (1:1 volume ratio), prepared by rapid cooling to 0–5°C of the hot (50–60°C) emulsion, a solution of 0.5 g (3.7 mmol) of CuCl₂ in 14.8 ml (168.9 mmol) of concentrated hydrochloric acid was added. To the obtained mixture, 16.5 ml (160.1 mmol) of 30% aqueous H₂O₂ was added dropwise during 1 h upon cooling with ice and stirring. A self-heating of the reaction mixture to 20–22°C was observed and the mixture color turned from brown to light green. The mixture was stirred for an additional 0.5 h at rt. The aqueous layer thus formed was separated and the organic layer was twice washed with water. After that, water and unreacted ethanol were removed from the combined aqueous solutions using a rotary evaporator, the residue was distilled in vacuum and a fraction with b.p._{5.0} of 70–80°C was collected. A total of 2.6 g of a mixture of diethylphosphite and triethylphosphate was obtained. According to the ³¹P NMR data, the mixture contained 14% of diethylphosphite (δ_P 10.4 ppm, J_{P-H} 690 Hz) and 11% of triethylphosphate (δ_P 2.1 ppm).

Phosphorylation of n-butanol (Table I, run 2). To a suspension of 2 g (16.1 mmol) of white phosphorus in 100 ml of benzene-*n*-butanol mixture (1:1 volume ratio), prepared by rapid cooling to 0–5°C of the hot (50–60°C) emulsion, a solution of 0.4 g (3.0 mmol) of CuCl₂ in 11.8 ml (134.6 mmol) of concentrated hydrochloric acid was added. To the obtained mixture, 13.2 ml (128.1 mmol) of 30% aqueous H₂O₂ was added dropwise during 1 h upon cooling with ice and stirring. A self-heating of the reaction mixture to 20–22°C was observed and the mixture color turned from brown to light green. The mixture was stirred for an additional 0.5 h at rt. The aqueous layer thus formed was separated and the organic layer was twice washed with water. After removal of the volatile components from the organic phase using a rotary evaporator the residue was distilled in vacuum and a fraction with b.p._{1.0} 110–130°C was collected. A total of 4 g of a mixture of dibutylphosphite and tributylphosphate was thus obtained. According to the ³¹P NMR data, the mixture contained 18% of dibutylphosphite (δ_P 10.7 ppm, J_{P-H} 683 Hz) and 12% of tributylphosphate (δ_P 2.3 ppm).

Dibutylphosphite (IIa) (Table I, run 4). To a cooled to 5–10°C mixture of 28.6 g (386.5 mmol) of *n*-BuOH and 0.6 g (4.4 mmol) of copper(II) chloride in 30 ml of benzene, a solution of 3 g (24.2 mmol) of white phosphorus in 120 ml of benzene, and 21.7 g (191.5 mmol) of 30% aqueous solution of hydrogen peroxide, preliminarily neutralized with barium hydroxide to pH = 7, were simultaneously added dropwise using two dropping funnels during 1.5 h. A self-heating of the reaction mixture to 30–35°C was observed and the mixture color turned from dark

brown to light blue. Two layers thus formed were separated. The upper organic layer was evaporated and the residue was distilled in vacuum to give 2.8 g (15%) of dibutylphosphite, b.p._{1.0} 75–77°C. ³¹P NMR spectrum: δ_P 7.68 ppm (a doublet, J_{P–H} 680 Hz).

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