Catalytic Synthesis of the Esters of Phosphorus Acids from White Phosphorus and Aliphatic or Aromatic Alcohols


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Abstract

The various esters of the phosphoric and phosphorous acids have been obtained directly from white phosphorus and aliphatic (or aromatic) alcohols under aerobic atmosphere in the presence of the CuX₂ or FeX₃ (X = Cl, NO₃, C₃H₇CO₂) salts. Irrespective of the variable nature of the used alcohols and catalysts, trialkyl(aryl) phosphates and dialkyl phosphites are a major products, whereas trialkyl(aryl) phosphites and dialkyl phosphates are a minor products of the phosphorylation process. Thanks to the presence of catalysts, the possible side reaction route of the radical chain oxidation of white phosphorus by oxygen to phosphorus oxides has been precluded. A comparison between the catalytic properties of CuX₂ and FeX₃ has been done. Although both of them have been found an efficient catalysts for the syntheses, the Cu(II) salts are active at 50-65°C, whereas the Fe(III) based catalytic systems become competitive in terms of catalytic efficiency when reaction is carried out at 70-90°C. Aromatic alcohols are characterised by less reactivity in this catalytic reaction as compared with an aliphatic ones. The same coordinative redox mechanism of the oxidative P-O coupling of P₄ to ROH in the presence of both Cu(II) and Fe(III) catalysts has been proposed. Relevant steps of the catalytic cycle including the complexation of both white phosphorus and alcohol molecules to metal ion, the reduction of catalyst by white phosphorus, and the oxidation of reduced form of catalyst by oxygen have been also considered.

Introduction

White phosphorus, P₄, is a precursor of many useful organophosphorus compounds including the esters of phosphorus acids that are produced in multitons amount and are widely employed in different technological areas as extractors of rare and radioactive elements, flame-retardants for plastic materials, additives for combustible and lubricating materials, bioactive substances for further elaboration in pharmaceutical and agricultural industries, etc. The traditional way for the synthesis of the esters is based on the preliminary oxidative chlorination of P₄ followed by the substitutive P-O coupling of phosphorus chlorides with alcohols or phenols [1]. This productive cycle demands consumption of toxic Cl₂ and causes the evolution of HCl, which has a negative influence on the product yield because may split the resulting organophosphorus compounds to undesired by-products. In consequence of neutralization, HCl is converted to inorganic chlorides, whose removal from waste may still cause problems in large-scale production plants. Moreover, the present methods of air purification do not secure a cheap and complete removal of both Cl₂ and HCl impurities from the technological workshops air. For the reasons, the search for an alternative technology, which does not use chlorine for the preparation of organophosphorus compounds, is attracting considerable industrial and environmental interest.

We have first proposed an original “chlorine-free” method of the oxidative alko(aro)xylation of white phosphorus under mild reaction conditions in the presence of CuX₂ or FeX₃ salts (X = Cl, Br, NO₃, CH₃CO₂, C₃H₇CO₂, C₁₇H₃₅CO₂) which uses dioxygen as a cheap and efficient oxidant [2-5]. The new catalytic protocol allows to remove both Cl₂ and HCl from the productive cycle and to incorporate into the catalytic cycle all the advantages of a homogeneous catalytic reac-
Catalytic Synthesis of the Esters from \( \text{P}_4 \) and Alcohols

As both \( \text{P}_4 \) and catalyst are taken in the reaction in the dissolved forms, depending on the reaction conditions, four types of organophosphorus derivatives bearing P-O bonds are formed and identified by chromatography and NMR: trialkyl(aryl) phosphate \( \text{PO(OR)}_3 \), dialkyl phosphite \( \text{P(OH)(OR)}_2 \), dialkyl phosphate \( \text{P(O)(OH)(RO)}_2 \), and trialkyl(aryl)phosphite \( \text{P(OR)}_3 \) (see Scheme 1).

\[
\begin{align*}
\text{P} + 12\text{ROH} + 5\text{O}_2 & \xrightarrow{\text{Catalyst}} 4\text{R} - \text{O} \Rightarrow \text{P} = \text{O} + 6\text{H}_2\text{O} \\
\text{P} + 8\text{ROH} + 3\text{O}_2 & \xrightarrow{\text{Catalyst}} 4\text{R} - \text{O} \Rightarrow \text{P} = \text{O} + 2\text{H}_2\text{O} \\
\text{P} + 8\text{ROH} + 5\text{O}_2 & \xrightarrow{\text{Catalyst}} 4\text{R} - \text{O} \Rightarrow \text{P} = \text{O} + 2\text{H}_2\text{O} \\
\text{P} + 12\text{ROH} + 3\text{O}_2 & \xrightarrow{\text{Catalyst}} 4\text{R} - \text{O} \Rightarrow \text{P} + 6\text{H}_2\text{O}
\end{align*}
\]

Scheme 1.

It has been shown by the volumetry method [2-5] that the experimental \( \text{O}_2/\text{P}_4 \) ratio between amounts of oxygen and phosphorus consumed is around 3-5, i.e. close to the stoichiometry of the above reactions. Thus, it appeared interesting to conduct the reaction at a preparative scale, to get more precise information about the type of organophosphorus compounds formed and the product composition. We report here several experiments concerning the reaction of white phosphorus with aliphatic and aromatic alcohols in the presence of air and different Cu(II) and Fe(III) salts which were carried out at a laboratory scale (grams) in order to isolate the individual products and characterise them by NMR.

**Experimental**

**Starting materials**

The most attention has been given to drying of reagents because \( \text{H}_2\text{O} \) stimulates the side reaction of the oxidative hydroxylation of \( \text{P}_4 \) to phosphoric acid. Air was dried over CaCl\(_2\). The alcohols and arenes were purified and dried by the usual methods. The catalysts were used after drying by heating when possible. Since iron(III) and copper(II) nitrates are not stable under heating, these catalysts were used as received. The solid \( \text{P}_4 \) was weighed in a beaker under water, dipped into two successive beakers containing ethanol and arene and then dissolved in a dried arene at 45°C. The concentration of \( \text{P}_4 \) in the solution was determined by iodometry.

**Caution**

White phosphorus is flammable and explosive in air and must be handled as soon and carefully as possible. It is known that bubbling oxygen through solutions of \( \text{P}_4 \) may result in violent explosions. However, no explosions occurred during these experiments,
thanks to the presence of catalysts. Nevertheless, it is strongly recommended to conduct these reactions behind shields.

**Products analysis**

Nuclear magnetic resonance (NMR) spectra of the organophosphorus esters were recorded on Bruker WM-250 and AC-200 spectrometers at 25°C, and on AC-80 at 35°C. Chemical shifts are expressed in ppm upfield from Me$_3$Si (H and $^{13}$C) and 85% H$_3$PO$_4$ ($^{31}$P). Coupling constants (J) are given in hertz (Hz). In order to eliminate paramagnetic CuCl$_2$ from the crude reaction solutions, Na$_2$SO$_3$ (3 to 10 g) was added, and the resulting suspension was stirred overnight. Such procedure did not remove paramagnetism when FeCl$_3$ was used; thus the crude reaction products were not analyzed by $^{31}$P NMR in these cases. Elemental analysis was obtained on Perkin-Elmer Model 2400. Gas chromatography analysis were recorded on Chrompack 9002 chromatograph equipped with flameionization detector and the capillary columns CP SIL 19CB (25m × 0.25mm) and CP SIL 5CB (10m × 0.25mm).

**Typical procedure**

A round three-neck flask (with volume about 250 cm$^3$) fitted with a refluxing condenser and a gas-inlet tube for air barbotage was used for catalytic synthesis of organophosphorus products. The constant reaction temperature (65-90°C) was supported with an oil bath, under vigorous magnetic stirring. An arene solution of P$_4$ (30-100 mL) was portionally added to the alcohol solution (10-180 mL) containing the catalyst by syringe through a rubber plug during 5-30 hours. The gradual addition of P$_4$ was aimed to prevent the formation of white smoke of P$_2$O$_5$ and P$_4$O$_{10}$. The rate of P$_4$ conversion was slowly decreased from portion to portion because the catalytic solution was gradually diluted by solvent (arene). The flow rate of air barbotage was 80-120 mL/min. The reactions were monitored by GC and $^{31}$P NMR (when applicable), which indicates in most cases the formation of several products in variable amounts. After completing the synthesis, the catalyst was precipitated by K$_2$CO$_3$ and filtered from the solution. High vacuum distillation (BUCHI GKR-51) of dark oil remaining after stripping off the excess of alcohol and arene (the rotation evaporator ER-1M2) yields the individual organophosphorus products as colourless oils.

**Physical and spectroscopic data**

1a. Tributyl phosphate: bp. 130-132°C (2 mm Hg); $^3$[H] NMR (CDCl$_3$): $\delta$ 0.51 ppm. $^{31}$P NMR (CDCl$_3$): $\delta$ -0.50 (sept., $^3$J$_{P-O}$ = 6.8 Hz) ppm. $^1$H NMR (CDCl$_3$): $\delta$ 3.92 (m, 6H, CH$_2$), 1.56 (m, 6H, CH$_2$), 1.30 (m, 6H, CH$_2$), 0.83 (m, 9H, CH$_3$) ppm. $^{13}$C[$^1$H] NMR (CDCl$_3$): $\delta$ 67.24 (d, $^3$J$_{CP} = 5.9$ Hz, CH$_2$), 32.12 (d, $^3$J$_{CP} = 6.0$ Hz, CH$_3$), 18.53 (s, CH$_3$), 13.42 (s, CH$_3$) ppm. Anal. Calcd for C$_9$H$_{22}$O$_4$P; C, 54.07; H, 10.10. Found: C, 54.70; H, 10.10.

2a. Dibutyl phosphate: bp. 110°C (5 mm Hg); $^3$[H] NMR (CDCl$_3$): $\delta$ 7.94 ppm. $^{31}$P NMR (CDCl$_3$): $\delta$ 7.9 (dt, $^3$J$_{PH} = 692$ Hz, $^3$J$_{P-O}$ = 8.5 Hz) ppm. $^1$H NMR (CDCl$_3$): $\delta$ 6.7 (d, $^3$J$_{HH} = 692$ Hz, 1H, H-P), 3.95 (m, 4H, CH$_2$), 1.55 (m, 4H, CH$_2$), 1.31 (m, 4H, CH$_2$), 0.84 (t, $^3$J$_{HH} = 7.2$ Hz, 6H, CH$_3$) ppm. $^{13}$C[$^1$H] NMR (CDCl$_3$): $\delta$ 65.39 (d, $^3$J$_{CP} = 5.8$ Hz, CH$_2$), 32.21 (d, $^3$J$_{CP} = 5.9$ Hz, CH$_2$), 18.57 (s, CH$_2$), 13.37 (s, CH$_3$) ppm. Anal. Calcd for C$_9$H$_{18}$O$_4$P; C, 49.5; H, 9.8. Found: C, 49.20; H 9.79.

3a. Tributyl phosphate: bp. 100°C (10$^{-3}$ mm Hg); $^3$[H] NMR (CDCl$_3$): $\delta$ 0.88 ppm. $^1$H NMR (CDCl$_3$): $\delta$ 11.8 (br s, 1H, OH), 3.97 (m, 4H, CH$_2$), 1.60 (m, 4H, CH$_2$), 1.38 (m, 4H, CH$_2$), 0.89 (t, $^3$J$_{HH} = 7$ Hz, 6H, CH$_3$) ppm. $^{13}$C[$^1$H] NMR (CDCl$_3$): $\delta$ 67.18 (d, $^3$J$_{CP} = 6.0$ Hz, CH$_2$), 32.06 (d, $^3$J$_{CP} = 7.8$ Hz, CH$_2$), 18.56 (s, CH$_2$), 13.48 (s, CH$_3$) ppm. Anal. Calcd for C$_9$H$_{18}$O$_4$P; C, 45.7; H, 9.0. Found: C, 46.33; H 9.29.

1b. Tri-isopropyl phosphate: bp. 83-84°C (5 mm Hg); $^3$[H] NMR (THF-d$_4$): $\delta$ 0.97 ppm. $^1$H NMR (THF-d$_4$): $\delta$ 4.55 (m, 3H, CH$_2$), 1.27 (d, $^3$J$_{HH} = 6.2$ Hz, 18H, CH$_3$) ppm. $^{13}$C[$^1$H] NMR (THF-d$_4$): $\delta$ 72.28 (d, $^3$J$_{CP} = 5.8$ Hz, CH$_2$), 24.38 (d, $^3$J$_{CP} = 4.0$ Hz, CH$_3$) ppm.

2b. Di-isopropyl phosphate: bp. 91-92°C (20 mm Hg); $^3$[H] NMR (CDCl$_3$): $\delta$ 4.6 ppm. $^{31}$P NMR (CDCl$_3$): $\delta$ 4.6 (d, $^3$J$_{HH} = 690$ Hz) ppm. $^1$H NMR (CDCl$_3$): $\delta$ 6.72 (d, $^3$J$_{HH} = 687$ Hz, 1H, HP), 4.6 (m, 2H, CH), 1.24 (d, $^3$J$_{HH} = 6.2$ Hz, 12H, CH$_3$) ppm. $^{13}$C[$^1$H] NMR (CDCl$_3$): $\delta$ 70.5 (d, $^3$J$_{CP} = 6$ Hz, CH), 23.6 (br d, $^3$J$_{CP} = 5$ Hz, CH$_3$) ppm.

3b. Di-isopropyl phosphate: bp. 94°C (10$^{-4}$ mm Hg); $^3$[H] NMR (THF-d$_4$): $\delta$ 2.98 ppm. $^{31}$P[$^1$H] NMR (THF-d$_4$): $\delta$ 8.8 (s, 1H, HO-P), 4.54 (m, 2H, CH), 1.28 (d, $^3$J$_{HH} = 6.1$ Hz, 12H, CH$_3$) ppm. $^{13}$C[$^1$H] NMR (THF- d$_4$): $\delta$ 72.43 (d, $^3$J$_{CP} = 5.9$ Hz, CH$_2$), 24.25 (d, $^3$J$_{CP} = 4.5$ Hz, CH$_3$) ppm.

1d. Triphenyl phosphate: bp. 244°C (10 mm Hg);
Results and discussion

We have carried out reactions between white phosphorus and alcohols under aerobic atmosphere in the presence of two types of catalysts, either CuX₂ or FeX₃. Table 1 summarises the conditions used for all the experiments and the results. It should be emphasised that no organophosphorus products but only phosphorus oxides such as P₄O₆ and P₄O₁₀ are yielded in the absence of the catalysts. In order to fasten the phosphorylation reactions, the metal salt is used in a large amount, between 0.7 and 4.0 equivalent of metal salt for each P₄. Such a large amount of catalyst is needed for productivity and safety reasons. Indeed, P₄ is introduced in the reaction under aerobic conditions, and the only way to preclude its radical chain reaction with O₂, which affords various phosphorus oxides, is to use also the catalyst as electron receptor.

Catalyst CuX₂

At using the CuX₂ catalysts, the reaction solution is characterised by a versatile colour in the course of the experiment. The initial transparent green alcohol solution of CuCl₂ is immediately converted in a turbid brown at adding the arene solution of P₄ at 60°C. In the course of air barbotage, the reaction solution is gradually clearing up to a colourless solution including white residue of CuCl. Finally, the residue is gradually disappeared, afterwards the catalytic solution is again turned in a transparent green one, as at the beginning of the reaction. The catalytic solution colour is determined by the correlative rates of the reduction of Cu(II) by P₄ and the oxidation of Cu, Cu(I) by oxygen. White smoke of phosphorus oxides above the catalytic solution is not observed. This means that the branched-chain route of the P₄ oxidation in the gas phase is precluded. Under optimal reac-

Table 1

Conditions for preparative-scale runs at the flow rate of air barbotage 80-120 mL/min.

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalytic solution</th>
<th>Phosphorus solution</th>
<th>Temp. °C</th>
<th>Time hr</th>
<th>Compounds isolated g (mmol; %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alkohol mL</td>
<td>Catalyst g (mmol)</td>
<td>Arene mL</td>
<td>P₄ g (mmol)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>BuOH 140</td>
<td>CuCl₂ 3.5 (26.0)</td>
<td>Benzene 94</td>
<td>1.8 (14.5)</td>
<td>60 24 1a 13.6 (51.0; 87.9, 2a (traces)</td>
</tr>
<tr>
<td>2</td>
<td>BuOH 20</td>
<td>CuCl₂ 3.0 (22.3)</td>
<td>Toluene 50</td>
<td>1.0 (8.0)</td>
<td>65 5 1a 4.3 (16.1; 50.3, 2a 1.0 (5.1; 15.9), 3a 0.6 (2.8; 8.7)</td>
</tr>
<tr>
<td>3</td>
<td>95% EtOH 150</td>
<td>CuCl₂ 3.0 (17.6)</td>
<td>Toluene (95)</td>
<td>1.2 (9.6)</td>
<td>50 15 1a 3.7 (20.3; 52.8, 2a (traces)</td>
</tr>
<tr>
<td>4</td>
<td>i-PrOH 20</td>
<td>CuCl₂ 2.0 (14.9)</td>
<td>Toluene (30)</td>
<td>0.7 (5.6)</td>
<td>65 5 1b 1.9 (8.5; 37.9), 2b 0.5 (3.0; 13.4), 3b 0.2 (1.1; 4.9)</td>
</tr>
<tr>
<td>5</td>
<td>tert-BuOH 20</td>
<td>CuCl₂ 3.0 (22.3)</td>
<td>Toluene (30)</td>
<td>0.7 (5.6)</td>
<td>55 5 1c, 2c, 4c (5/2/1, not separated)</td>
</tr>
<tr>
<td>6</td>
<td>i-AmOH 150</td>
<td>Cu(NO₃)₂ 3H₂O 3.0 (12.4)</td>
<td>Toluene (100)</td>
<td>1.2 (9.6)</td>
<td>65 30 1a 7.4 (24.0; 62.5, 2a 1.1 (4.9; 12.8)</td>
</tr>
<tr>
<td>7</td>
<td>BuOH 150</td>
<td>CuC₆H₄CO₂J 2 5.0 (21.0)</td>
<td>Toluene (100)</td>
<td>1.4 (11.3)</td>
<td>65 20 1a 10.2 (38.3; 84.7), 2a 0.6 (3.0; 6.6)</td>
</tr>
<tr>
<td>8</td>
<td>i-AmOH 150</td>
<td>FeCl₃ 3.0 (11.1)</td>
<td>Benzene (100)</td>
<td>1.9 (15.3)</td>
<td>70 12 1a 8.2 (26.6; 43.4), 2a 2.9 (13.0; 21.2)</td>
</tr>
<tr>
<td>9</td>
<td>BuOH 150</td>
<td>FeCl₃ 4.0 (14.8)</td>
<td>Toluene (60)</td>
<td>1.4 (11.3)</td>
<td>80 12 1a 7.2 (26.9; 59.7), 2a 3.0 (15.6; 34.5)</td>
</tr>
<tr>
<td>10</td>
<td>i-AmOH 180</td>
<td>FeCl₃ 3.0 (11.1)</td>
<td>Benzene (90)</td>
<td>1.7 (13.7)</td>
<td>90 22 1a 12.3 (39.8; 72.6), 2a 2.8 (12.6; 23.0)</td>
</tr>
<tr>
<td>11</td>
<td>i-AmOH 150</td>
<td>Fe(NO₃)₃ 9H₂O 5.0 (12.4)</td>
<td>Toluene (70)</td>
<td>1.2 (9.6)</td>
<td>70 20 1a 0.2 (0.6; 1.5), 2a 1.4 (6.3; 16.4)</td>
</tr>
<tr>
<td>12</td>
<td>PhOH 6.2 g</td>
<td>FeCl₃-I₂ 0.5 (3.0)-0.24 (0.9)</td>
<td>Toluene (20)</td>
<td>0.4 (3.2)</td>
<td>80 7 1d 1.2 (3.6; 28.1)</td>
</tr>
</tbody>
</table>
tion conditions, the use of CuCl₂ as catalyst leads to the formation of almost a single product 1a (87.9%; run 1, Table 1). However, the process selectivity depends largely on the reaction time and amount of alcohol used. In particular, three compounds 1a (50.3%), 2a (15.9%) and 3a (8.7%) are formed when the reaction is hastily conducted with a small volume of alcohol (run 2). The H₂O admixtures in alcohol or/and catalyst leads to formation of an inorganic phosphorus derivatives and to decreasing the 1a yield (52.8%; run 3).

Copper chloride exhibits catalytic activity also in the phosphorylation of a secondary and tertiary alcohols. When isopropanol is taken in the reaction (run 4), high vacuum distillation affords PO(OiPr)₃(37.9%), P(O)(OH)(OiPr)₂(13.4%) and several drops of P(O)(OH)(OiPr)₃(4.9%). We did not succeed in isolating a compound when the tertiary alcohol (tert-BuOH) was used (run 5), since vacuum distillation of the products was difficult because of the high viscosity of the residual liquid and the small amount of products. However, the ³¹P NMR spectrum of the crude reaction products reveals not only PO(OtertBu), 1c (δₚ = -0.39 ppm) and P(O)(OH)(OtertBu)₁, 2c (δₚ = 2.98 ppm) but also the third product P(OtertBu)₃, 4c (δₚ = 141.73 ppm). With primary or secondary alcohols, trialkyl phosphate 4 was observed by gas chromatography only at the beginning of reaction; then it was readily oxidized to 1 under influence of catalyst and oxygen. Accumulation of this intermediate in tertiary alcohols suggests that the bulky tert-alkyl groups make 4c more stable as compared with 4a,b.

In the presence of Cu(NO₃)₂ (run 6), the oxidative alkoxylation of P₄ proceeds slower than with CuCl₂ due to the lesser solubility of copper nitrate in alcohols. The initial turbid blue alcohol solution of Cu(NO₃)₂⋅3H₂O becomes brown after addition of P₄. With the air babbling, the colour of catalytic solution is gradually converted to a blue one. The phosphorus oxides above the catalytic solution are not observed. Distillation allows isolating the phosphate 1a (62.5% yield) and phosphate 2a (12.8% yield).

The better result is obtained with copper butyrate, which is well soluble in alcohols. The initial bright-green alcohol solution of Cu(C₂H₅CO₂)₂ becomes dark-green and brown after addition of P₄. In the course of the air babottage, the catalytic solution colour is changed from brown to green. White smoke of phosphorus oxides over the reaction solution is not appeared. Distillation affords phosphate 1a and phosphite 2a in 84.7% and 6.6% yield, respectively (run 7). Thus, based on the above experiments, one can see that the CuX₂ salts exhibit a high catalytic activity in the reaction of the oxidative alkoxylation of white phosphorus at 50-65°C.

**Catalyst FeX₃**

The iron based systems become competitive in terms of catalytic efficiency, when the phosphorylation reactions are carried out at 70-90°C. The reaction temperature dependence of the product composition should be also noted at using the FeX₃ catalysts. At 70°C, the initial light-brown colour of alcohol solution of FeCl₃ is not practically changed neither at the moment of P₄ addition, nor in the course of air bubbling. Some white smoke of phosphorus oxides is observed above the catalytic solution. When the reaction is conducted at 80 or 90°C (runs 9, 10), the reaction solution colour turns into a dark-brown and the white smoke is disappeared. At 90°C, the oxidative alkoxylation of P₄ results in higher yields of 1a and 2a (72.6% and 23.0%; run 10) as compared to reaction carried out at 70°C (43.4% and 21.2%; run 8).

The same products are formed in the presence of iron nitrate although the product yields are lower. The addition of toluene solution of P₄ to alcohol solution of Fe(NO₃)₃⋅9H₂O leads to appearance of the white smoke of phosphorus oxides above the solution and to formation of an yellow precipitate (presumably, the iron hydroxycomplexes) which are not catalytically active in this reaction. The product yields are therefore low, only 1.5% for 1a and 16.4% for 2a (run 11). Nevertheless, the identity of esters of phosphorus acids obtained from P₄ and alcohols in the presence of both chloride-including and chloride-free catalysts (CuCl₂, Cu(NO₃)₂, Cu(C₂H₅CO₂)₂, FeCl₃, Fe(NO₃)₃) allow us to exclude a probable reaction route via formation of PCl₃ in situ followed with its alcoholysis and to suppose a coordinative mechanism of the reaction.

Finally, we tried to extend the phosphorylation reactions to an aromatic alcohol, PhOH, but we did not succeeded in isolating a product when FeCl₃ alone was used as catalyst. This may be explained by less nucleophility of the phenoxide anion and its stronger association in organic solutions as compared with alkoxide one [6]. Thus, a promoting additive is needed to carry out the coupling reaction of P₄ with phenol. We used iodine as a reversible co-oxidant whose reduced form (iodide) can be reoxidized by FeCl₃. At
adding the toluene solution of P₄ into a viscous mixture of PhOH, FeCl₃, and I₂ at 80°C followed by the air babbling, the initial red-brown solution is not undergone a visible change and the white smoke of a phosphorus oxides is not observed above the solution. Both triphenyl phosphate 1d and triphenyl phosphate 4d are determined by gas chromatography during reaction, however, only 1d (28.1%) is isolated by high vacuum distillation as a yellow fastly thickening oil (run 12).

Thus, one can notice that catalytic reactions of the oxidative alko(aro)xylation of white phosphorus are quite innovative and not characteristic for the known chemistry of elemental phosphorus. The novelty and potentiality of the catalytic functionalisation of white phosphorus is confirmed by the patent [7] illustrating this approach.

Despite of a variable nature of the catalytic systems and alcohols used, the experimental data and products composition indicate to a general features of the oxidative P-O coupling of P₄ with aliphatic and aromatic alcohols described in Scheme 2. Relevant steps of the process may be considered: (i) the oxidative alko(aro)xylation of P₄ to P(OR)₃, (ii) the oxidation of P(OR)₃ to PO(OR)₂, (iii) the dealkylation of P(OR)₃ to P(O)H(OR)₂, and (iv) the oxidation of P(O)H(OR)₂ to P(O)(OH)(OR)₃.

In their turn, the steps (i), (ii), and (iv) with CuX₂ and FeX₃ proceed via the repeated stages of the complexation of both ROH and P₄ (as well as 4 or 2) to metal ion, the reduction of catalyst by P₄ (as well as by 4 or 2), and its reoxidation by oxygen. In the presence of the catalytic FeCl₃-I₂ system, the stages of the oxidation of P₄ by I₂ followed by the reduction of Fe(III) by I⁻ and the oxidation of Fe(II) by oxygen are supposed. It should be mentioned that the above stages of the complexation of reagents to Cu(II) and Fe(III) ions followed by the oxidative P-O coupling of white phosphorus to alcohol have been established and studied by the kinetic, potentiometric, thermodynamic, IR, ESR [2-5] and quantum chemical CNDO [8,9] methods. Dealkylation of P(OR)₂ (iii) occurs as a result of interaction with water or acid both generated in situ. The products composition is determined by the rates of the key steps (i-iv). The predominant formation of 1 with CuX₂ and mixed FeCl₃-I₂ system points to the relatively higher step (ii) velocity. The step (iv) seems to be accelerated at using of the primary and secondary aliphatic alcohols.

**Conclusion**

Thus, we have shown that the new processes of the oxidative alko(aro)xylation of P₄ catalysed by the CuX₂ or FeX₃ based catalytic systems allows to synthesize an organophosphorus derivatives which have a high added value directly from cheap and abundant white phosphorus, aliphatic or aromatic alcohols and oxygen under mild reaction conditions. The variable nature of the used alcohols and transition metal salts does not dramatically change the type of reactions observed. In all cases, compounds bearing P-O bonds are obtained, only the ratio of the various P-O compounds changes. Aromatic alcohols are characterised by less reactivity in this catalytic reaction as compared with an aliphatic ones. Both CuX₂ and FeX₃ are found an efficient catalysts for the syntheses, however copper(II) salts exhibit the most catalytic activity at 50-65°C, whereas the iron(III) based catalytic
systems become competitive and give better results in terms of catalytic efficiency when reaction is carried out at 70-90°C. On the basis of our present and previously published results, we have proposed that both Cu(II) and Fe(III) catalysts entail the same coordinative redox mechanism comprised of the major stages of the complexation of both P₄ (or its derivative) and ROH to metal ion, the reduction of catalyst by P₄ (or its derivative), liberating organophosphorus products, and the oxidation of reduced form of catalyst by oxygen. Work is in progress to achieve optimisation of the catalytic production of the esters of phosphorus acids through the metal-mediated functionalisation of white phosphorus.

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