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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 CuX_2 or FeX_3 (X = Cl, NO_3, $C_3H_7CO_2$) 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 CuX_2 and FeX_3 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 P_4 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, P_4, 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 substanses for furter elaboration in pharmaceutical and agricultural industries, *etc*. The traditional way for the synthesis of the esters is based on the preliminary oxidative chlorination of P_4 followed by the substitutive P-O coupling of phosphorus chlorides with alcohols or phenols [1]. This productive cycle demands consumption of toxic Cl_2 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 Cl_2 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 CuX_2 or FeX_3 salts (X = Cl, Br, NO_3, CH_3CO_2, $C_3H_7CO_2$, $C_{17}H_{35}CO_2$) which uses dioxygen as a cheap and efficient oxidant [2-5]. The new catalytic protocol allows to remove both Cl_2 and HCl from the productive cycle and to incorporate into the catalytic cycle all the advantages of a homogeneous catalytic reac-

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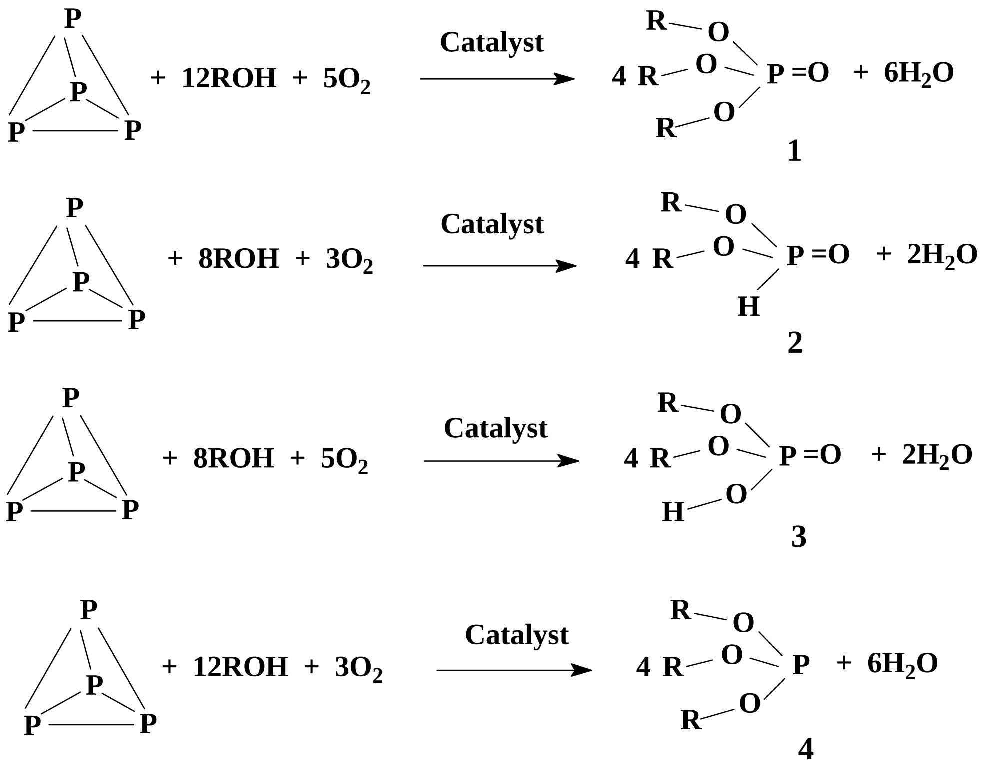
*corresponding author. E-mail: abdreimioce@nursat.kz tion as both P_4 and catalyst are taken in the reaction in the dissolved forms. Depending on the reactions conditions, four types of organophosphorus derivatives bearing P-O bonds are formed and identified by chromatography and NMR: trialkyl(aryl) phosphate $PO(OR)_3$ **1**, dialkyl phosphite $P(O)H(OR)_2$ **2**, dialkyl phosphate $P(O)(OH)(RO)_2$ **3**, and trialkyl(aryl)phosphite $P(OR)_3$ **4** (see Scheme 1).



Scheme 1.

It has been shown by the volumometry method [2-5] that the experimental O_2/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 H_2O stimulates the side reaction of the oxidative hydroxylation of 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 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 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 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_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants (J) are given in hertz (Hz). In order to eliminate paramagnetic $CuCl_2$ from the crude reaction solutions, Na_2SO_3 (3 to 10 g) was added, and the resulting suspension was stirred overnight. Such procedure did not removed 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_2O_3 and P_4O_{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_2CO_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); ^{31}P{^{1}H}NMR ($CDCl_3$): δ - 0.51 ppm. ^{31}P NMR ($CDCl_3$): δ - 0.50 (sept., $^{3}J_{P\text{-}O\text{-}CH2}$ = 6.8 Hz) ppm. ^{1}H NMR ($CDCL_3$): δ 3.92 (m, 6H, CH_2 α), 1.56 (m, 6H, CH_2 β), 1.30 (m, 6H, CH_2 γ), 0.83 (m, 9H, CH_3) ppm. ^{13}C{^{1}H}NMR ($CDCl_3$): δ 67.24 (d, $^{2}J_{CP}$ = 5.9 Hz, CH_2 α), 32.12 (d, $^{3}J_{CP}$ = 6.0 Hz, CH_2 β), 18.53 (s, CH_2 γ), 13.42 (s, CH_3) ppm. Anal. Calcd for $C_{12}H_{27}O_4P$: C, 54.07; H, 10.10. Found: C, 54.70; H, 10.10.

2a. Dibutyl phosphite: bp. 110°C (5 mm Hg); ^{31}P{^{1}H}NMR ($CDCl_3$): δ 7.94 ppm. ^{31}P NMR ($CDCl_3$): δ 7.9 (dt, $^{1}J_{PH}$ = 692 Hz, $^{3}J_{P\text{-}O\text{-}CH2}$ = 8.5 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ 6.7 (d, $^{1}J_{HP}$ = 692 Hz, 1H, H-P), 3.95 (m, 4H, CH_2 α), 1.55 (m, 4H, CH_2 β), 1.31 (m, 4H, CH_2 χ), 0.84 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 65.39 (d, $^{2}J_{PC}$ = 5.8 Hz, CH_2 α), 32.21 (d, $^{3}J_{CP}$ = 5.9 Hz, CH_2 β), 18.57 (s, CH_2 χ), 13.37 (s, CH_3) ppm. Anal. Calcd for $C_8H_{19}O_3P$: C, 49.5; H, 9.8. Found: C, 49.20; H 9.79.

3a. Dibutyl phosphate: bp. 100°C (10^{-4} mm Hg); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 0.88 ppm. ^{1}H NMR ($CDCl_3$): δ 11.8 (br s, 1H, OH), 3.97 (m, 4H, CH_2 α), 1.60 (m, 4H, CH_2 β), 1.38 (m, 4H, CH_2 χ), 0.89 (t, $^{3}J_{HH}$ = 7 Hz, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 67.18 (d, $^{2}J_{CP}$ =6.0 Hz, CH_2 α), 32.06 (d, $^{3}J_{CP}$ = 7.8 Hz, CH_2 β), 18.56 (s, CH_2 χ), 13.48 (s, CH_3) ppm. Anal. Calcd for $C_8H_{19}O_4P$: C, 45.7; H, 9.0. Found: C, 46.33; H 9.29.

1b. Tri-isopropyl phosphate: bp. 83-84°C (5 mm Hg); ^{31}P{^{1}H}NMR (THF-d_8): δ 0.97 ppm. ^{1}H NMR (THF-d_8): δ 4.55 (m, 3H, CH α), 1.27 (d, $^{3}J_{HH}$ = 6.2 Hz, 18H, CH_3) ppm. ^{13}C{^{1}H}NMR (THF-d_8): δ 72.28 (d, $^{2}J_{CP}$ = 5.8 Hz, CH α,), 24.38 (d, $^{3}J_{CP}$ = 4.0 Hz, CH_3) ppm.

2b. Di-isopropyl phosphite: bp. 91-92°C (20 mm Hg); ^{31}P{^{1}H} NMR ($CDCI_3$): δ 4.6 ppm. ^{31}P{^{1}H} NMR ($CDCI_3$): δ 4.6 (d, $^{1}J_{PH}$ = 690 Hz) ppm. ^{1}H NMR ($CDCI_3$): δ 6.72 (d, $^{1}J_{PH}$ = 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 ($CDCI_3$): δ 70.5 (d, $^{2}J_{CP}$ = 6 Hz, CH), 23.6 (br d, $^{2}J_{CP}$ = 5 Hz, CH_3) ppm.

3b. Di-isopropyl phosphate: bp. 94°C (10^{-4} mm Hg); ^{31}P{^{1}H}NMR (THF-d_8): δ 2.98 ppm.

^{31}P{^{1}H}NMR (THF- d_8): δ 8.8 (s, 1H, HO-P), 4.54 (m, 2H, CH α), 1.28 (d, $^{3}J_{HH}$ = 6.1 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H}NMR (THF- d_8): δ 72.43 (d, $^{2}J_{CP}$ = 5.9 Hz, CH α), 24.25 (d, $^{3}J_{CP}$ = 4.5 Hz, CH_3) ppm.

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

$^{31}P\{^1H\}$NMR ($CDCI_3$): δ -17.3 ppm; ^1H NMR ($CDCI_3$): δ 7.2-7.4 (m, 15H, C_6H_5) ppm; $^{13}C\{^1H\}$ NMR ($CDCI_3$): δ 150.5 (d, $^2J_{CP}$ = 8 Hz, i-C_6H_5), 129.9 (s, m-C_6H_5), 125.7 (s, p-C_6H_5), 120.1 (d, $^3J_{CP}$ = 4 Hz, o-C_6H_5) ppm.

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 CuX_2 or FeX_3. 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 P_4O_6 and P_4O_{10} 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 P_4. Such a large amount of catalyst is needed for productivity and safety reasons. Indeed, P_4 is introduced in the reaction under aerobic conditions, and the only way to preclude its radical chain reaction with O_2, which affords various phosphorus oxides, is to use also the catalyst as electron receptor.

Catalyst CuX_2

At using the CuX_2 catalysts, the reaction solution is characterised by a versatile colour in the course of the experiment. The initial transparent green alcohol solution of $CuCl_2$ is immediately converted in a turbid brown at adding the arene solution of P_4 at 60°C. In the course of air barbbling, 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 P_4 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 P_4 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.

Run	Catalytic solution		Phosphorus solution		Temp. °C	Time hr	Compounds isolated g (mmol; %)
	Alcohol mL	Catalyst g (mmol)	Arene mL	P_4 g (mmol)			
1	BuOH 140	$CuCl_2$ 3.5 (26.0)	Benzene 94	1.8 (14.5)	60	24	**1a** 13.6 (51.0; 87.9), **2a** (traces)
2	BuOH 20	$CuCl_2$ 3.0 (22.3)	Toluene 50	1.0 (8.0)	65	5	**1a** 4.3 (16.1; 50.3), **2a** 1.0 (5.1; 15.9), **3a** 0.6 (2.8; 8.7)
3	95% EtOH 150	$CuCl_2{\cdot}2H_2O$ 3.0 (17.6)	Toluene (95)	1.2 (9.6)	50	15	**1a** 3.7 (20.3; 52.8), **2a** (traces)
4	i-PrOH 20	$CuCl_2$ 2.0 (14.9)	Toluene (30)	0.7 (5.6)	65	5	**1b** 1.9 (8.5; 37.9), **2b** 0.5 (3.0; 13.4), **3b** 0.2 (1.1; 4.9)
5	tert-BuOH 20	$CuCl_2$ 3.0 (22.3)	Toluene (30)	0.7 (5.6)	55	5	**1c**, **2c**, **4c** (5/2/1, not separated)
6	i-AmOH 150	$Cu(NO_3)_2{\cdot}3H_2O$ 3.0 (12.4)	Toluene (100)	1.2 (9.6)	65	30	**1a** 7.4 (24.0; 62.5), **2a** 1.1 (4.9; 12.8)
7	BuOH 150	$Cu(C_3H_7CO_2)_2$ 5.0 (21.0)	Toluene (100)	1.4 (11.3)	65	20	**1a** 10.2 (38.3; 84.7), **2a** 0.6 (3.0; 6.6)
8	i-AmOH 150	$FeCl_3$ 3.0 (11.1)	Benzene (100)	1.9 (15.3)	70	12	**1a** 8.2 (26.6; 43.4), **2a** 2.9 (13.0; 21.2)
9	BuOH 150	$FeCl_3$ 4.0 (14.8)	Toluene (60)	1.4 (11.3)	80	12	**1a** 7.2 (26.9; 59.7), **2a** 3.0 (15.6; 34.5)
10	i-AmOH 180	$FeCl_3$ 3.0 (11.1)	Benzene (90)	1.7 (13.7)	90	22	**1a** 12.3 (39.8; 72.6), **2a** 2.8 (12.6; 23.0)
11	i-AmOH 150	$Fe(NO_3)_3{\cdot}9H_2O$ 5.0 (12.4)	Toluene (70)	1.2 (9.6)	70	20	**1a** 0.2 (0.6; 1.5), **2a** 1.4 (6.3; 16.4)
12	PhOH 6.2 g	$FeCl_3$-I_2 0.5 (3.0)-0.24 (0.9)	Toluene (20)	0.4 (3.2)	80	7	**1d** 1.2 (3.6; 28.1)

tion conditions, the use of $CuCl_2$ 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 H_2O 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 $PO(OiPr)_3$ **1b** (37.9%), $P(O)H(OiPr)_2$ **2b** (13.4%) and several drops of $P(O)(OH)(OiPr)_2$ **3b** (4.9%). We did not succeeded 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 ^{31}P NMR spectrum of the crude reaction products reveals not only $PO(OtertBu)_3$ **1c** ($\delta_p = -0.39$ ppm) and $P(O)H(OtertBu)_2$ **2c** ($\delta_p = 2.98$ ppm) but also the third product $P(OtertBu)_3$ **4c** ($\delta_p = 141.73$ ppm). With primary or secondary alcohols, trialkyl phosphite **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 $Cu(NO_3)_2$ (run 6), the oxidative alkoxylation of P_4 proceeds slower than with $CuCl_2$ due to the lesser solubility of copper nitrate in alcohols. The initial turbid blue alcohol solution of $Cu(NO_3)_2\cdot 3H_2O$ becomes brown after addition of P_4. 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 phosphite **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 $Cu(C_3H_7CO_2)_2$ becomes dark-green and brown after addition of P_4. In the course of the air barbotage, 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 CuX_2 salts exhibit a high catalytic activity in the reaction of the oxidative alkoxylation of white phosphorus at 50-65°C.

Catalyst FeX_3

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 FeX_3 catalysts. At 70°C, the initial light-brown colour of alcohol solution of $FeCl_3$ is not practically changed neither at the moment of P_4 addition, nor in the course of air babbling. 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 P_4 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 P_4 to alcohol solution of $Fe(NO_3)_3\cdot 9H_2O$ 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 P_4 and alcohols in the presence of both chloride-including and chloride-free catalysts ($CuCl_2$, $Cu(NO_3)_2$, $Cu(C_3H_7CO_2)_2$, $FeCl_3$, $Fe(NO_3)_3$) allow us to exclude a probable reaction route *via* formation of PCl_3 *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 $FeCl_3$ 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 P_4 with phenol. We used iodine as a reversible co-oxidant whose reduced form (iodide) can be reoxidized by $FeCl_3$. At adding the toluene solution of P_4 into a viscous mixture of PhOH, $FeCl_3$ and I_2 at 80°C followed by the air babbling, the initial red-brown solution is not underwent a visible change and the white smoke of a phosphorus oxides is not observed above the solution. Both triphenyl phosphate **1d** and triphenyl phosphite **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).

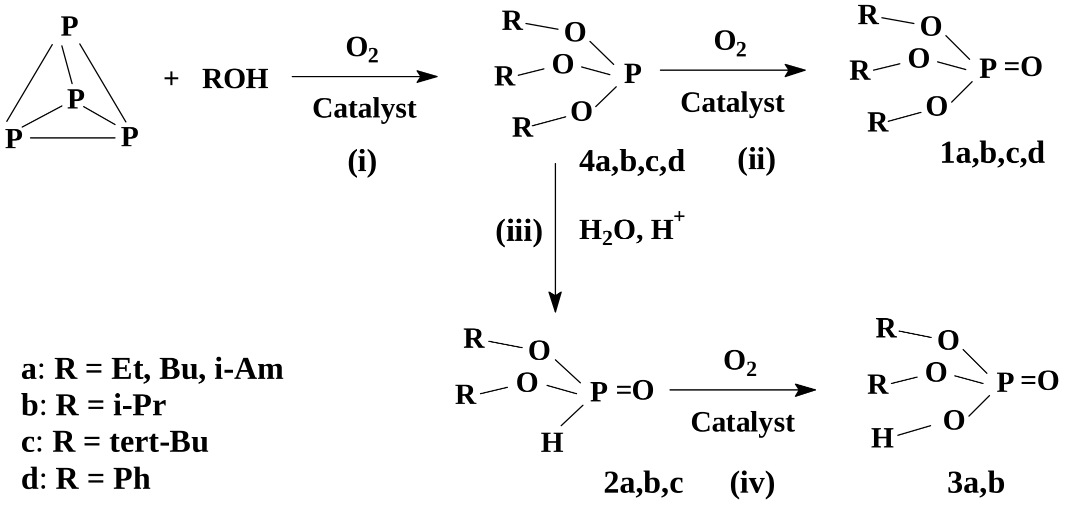
Thus, one can notice that catalytic reactions of the oxidative alko(aro)xylation of white phosphorus are quite innovative and not characteristic for the known chemistry of elemental phosphorus. The novelty and potentiality of the catalytic functionalisation of white phosphorus is confirmed by the patent [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 P_4 with aliphatic and aromatic alcohols described in Scheme 2. Relevant steps of the process may be considered: (i) the oxidative alko(aro)xylation of P_4 to $P(OR)_3$ **4**, (ii) the oxidation of $P(OR)_3$ **4** to $PO(OR)_3$ **1**, (iii) the dealkylation of $P(OR)_3$ **4** to $P(O)H(OR)_2$ **2**, and (iv) the oxidation of $P(O)H(OR)_2$ **2** to $P(O)(OH)(OR)_2$ **3**.

In their turn, the steps (i), (ii), and (iv) with CuX_2 and FeX_3 proceed *via* the repeated stages of the complexation of both ROH and P_4 (as well as **4** or **2**) to metal ion, the reduction of catalyst by P_4 (as well as by **4** or **2**), and its reoxidation by oxygen. In the presence of the catalytic $FeCl_3$-I_2 system, the stages of the oxidation of P_4 by I_2 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 $P(OR)_3$ (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 CuX_2 and mixed $FeCl_3$-I_2 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 P_4 catalysed by the CuX_2 or FeX_3 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 CuX_2 and FeX_3 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



Scheme2

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 P_4 (or its derivative) and ROH to metal ion, the reduction of catalyst by P_4 (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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