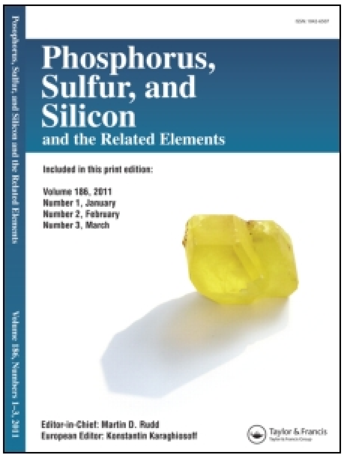

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# CHLORINE FREE SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS BASED ON THE FUNCTIONALIZATION OF WHITE PHOSPHORUS ($P_4$)

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# CHLORINE FREE SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS BASED ON THE FUNCTIONALIZATION OF WHITE PHOSPHORUS ($P_4$)*

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Oxidative alkoxylations of $P_4$ in toluene-alcohol solutions are studied. These reactions need oxygen, a catalyst ($PdCl_2$, $RuOHCl_3$, $RuCl_3$) and a co-oxidant ($CuCl_2$, $NaNO_2$, $FeCl_3$, 1,4-benzoquinone, $NaBrO_3$). Trialkylphosphates $(RO)_3P(O)$ and dialkylphosphites $(RO)_2P(O)H$ are the major products of the reaction. Kinetic experiments concerning the rate of absorption of $O_2$ during these reactions are also reported.

*Keywords:* white phosphorus; phosphate; phosphite; catalysis

## INTRODUCTION

Organic phosphorus derivatives are widely known and used since more than one century. Most of the methods of synthesis of such compounds involve the use of $POCl_3$or $PCl_5$, which are obtained using chlorine,[1] a gas highly toxic for the environment. Thus, the search for environmental friendly methods of synthesis of organophosphorus derivatives remains a challenge. Phosphorus sludge from manufacturing plants, not utilized nowadays, contains white phosphorus ($P_4$), which could be a good precur-

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* Dedicated to the memory of Professor Ya. A. Dorfman (1938–1996)

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sor for the synthesis of organophosphorus compounds. The use of such wastes should offer a way both to eliminate them and to valorize them. The problem in this perspective is to find a way to activate $P_4$.

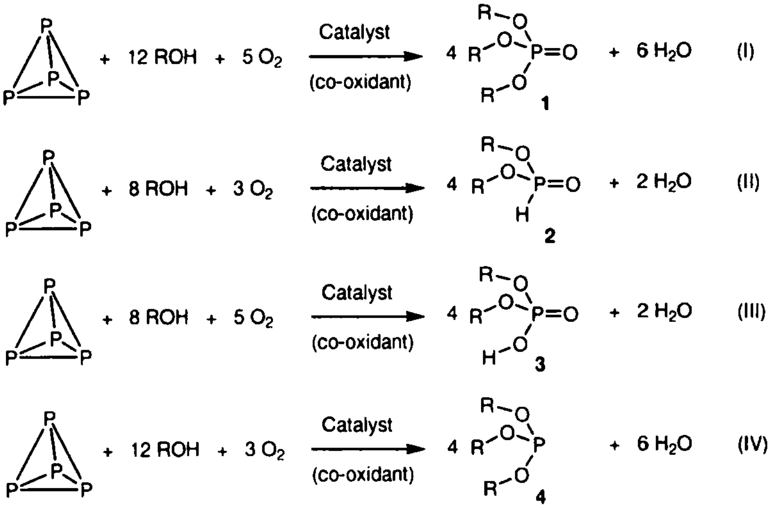
Some of us have reported that white phosphorus is converted to organic phosphates and phosphites via oxidation by oxygen in alcohol-arene solutions of copper (II) salts (halides, carboxylates).[2] At least four types of organophosphorus derivatives with P-O bonds are obtained in this case: trialkylphosphate $(RO)_3P{=}O$ **1**, dialkylphosphite $(RO)_2P(O)H$ **2**, dialkylphosphate $(RO)_2P(O)OH$ **3**, and trialkylphosphite $(RO)_3P$ **4** (Scheme 1, ways (I)-(IV), with $CuX_2$ as catalyst and no co-oxidant). Depending on the ligands of copper, the ratio of products changes; for instance, $CuCl_2$ favors the ways (I) and (II). Thus, it appeared interesting to test other types of transition metal catalysts, to have a more precise insight into the coupling reaction between alcohols and $P_4$, and to see if it is possible to direct the reaction toward the predominant formation of one compound with P-O bonds, or even toward the formation of compounds with P-C bonds. Indeed, it is well known that $P_4$ reacts with transition metal derivatives to afford complexes containing a large variety of $P_x$ ligands ($1 \leq x \leq 12$)[3] even if few examples result in the functionalization of the $P_4$ molecule.[4] In this perspective, we decided to test noble transition metal catalysts such as Pd and Ru derivatives, which could induce the reaction of the C-H bond of alcohol in addition to (or instead of) the reaction of the O-H bond.

We report here several experiments concerning the reaction of white phosphorus with 1-butanol in the presence of various catalysts, and the extension of this reaction to other alcohols. First experiments were kinetic and gas chromatography studies. Other experiments were carried out at a laboratory scale (grams) in order to identify the products by $^{31}P$ NMR, and to isolate them.

## RESULTS AND DISCUSSION

### Kinetic experiments

We have carried out reactions between $P_4$ in toluene solution, and butanol at 70°C in the presence of oxygen (60%) and of two types of catalysts, either $PdCl_2$ or $RuOHCl_3$. In order to hasten the reactions, the metal salt is used in a large amount, between 2.5 and 3.12 equivalents for each phos-



SCHEME 1

phorus atom, i.e. between 10 and 12.5 equivalents of metal salt for each $P_4$ (Table I). Such a large amount of catalyst is needed for productivity and safety reasons. Indeed, $P_4$ is added at once for these kinetic experiments, and the only way to preclude the radical chain reaction of $O_2$, which affords various phosphorus oxides such as $P_4O_6$ and $P_4O_{10}$, is to use also the catalyst as electrons receptor. The reaction is monitored by the absorption of $O_2$, and the percentage of tributylphosphate formed is determined by gas chromatography at periodic intervals.

A brown precipitate appears when $PdCl_2$ is used as catalyst, but no organophosphorus compounds are yielded, and no oxygen is absorbed, even if it is known that $P_4$ may react with $O_2$ to form $P_4O_{10}$. It means that $PdCl_2$ alone cannot oxidize $P_4$ and presumably forms stable phosphides (the brown precipitate) which do not undergo alcoholysis. Thus, a co-oxidant is needed to carry out the reaction. We used three types of reversible co-oxidants: $CuCl_2$, $NaNO_2$, and $FeCl_3$, whose reduced forms (CuCl, NaNO, $FeCl_2$) can be reoxidized by $O_2$ (Table I, runs 1–3). The kinetic curves concerning the rate of $O_2$ absorption illustrate the influence of the nature of the co-oxidant on the course of $P_4$ oxidation (Figure 1). The three curves have a fallen form, due to the fact that the reaction rates are fast at the beginning but rapidly decreases. The reaction is finished within 60 min

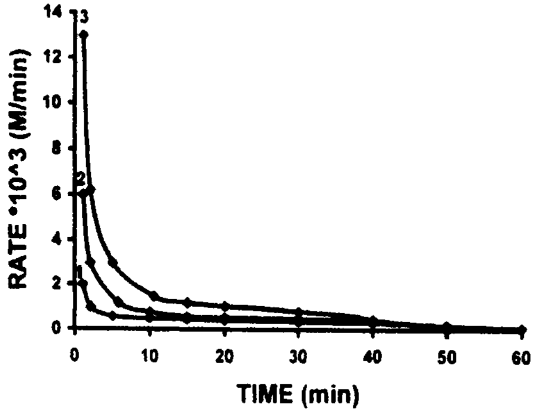


FIGURE 1 Kinetic curves of $O_2$ absorption at 70°C by a catalytic solution including the following components (concentrations in M): – 1: $PdCl_2$ (0.1), $CuCl_2$ (0.15), BuOH (9.8), PhMe (0.9), $P_4$ ($9\ 10^{-3}$), $O_2$ ($1.9\ 10^{-3}$) – 2: $PdCl_2$ (0.1), $NaNO_2$ (0.4), BuOH (9.8), PhMe (0.9), $P_4$ ($8\ 10^{-3}$), $O_2$ ($1.9\ 10^{-3}$) – 3 : $PdCl_2$ (0.1), $FeCl_3$ (0.11), BuOH (9.8), PhMe (0.9), $P_4$ ($9\ 10^{-3}$), $O_2$ ($1.9\ 10^{-3}$)

with $CuCl_2$ (run 1), and within 40 min. with $FeCl_3$ (run 3). Thus, the reaction rate increases in the series $CuCl_2 < NaNO_2 < FeCl_3$. Gas chromatography analysis of the reaction products indicates the formation of $(BuO)_3P(O)$ **1a** as the major product when $CuCl_2$ is used as co-oxidant (69% yield for run 1) (Scheme 1, way (I), R = Bu). The phosphate **1a** is also obtained in runs 2 and 3, but only in 16 and 9% yield, respectively.

In a second series of experiments, we used $RuOHCl_3$ as catalyst. Addition of a toluene solution of $P_4$ to a butanol solution of $RuOHCl_3$ at 70°C in 60% $O_2$ atmosphere is accompanied by some $O_2$ absorption, but no organophosphorus compounds are formed, as evidenced by gas chromatography. Thus, a co-oxidant is needed in this case also, and we choose again $CuCl_2$, $NaNO_2$ and $FeCl_3$ for this purpose (Table I, runs 4–6). Kinetic curves concerning the rate of absorption of oxygen have also a fallen form (Figure 2). The reaction rate increases in the series $CuCl_2 <$ $NaNO_2 < FeCl_3$ as seen previously for the $PdCl_2$ series. The reaction is finished within 100 minutes with $CuCl_2$ and within 30 minutes with $FeCl_3$. Gas chromatography analysis indicates that the larger amount of phosphate **1a** is obtained again with $CuCl_2$ as oxidant (47% yield, run 4). Compound **1a** is obtained only in 6 and 17% yield for runs 5 and 6, respectively (Table I).

TABLE I Conditions for kinetic experiments with butanol and 60% $O_2$ at 70°C

| Catalyst | Ratio Cat./P | Co-oxidant | Ratio Co-oxid./P | Ratio Cat./Co-ox | $O_2$ absorption | %. of 1a$^a$ $(BuO)_3$ |
|---|---|---|---|---|---|---|
| $PdCl_2$ | 2.78 | $CuCl_2$ | 4.17 | 0.7 | slow | 69 |
| $PdCl_2$ | 3.12 | $NaNO_2$ | 12.5 | 0.25 | moderate | 16 |
| $PdCl_2$ | 2.78 | $FeCl_3$ | 3.06 | 0.7 | high | 9 |
| $RuOHCl_3$ | 2.5 | $CuCl_2$ | 2.08 | 1.2 | slow | 47 |
| $RuOHCl_3$ | 2.81 | $NaNO_2$ | 4.69 | 0.6 | moderate | 6 |
| $RuOHCl_3$ | 2.81 | $FeCl_3$ | 2.34 | 1.2 | high | 17 |

ed by gas chromatography

## Characterization and isolation of phosphates and phosphites

In order to get more precise information concerning the type of organophosphorus compounds formed, we have carried out again reactions with the systems $PdCl_2$ – co-oxidant and $RuOHCl_3$ – co-oxidant (co-oxidant = $CuCl_2$, $NaNO_2$, $FeCl_3$) in different conditions. These experiments have been done at a preparative scale, to get $^{31}P$ NMR spectra and to isolate the products. The main difference with the kinetic experiments concerns the amount of reagents used, and particularly the catalyst/phosphorus ratio which is much lower for the preparative scale experiments (Table II, runs $1^*$-$6^*$). $P_4$ is added portionnaly in these cases, thus the relative instantaneous ratio catalyst/$P_4$ is always in favor of the catalyst. In addition to the preparative scale experiments done for comparison with the kinetic experiments, other conditions have been used such as changes in the nature of: *i*) the co-oxidant (benzoquinone, $NaBrO_3$), *ii*) the catalyst ($RuCl_3,xH_2O$), *iii*) the alcohol (isopropyl alcohol). Table II summarizes the conditions used for all the experiments and the results. The reactions are monitored by $^{31}P$ NMR (when applicable), which indicates in most cases the formation of several products in variable amounts.

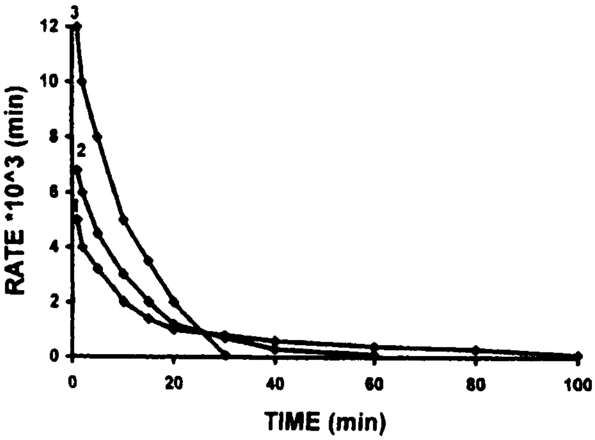


FIGURE 2 Kinetic curves of $O_2$ absorption at 70°C by a catalytic solution including the following components (concentrations in M): – 1: $RuOHCl_3$ (0.18), $CuCl_2$ (0.15), BuOH (8.7), PhMe (1.9), $P_4$ ($1.8\ 10^{-2}$), $O_2$ ($1.9\ 10^{-3}$) – 2: $RuOHCl_3$ (0.18), $NaNO_2$ (0.30), BuOH (8.7), PhMe (1.9), $P_4$ ($1.6\ 10^{-2}$), $O_2$ ($1.9\ 10^{-3}$) – 3: $RuOHCl_3$ (0.18), $FeCl_3$ (0.15), BuOH (8.7), PhMe (1.9), $P_4$ ($1.6\ 10^{-2}$), $O_2$ ($1.9\ 10^{-3}$)

TABLE II Conditions for preparative-scale runs

| *Catalyst* | *Ratio Cat./P* | *Co-oxidant* | *Ratio Co-ox./P* | *Ratio Cat ./Co-ox.* | *Oxidant* | *Temp. °C* | *Compounds identified by $^{31}P$ NMR* | *Compou isolated* |
|---|---|---|---|---|---|---|---|---|
| $PdCl_2$ | 0.08 | $CuCl_2$ | 0.79 | 0.1 | air | 80 | **1a** (maj.), **2a** (min.)[a] | **1a** (54.2), **2** |
| $PdCl_2$ | 0.09 | $NaNO_2$ | 0.86 | 0.1 | air | 80 | **1a** (ε), **2a** (maj.), **3a** (min.) | **1a** (3.8), **2** |
| $PdCl_2$ | 0.09 | $FeCl_3$ | 0.09 | 0.1 | air | 70 | [b] | **1a** (ε), **2a** |
| $RuOHCl_3$ | 0.05 | $CuCl_2$ | 0.37 | 0.09 | air | 80 | **1a** (maj.), **3a** (min.)[a] | **1a** (33.7), **3** |
| $RuOHCl_3$ | 0.16 | $NaNO_2$ | 1.49 | 0.16 | air | 80 | **1a** (min.), **2a** (maj.), **3a** (min.) | **1a, 2a** ( |
| $RuOHCl_3$ | 0.08 | $FeCl_3$ | 0.33 | 0.24 | air | 80 | [b] | **1a** (13), |
| $RuOHCl_3$ | 0.16 | $O=(C_6H_4)=O$ | 0.95 | 0.35 | air | 80 | **4a** | **1a, 2a** ( |
| $RuOHCl_3$ | 0.28 | $NaBrO_3$ | 3.17 | 0.09 | $NaBrO_3$ | 70 | **1a** (almost single), **3a** (ε) | **1a** |
| $RuCl_3.xH_2O$ | 0.16 | $NaBrO_3$ | 0.70 | 0.25 | air | 70 | **1a** (maj.), **2a** (min.), **3a** (ε), **4a** (min.) | **1a** (8), **2a** |
| $RuOHCl_3$ | 0.37 | $NaBrO_3$ | 2.26 | 0.16 | $NaBrO_3$ | 65 | **1b** (min.), **3b** (maj.) | **1b, 3b** ( |

udies have been carried out with these catalysts and co-oxidants, see Table I

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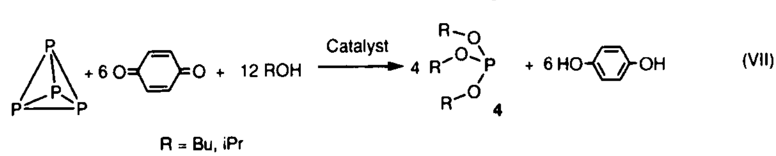
First experiments were conducted with $PdCl_2$ as catalysts, by bubbling air through a toluene solution containing $P_4$, butanol, and various co-oxidants. The $^{31}P$ NMR spectrum of the crude reaction products obtained with $NaNO_2$ as co-oxidant (run $2^*$) indicates the formation of one major compound, the phosphite $(BuO)_2P(O)H$ **2a** ($\delta$ $^{31}P = 7.9$ ppm, $^1J_{PH} = 692$ Hz, $^3J_{PH} = 8.5$ Hz) (Scheme 1, way (II), R = Bu). One minor compound, the phosphate $(BuO)_2P(O)OH$ **3a** ($\delta$ $^{31}P = 0.9$ ppm) and a few small signals, including one corresponding to the phosphate $(BuO)_3P(O)$ **1a** ($\delta$ $^{31}P = -0.5$ ppm) are also observed. High vacuum distillation allows isolating compound **2a** in 52% yield, and compound **1a** in 3.8% yield.

The presence of $CuCl_2$ (run $1^*$) or $FeCl_3$ (run $3^*$) as co-oxidant precludes the use of $^{31}P$ NMR to characterize the crude reaction product, due to paramagnetism. In the case of $CuCl_2$, addition of $Na_2SO_3$, stirring overnight of the resulting suspension, then filtration gives a solution that does not contain paramagnetic compounds, and is suitable for NMR experiments. Two main peaks are observed, the major one corresponding to compound **1a**, and the minor one to compound **2a**. It must be noted that both compounds are also obtained when $CuCl_2$ alone is used.[3] High vacuum distillation allows isolating both compounds in 54.2% and 21.6% yield, respectively. In the case of the use of $FeCl_3$ as co-oxidant, we did not succeeded to eliminate paramagnetism; thus it was impossible to run $^{31}P$ NMR of the crude reaction products. High vacuum distillation affords compound **2a** as the major product (35.6% yield) and one drop of compound **1a** (Table II, run $3^*$).

A second series of preparative scale experiments has been carried out with $RuOHCl_3$ as catalyst. The use of $CuCl_2$, $NaNO_2$, and $FeCl_3$ as co-oxidant (Table II, runs $4^*$-$6^*$) deserves the same remarks than with $PdCl_2$: the crude reaction products can be analyzed by $^{31}P$ NMR with $NaNO_2$ and with $CuCl_2$ (after treatment with $Na_2SO_3$ in this case), but not with $FeCl_3$. The phosphate **1a** is isolated as the major product when $CuCl_2$ is used (33.7% yield, run $4^*$), whereas the phosphate **3a** is isolated in 11.3% yield. The later compound may be formed either according to way (III) (Scheme 1) or by direct reaction of water generated in situ, instead of butanol. We did not succeeded in isolating a compound when $NaNO_2$ was used, only a 1/1 mixture of **1a** and **2a** was obtained after distillation; however, $^{31}P$ NMR of the crude reaction products indicates that compound **1a** is a minor component (run $5^*$). Compound **1a** is also obtained and isolated when $FeCl_3$ was used, but in a small yield (13%, run $6^*$).

Thus, one can notice that there is a fairly good correlation between the results of the kinetic (runs 1–6) and preparative scale (runs 1*-6*) experiments concerning the amount of tributylphosphate formed in each case.

Then we have extended these preparative scale experiments to other co-oxidants such as benzoquinone and $NaBrO_3$. These are unreversible co-oxidants in the conditions used, since their reduced forms ($C_6H_4(OH)_2$ and NaBr) cannot be reoxidized by $O_2$. Benzoquinone leads to the initial formation of a single product, identified as the tributylphosphite $(BuO)_3P$ **4a** ($\delta\ ^{31}P = 133$ ppm). High vacuum distillation of this compound leads to the formation of the oxide **1a** and the phosphite **2a** (run 7). The latter compound comes from acidolysis of **4a**, certainly due to acid generated in situ, owing to the solvolysis of the transition metal salt in polar solvents. The use of $NaBrO_3$ as co-oxidant leads to the formation of almost a single product, the phosphate **1a** (run 8). This experiment has been carried out in the absence of oxygen, $NaBrO_3$ plays both the role of oxidant and co-oxidant in this case. Indeed, $NaBrO_3$ and benzoquinone independently oxidize $P_4$ without $O_2$, according to the catalytic ways (V-VII) (Scheme 2).

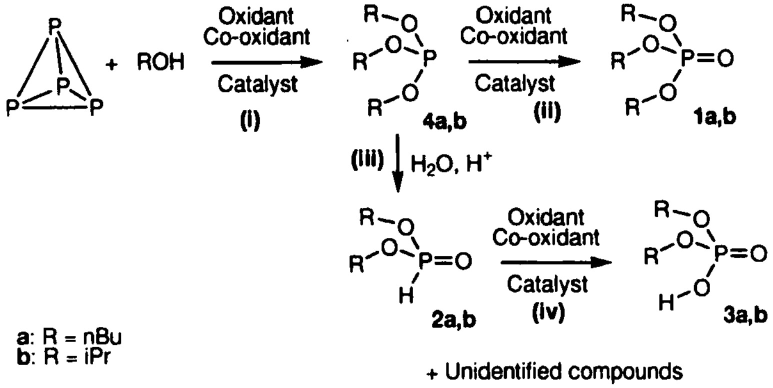


SCHEME 2

$NaBrO_3$ gives the cleanest results with $RuOHCl_3$ as catalyst; it was interesting to test if this co-oxidant gives analogous results with another catalyst ($RuCl_3$,$xH_2O$) or with another alcohol (iPrOH). In fact, the use of the system $RuCl_3$-$NaBrO_3$ induces the formation of a complex mixture, according to $^{31}P$ NMR (run 9). The major compound is the phosphate **1a**, and many other peaks are observed, three of them corresponding to the phosphite **2a**, the phosphate **3a**, and the phosphite **4a**. The large number of products formed explains the low yield of the products isolated after distillation (8% for **1a** and 7% for **2a**).

Finally, we tried to extend the catalytic alkoxylation of $P_4$ to a secondary alcohol, iPrOH. We used the $RuOHCl_3$-$NaBrO_3$ system in the absence of $O_2$, which gave the best results in the case of butanol. The result obtained with isopropanol is different (run 10). The major product is $(iPrO)_2P(O)OH$ **3b**, whereas $(iPrO)_3P(O)$ **1b** is a minor product (Scheme 1, R = iPr).

Thus, experimental data and products composition suggest the redox multi-step mechanism of the catalytic conversion of $P_4$ described in Scheme 3. Key steps in the process are: i) oxidative alkoxylation of $P_4$ to $(RO)_3P$ **4**, ii) oxidation of $(RO)_3P$ **4** to $(RO)_3P(O)$ **1**, iii) dealkylation of $(RO)_3P$ **4** to $(RO)_2P(O)H$ **2**, and iv) oxidation of $(RO)_2P(O)H$ **2** to $(RO)_2P(O)OH$ **3**. The stages i), ii), and iv) proceed into the coordination sphere of the catalyst. Dealkylation of $(RO)_3P$ (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 stages (i-iv). The predominant formation of **3b** with iPrOH points that step (iv) is accelerated in the case of secondary alcohols.



Oxidant: $O_2$, $NaBrO_3$
Co-oxidant: $CuCl_2$, $NaNO_2$, $FeCl_3$, $O=(C_6H_4)=O$, $NaBrO_3$
Catalyst: $PdCl_2$, $RuOHCl_3$, $[RuCl_3.xH_2O]$

SCHEME 3

## CONCLUSION

We have shown that many parameters influence the catalytic oxidative alkoxylation of white phosphorus. The most important factors are the type of catalyst, the type of co-oxidant, and the type of alcohol used. Noble transition metal catalysts do not dramatically change the type of reactions observed, when compared to $CuCl_2$ alone. Indeed, in all cases, compounds with P-O bonds are obtained; only the ratio of the various P-O compounds changes. If compounds with P-C bonds are obtained, it is only as traces, which may correspond to some of the very small peaks observed by $^{31}P$ NMR in most experiments (for instance $\delta = 31$ ppm might correspond to $(O)P(Bu)(OBu)_2$). However, none of them are isolable. The type of co-oxidant seems to play a major role; both $CuCl_2$and $NaBrO_3$ favors the formation of the trialkylphosphate, as evidenced by chromatography analyses and $^{31}P$ NMR spectroscopy. Work is in progress to test other systems using cheaper catalysts to functionalize the $P_4$ molecule.

## EXPERIMENTAL SECTION

### General

#### *Starting materials*

The gases ($O_2$, $N_2$, and Ar) were dried over $CaCl_2$. The alcohols and arenes were purified and dried by the usual methods. The catalysts and co-oxidants ($RuOHCl_3$, $RuCl_3$, $PdCl_2$, $CuCl_2$, $FeCl_3$, $NaNO_2$, $NaBrO_3$, 1,4-benzoquinone) were used after drying under vacuum. The solid $P_4$ was weighed in a beaker under water, dipped into two successive beakers containing THF, dried under vacuum at $10^{-2}$ mm Hg for ca. 30 min and then dissolved in toluene at its melting temperature 45–50°C. The concentration of $P_4$ in the solution ($[P_4]$, mol/l) was determined by iodometry.

#### *Safety Note*

White phosphorus is flammable in air and must be handled as soon and carefully as possible. No explosions occurred during these experiments, thanks to the presence of catalysts and co-oxidants. However, it is known that bubbling oxygen through solutions of $P_4$ may frequently result in violent explosions. Thus, it is strongly recommended to conduct these reactions behind shields.

### *Products analysis*

Tributylphosphate **1a** was detected by gas chromatography (Model-3700 Chromatograph equipped with a flameionization detector, and column packed with Chromaton impregnated with 5% Apiezon-L). Nuclear magnetic resonance (NMR) spectra 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 $Me_4Si$ ($^1H$ and $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$). Coupling constants (J) are given in hertz. Elemental analysis was obtained on Perkin-Elmer Model 2400, by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. Vacuum distillation of products was perfomed on BUCHI GKR-51.

### *Kinetic studie*

Kinetics of the catalytic reactions of the oxidative alkoxylation of $P_4$ were studied with a volumetric installation consisting of a thermostated glass reactor (total volume of the solution is 10–15 mL) connected with a gasometric burette for the measurement of $O_2$ absorbed. The reactions were conducted at 70°C under non-stationary conditions in which kinetic control is ensured until $P_4$ is completely consumed. The kinetic regime was reached at shaking of the reactor with frequency about 250–300 swingings per minute.

The experiments were performed as follows. Alcohol was poured into the reactor, then the catalytic system ($PdCl_2$-$CuCl_2$, $PdCl_2$-$NaNO_2$, $PdCl_2$-$FeCl_3$, $RuOHCl_3$-$CuCl_2$, $RuOHCl_3$-$NaNO_2$, $RuOHCl_3$-$FeCl_3$) was added and the shaking and heating to the required temperature (70°C) were switched on, untill catalyst was dissolved. Then, the shaker was stopped to add the toluene solution of $P_4$ ($P_4$/PhMe) through tube into the catalyst solution. The atmosphere contains 60% $O_2$. Usually the initial volume of the liquid phase in the reactor was 10 mL. We took as a zero point for the kinetic measurements that instant of time when the shaker was switched on and heated for the second time. In the course of the reactions the rate of $O_2$ absorption was continuously measured. Samples were taken at periodic intervals and subjected to GC analysis.

### *Kinetic runs 1–6*

The initial limpid solution (brown for the systems $PdCl_2$-$CuCl_2$, $PdCl_2$-$NaNO_2$, $PdCl_2$-$FeCl_3$, and $RuOHCl_3$-$FeCl_3$, dark-green for the systems $RuOHCl_3$-$CuCl_2$, and $RuOHCl_3$-$NaNO_2$) heated at 70°C became darker (dark-brown or black) after addition of the toluene solution of $P_4$. The colour of the solution did not changed in the course of $O_2$ absorption. A white deposit of CuCl appeared when $CuCl_2$ was used.

## Preparative scale studies

Laboratory-scale runs were carried out to be analyzed by $^{31}P$ NMR and to separate the reaction products. 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. The constant reaction temperature (65–80°C) was supported with an oil bath, under vigorous magnetic stirring. A toluene solution of $P_4$ (15–30 mL) was portionally added to the alcohol solution containing the catalyst (6–15 mL) by syringe through a rubber plug during 5–8 hours. The gradual addition of $P_4$ was aimed to prevent the formation of white vapor of $P_4O_{10}$. The volumetric rate of air barbotage was 40–60 $hour^{-1}$ (80–120 mL/min). The crude reaction products were analyzed by $^{31}P$ NMR when possible, it means when there were no paramagnetic species, neither $CuCl_2$, nor $FeCl_3$. In order to eliminate paramagnetic compounds, $Na_2SO_3$ (3 to 10 g) was added, and the resulting suspension was stirred overnight, when $CuCl_2$ was used. The suspension was filtered and the solution was analyzed by $^{31}P$ NMR. Such procedure did not removed paramagnetism when $FeCl_3$ was used; thus the crude reaction products were not analyzed in these cases. High vacuum distillation of dark oil remaining after stripping off the excess of alcohol and toluene yields the organophosphorus products as colorless oils.

## Preparative scale runs 1*-6*, 7–10

The toluene solution of $P_4$ was slowly added (four to eight hours) to a heated solution of catalyst and co-oxidant in alcohol. The solution was filtered when a precipitate was formed, then concentrated and distilled under high vacuum. The experimental data concerning these runs are gathered in Table III.

TABLE III Experimental data for preparative-scale runs

| *luene mL* | $P_4$ *g* | *Catalyst (g)* | *Co-oxidant (g)* | *alcohol (mL)* | *Temp. °C* | *Compounds isolated (* |
|---|---|---|---|---|---|---|
| 30 | 0.59 | $PdCl_2$ (0.27) | $CuCl_2$ (2.0) | BuOH (8) | 80 | **1a** (2.74), **2a** (0.8) |
| 25 | 0.50 | $PdCl_2$ (0.27) | $NaNO_2$(1.0) | BuOH (7) | 80 | **1a** (0.16), **2a** (1.6) |
| 30 | 0.50 | $PdCl_2$ (0.27) | $FeCl_3$ (0.24) | BuOH (7) | 70 | **1a** (traces), **2a** (1.1) |
| 50 | 1.18 | $RuOHCl_3$ (0.45) | $CuCl_2$ (2.88) | BuOH (15) | 80 | **1a** (3.4), **3a** (0.9) |
| 15 | 0.3 | $RuOHCl_3$ (1.0) | $NaNO_2$ (2.0) | BuOH (7) | 80 | **1a, 2a** (1/1, not separat |
| 30 | 0.7 | $RuOHCl_3$ (0.4) | $FeCl_3$ (1.2) | BuOH (9) | 80 | **1a** (0.78), **2a** (traces |
| 15 | 0.3 | $RuOHCl_3$ (0.75) | $O{=}(C_6H_4){=}O$ (1.0) | BuOH (7) | 80 | **1a, 2a** (1/3, not separat |
| 10 | 0.11 | $RuOHCl_3$ (0.22) | $NaBrO_3$ (1.7) | BuOH (9) | 80 | **1a** (traces) |
| 20 | 0.44 | $RuCl_3{,}xH_2O$ (0.51) | $NaBrO_3$ (1.5) | BuOH (9) | 70 | **1a** (0.3), **2a** (0.2) |
| 10 | 0.28 | $RuOHCl_3$ (0.74) | $NaBrO_3$ (3.0) | iPrOH (8) | 65 | **1b, 3b** (5/1, not separat |

## Spectroscopic data

### 1a. Tributyl phosphate

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ - 0.51 ppm. $^{31}P$ NMR ($CDCl_3$): δ - 0.50 (sept., $^3J_{P\text{-}O\text{-}CH2}$ = 6.8 Hz) ppm. $^1H$ NMR ($CDCl_3$): δ 3.92 (m, 6H, $CH_2\alpha$), 1.56 (m, 6H, $CH_2$ β), 1.30 (m, 6H, $CH_2$ γ), 0.83 (m, 9H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 67.24 (d, $^2J_{CP}$ = 5.9 Hz, $CH_2\alpha$), 32.12 (d, $^3J_{CP}$ = 6.0 Hz, $CH_2\beta$), 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, 10.1. Found: C, 54.70; H, 10.10.

### 2a. Dibutyl phosphite

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 7.94 ppm. $^{31}P$ NMR ($CDCl_3$): δ 7.9 (dt, $^1J_{PH}$ = 692 Hz, $^3J_{P\text{-}O\text{-}CH2}$ = 8.5 Hz) ppm. $^1H$ NMR ($CDCl_3$): δ 6.7 (d. $^1J_{HP}$= 692 Hz, 1H, H-P), 3.95 (m. 4H, $CH_2$ α), 1.55 (m, 4H, CH, β), 1.31 (m, 4H, $CH_2$ χ), 0.84 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 65.39 (d, $^2J_{CP}$ = 5.8 Hz, $CH_2\alpha$), 32.21 (d, $^3J_{CP}$= 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

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.88 ppm. $^1H$ 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, $^3J_{HH}$ = 7 Hz, 6H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 67.18 (d, $^2J_{CP}$ = 6.0 Hz, $CH_2\alpha$), 32.06 (d, $^3J_{PC}$ = 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 and 3b. Di-isopropyl phosphate (~5:1 ratio not separated)

**1b**. $^{31}P\{^1H\}$ NMR (THF- $d_8$): δ 0.97 ppm. $^1H$ NMR (THF- $d_8$): δ 4.55 (m, 3H, CH α), 1.27 (d, $^3J_{HH}$ = 6.2 Hz, 18H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR (THF- $d_8$): δ 72.28 (d, $^2J_{CP}$= 5.8Hz, CH α), 24.38 (δ, $^3J_{CP}$ = 4.0Hz, $CH_3$) ppm. **3b**. $^{31}P\{^1H\}$ NMR (THF-$d_8$): δ 2.98 ppm. $^1H$ NMR (THF- $d_8$): δ 8.8 (s, 1H, HO-P), 4.54 (m, 2H, CH α), 1.28 (d, $^3J_{HH}$= 6.1 Hz, 12H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR (THF- $d_8$): δ 72.43 (d, $^2J_{CP}$ = 5.9 Hz, CH α), 24.25 (d, $^3J_{CP}$ = 4.5 Hz, $CH_3$) ppm.

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