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 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 ³¹P 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(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 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(C₃H₇CO₂)₂ becomes dark-green and brown after addition of P₄. 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 phos-

phite **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 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 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(C₃H₇CO₂)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