

adding the toluene solution of P₄ into a viscous mixture of PhOH, FeCl₃ and I₂ at 80°C followed by the air bubbling, 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.

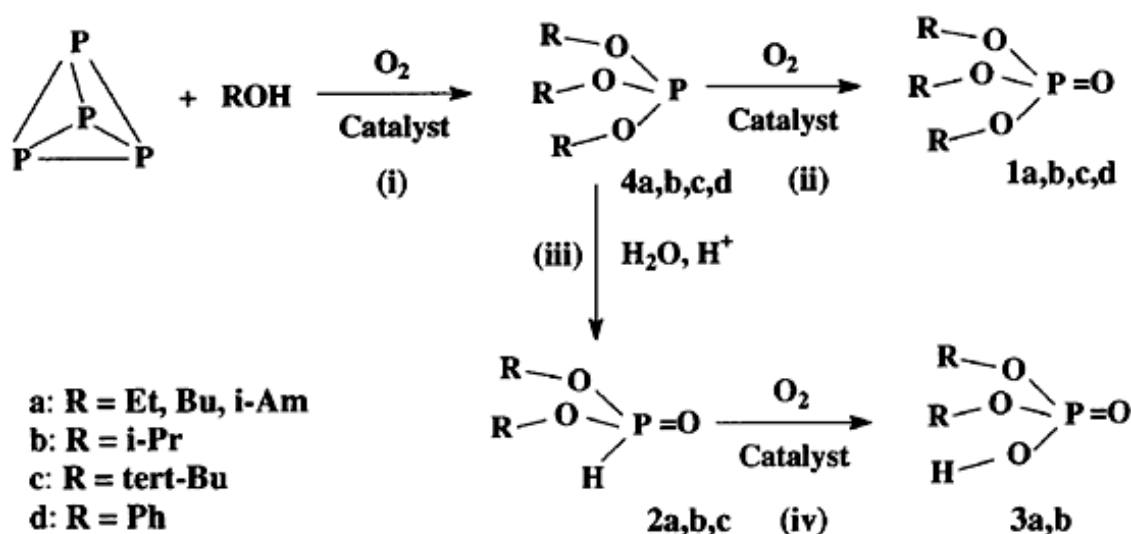
Despite of a variable nature of the catalytic systems and alcohols used, the experimental data and products composition indicate to a general features of the oxidative P-O coupling of P₄ with aliphatic and aromatic alcohols described in Scheme 2. Relevant steps of the process may be considered: (i) the oxidative alko(aro)xylation of P₄ to P(OR)₃ **4**, (ii) the oxidation of P(OR)₃ **4** to PO(OR)₂ **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 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)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 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



Scheme2