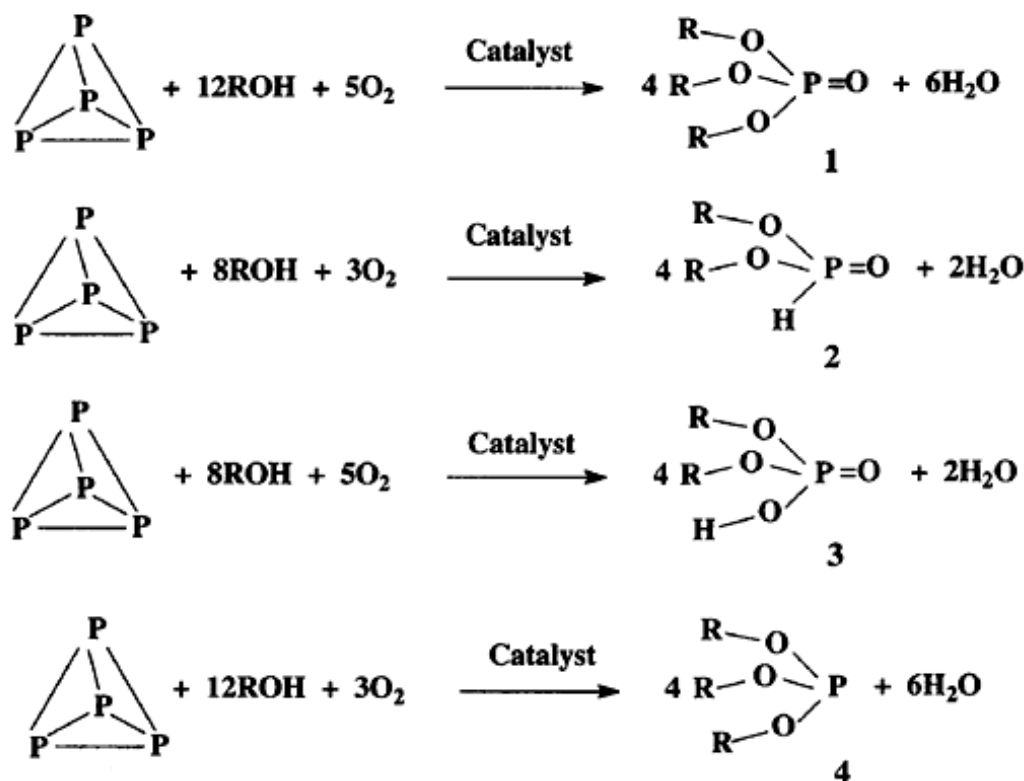


tion as both P₄ and catalyst are taken in the reaction in the dissolved forms. Depending on the reactions conditions, four types of organophosphorus derivatives bearing P-O bonds are formed and identified by

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).



It has been shown by the volumetry method [2-5] that the experimental O₂/P₄ 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 H₂O stimulates the side reaction of the oxidative hydroxylation of P₄ to phosphoric acid. Air was dried over CaCl₂. 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 P₄ 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 P₄ 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 P₄ may result in violent explosions. However, no explosions occurred during these experiments,