$^{31}P\{^1H\}$NMR ($CDCl_3$): δ -17.3 ppm; ^1H NMR ($CDCl_3$): δ 7.2-7.4 (m, 15H, C_6H_5) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): 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	$CuCl_2·2H_2O$ 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	$Cu(NO_3)_2·3H_2O$ 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	$Fe(NO_3)_3·9H_2O$ 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)