thanks to the presence of catalysts. Nevertheless, it is strongly recommended to conduct these reactions behind shields.

Products analysis

Nuclear magnetic resonance (NMR) spectra of the organophosphorus esters 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 (Hz). In order to eliminate paramagnetic $CuCl_2$ from the crude reaction solutions, Na_2SO_3 (3 to 10 g) was added, and the resulting suspension was stirred overnight. Such procedure did not removed paramagnetism when $FeCl_3$ was used; thus the crude reaction products were not analyzed by ^{31}P NMR in these cases. Elemental analysis was obtained on Perkin-Elmer Model 2400. Gas chromatography analysis were recorded on Chrompack 9002 chromatograph equipped with flameionization detector and the capillary columns CP SIL 19CB (25m × 0.25mm) and CP SIL 5CB (10m × 0.25mm).

Typical procedure

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 for catalytic synthesis of organophosphorus products. The constant reaction temperature (65-90°C) was supported with an oil bath, under vigorous magnetic stirring. An arene solution of P_4 (30-100 mL) was portionally added to the alcohol solution (10-180 mL) containing the catalyst by syringe through a rubber plug during 5-30 hours. The gradual addition of P_4 was aimed to prevent the formation of white smoke of P_2O_3 and P_4O_{10}. The rate of P_4 conversion was slowly decreased from portion to portion because the catalytic solution was gradually diluted by solvent (arene). The flow rate of air barbotage was 80-120 mL/min. The reactions were monitored by GC and ^{31}P NMR (when applicable), which indicates in most cases the formation of several products in variable amounts. After completing the synthesis, the catalyst was precipitated by K_2CO_3 and filtered from the solution. High vacuum distillation (BUCHI GKR-51) of dark oil remaining after stripping off the excess of alcohol and arene (the rotation evaporator ER-1M2) yields the individual organophosphorus products as colourless oils.

Physical and spectroscopic data

1a. Tributyl phosphate: bp. 130-132°C (2 mm Hg); $^{31}P\{^1H\}$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 α), 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 α), 32.12 (d, $^3J_{CP}$ = 6.0 Hz, CH_2 β), 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, 10.10. Found: C, 54.70; H, 10.10.

2a. Dibutyl phosphite: bp. 110°C (5 mm Hg); $^{31}P\{^1H\}$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_2 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, $^2J_{PC}$ = 5.8 Hz, CH_2 α), 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: bp. 100°C (10^{-4} mm Hg); $^{31}P\{^1H\}$ 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 α), 32.06 (d, $^3J_{CP}$ = 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: bp. 83-84°C (5 mm Hg); $^{31}P\{^1H\}$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, $^2J_{CP}$ = 5.8 Hz, CH α,), 24.38 (d, $^3J_{CP}$ = 4.0 Hz, CH_3) ppm.

2b. Di-isopropyl phosphite: bp. 91-92°C (20 mm Hg); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 4.6 ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 4.6 (d, $^1J_{PH}$ = 690 Hz) ppm. ^1H NMR ($CDCl_3$): δ 6.72 (d, $^1J_{PH}$ = 687 Hz, 1H, HP), 4.6 (m, 2H, CH), 1.24 (d, $^3J_{HH}$ = 6.2 Hz, 12H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 70.5 (d, $^2J_{CP}$ = 6 Hz, CH), 23.6 (br d, $^2J_{CP}$ = 5 Hz, CH_3) ppm.

3b. Di-isopropyl phosphate: bp. 94°C (10^{-4} mm Hg); $^{31}P\{^1H\}$NMR (THF-d_8): δ 2.98 ppm.

$^{31}P\{^1H\}$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.

1d. Triphenyl phosphate: bp. 244°C (10 mm Hg);