An efficient strategy for the synthesis of 1-chloroethyl phosphates and phosphoramidates

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General methods. All the described reactions were performed under argon atmosphere. Column chromatography was performed with silica gel (0.063-0.200 mm mesh). ^{1}H, ^{13}C and ^{31}P NMR-spectra were recorded at 500.13, 125.78 and 200.46 MHz at 25ºC, respectively. TMS was used as an internal reference for ^{1}H and ^{13}C measurements and H_3PO_4 as an external reference for ^{31}P measurements. The splitting pattern abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The ^{1}H NMR parameters have been solved precisely with the PERCHit iterator[23] under PERCH software.[24] Electron impact or positive chemical ionization mass spectra were acquired by an gas chromatograph- mass spectrometry system. All reagents obtained from commercial suppliers were used without further purifications. Most of the products were oily compounds and difficult to obtain as analytically pure products. However, the spectral and GC-MS data of the compounds were consistent with those of the proposed structures.

Phosphoric acid diethyl ester vinyl ester 2b: 64 %, colorless oil. Chromatography eluent EtOAc:petrol ether 1:3. ^{1}H NMR ($CDCl_3$) δ 6.584 (1H, ddd, J=13.54 Hz, 5.87 Hz, $^{3}J_{HP}$=6.50 Hz), 4.901 (1H, ddd, J=13.54 Hz, 2.05 Hz, $^{4}J_{HP}$=1.19 Hz), 4.568 (1H, ddd, J=5.87 Hz, 2.05 Hz, $^{4}J_{HP}$=2.71 Hz),

4.174 (4H, dq, J=7.08 Hz, $^{3}J_{HP}$=8.28 Hz), 1.363 (6H, td, J=7.08 Hz, $^{3}J_{HP}$=1.01 Hz); ^{13}C NMR ($CDCl_3$) δ 142.17 (d, $^{2}J_{CP}$ = 5.6 Hz), 99.63 (d, $^{3}J_{CP}$ = 10.4 Hz), 64.33 (d, $^{2}J_{CP}$ = 5.8 Hz), 16.00 (d, $^{3}J_{CP}$ = 6.6 Hz); ^{31}P NMR ($CDCl_3$) δ -4.28. GC-MS *m/z* 180 (M).

Phosphoric acid bis-(2,2,2-trichloro-ethyl) ester vinyl ester 2c: 68 %, colorless oil. Chromatography eluent EtOAc:petrol ether 1:2. ^{1}H NMR ($CDCl_3$) δ 6.630 (1H, ddd, J=13.44 Hz, 5.78 Hz, $^{3}J_{HP}$=6.71 Hz), 5.082 (1H, ddd, J=13.44 Hz, 2.59 Hz, $^{4}J_{HP}$=1.30 Hz), 4.758 (1H, ddd, J=5.78 Hz, 2.59 Hz, $^{4}J_{HP}$=2.66 Hz), 4.680 (4H, d, $^{3}J_{HP}$=6.90 Hz); ^{13}C NMR ($CDCl_3$) δ 141.34 (d, $^{2}J_{CP}$ = 6.2 Hz), 102.17 (d, $^{3}J_{CP}$ = 10.6 Hz), 94.34 (d, $^{3}J_{CP}$ = 10.6 Hz), 77.42 (d, $^{2}J_{CP}$ = 4.5 Hz); ^{31}P NMR ($CDCl_3$) δ -7.59. GC-MS *m/z* 387 (M).

Phosphoric acid methyl ester phenyl ester vinyl ester 2d: 54 %, colorless oil. Chromatography eluent EtOAc:petrol ether 1:4. ^{1}H NMR ($CDCl_3$) δ 7.346 (2H, m, J=8.05 Hz, 7.40 Hz, $^{4}J_{HH}$=-1.74 Hz, $^{5}J_{HH}$= 0.77 Hz) , 7.218 (2H, m, J=8.05 Hz, $^{4}J_{HH}$=-1.20 Hz, -1.17 Hz, $^{5}J_{HH}$= 0.77 Hz, $^{4}J_{HP}$=1.19 Hz), 7.195 (1H, m, J=7.40, $^{4}J_{HH}$=-1.17), 6.634 (1H, ddd, J=13.50 Hz, 5.82 Hz and $^{3}J_{HP}$=6.59 Hz), 4.966 (1H, ddd, J=13.50 Hz, 2.27 Hz and $^{4}J_{HP}$=1.19 Hz), 4.825 (1H, ddd, J=5.82 Hz, 2.27 Hz and $^{4}J_{HP}$=2.80 Hz), 3.908 (3H, d, $^{3}J_{HP}$=11.51 Hz); ^{13}C NMR ($CDCl_3$) δ 150.36 (d, $^{2}J_{CP}$ = 6.9 Hz), 141.99 (d, $^{2}J_{CP}$ = 5.9 Hz), 129.85, 125.47, 120.01 (d, $^{3}J_{CP}$ = 4.8 Hz), 100.70 (d, $^{3}J_{CP}$ = 10.5 Hz), 55.23 (d, $^{2}J_{CP}$ = 6.2 Hz); ^{31}P NMR ($CDCl_3$) δ -8.79. GC-MS *m/z* 215 (M + 1).

Phosphoric acid bis-(2,6-dimethyl-phenyl) ester vinyl ester 2e: 35 %, colorless oil. Chromatography eluent EtOAc:petrol ether 1:20. ^{1}H NMR ($CDCl_3$) δ 7.044-6.977 (6H, m), 6.661 (1H, ddd, J=13.49 Hz, 5.77 Hz and $^{3}J_{HP}$=5.78 Hz), 4.840 (1H, ddd, J=13.49 Hz, 2.19 Hz and $^{4}J_{HP}$=1.01 Hz), 4.525 (1H, ddd, J=5.77 Hz, 2.19 Hz and $^{4}J_{HP}$=3.91 Hz), 2.343 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 147.99 (d, $^{2}J_{CP}$ = 8.6 Hz), 142.45 (d, $^{2}J_{CP}$ = 5.4 Hz), 130.29 (d, $^{3}J_{CP}$ = 3.4 Hz), 129.16 (d, $^{4}J_{CP}$ = 1.5 Hz), 125.54 (d, $^{5}J_{CP}$ = 1.7 Hz), 99.57 (d, $^{3}J_{CP}$ = 11.3 Hz), 17.00; ^{31}P NMR ($CDCl_3$) δ -14.69. GC-MS *m/z* 333 (M + 1).

2-vinyloxy-[1,3,2]dioxaphosphinane 2-oxide 2f: 76 %, colorless oil. Chromatography eluent EtOAc:petrol ether 1:1. ^{1}H NMR ($CDCl_3$) δ 6.611 (1H, ddd, J=13.56 Hz, 5.87 Hz and $^{3}J_{HP}$=7.47 Hz),

4.962 (1H, ddd, J=13.56 Hz, 2.28 Hz and $^{4}J_{HP}$=1.21 Hz), 4.637 (1H, ddd, J=5.87 Hz, 2.28 Hz and $^{4}J_{HP}$=2.12 Hz), 4.520-4.400 (4H, m), 2.390-2.287 (1H, m), 1.834-1.779 (1H, m); ^{13}C NMR ($CDCl_3$) δ 141.64 (d, $^{2}J_{CP}$ = 5.7 Hz), 100.22 (d, $^{3}J_{CP}$ = 9.9 Hz), 69.23 (d, $^{2}J_{CP}$ = 6.3 Hz), 25.42 (d, $^{3}J_{CP}$ = 7.3 Hz); ^{31}P NMR ($CDCl_3$) δ -11.15. GC-MS *m/z* 165 (M + 1).

Phosphoric acid diphenyl ester vinyl ester 2g: 70 %, light-yellow oil. Chromatography eluent EtOAc:petrol ether 1:4. ^{1}H NMR ($CDCl_3$) δ 7.451 (4H, m, J=8.20 Hz, 7.44 Hz, $^{4}J_{HH}$=-2.35 Hz, $^{5}J_{HH}$= 0.55 Hz), 7.290 (2H, m, J=7.44, $^{4}J_{HH}$=-1.04), 7.265 (4H, m, J=8.20 Hz, $^{4}J_{HH}$=-2.06 Hz, -1.04 Hz, $^{5}J_{HH}$= 0.55 Hz, $^{4}J_{HP}$=1.22 Hz), 6.845 (1H, ddd, J=13.34 Hz, 5.76 Hz and $^{3}J_{HP}$=6.82 Hz), 5.056 (1H, ddd, J=13.34 Hz, 2.38 Hz and $^{4}J_{HP}$=1.23 Hz), 4.825 (1H, ddd, J=5.76 Hz, 2.38 Hz and $^{4}J_{HP}$=2.79 Hz).

Phosphoric acid dibenzyl ester vinyl ester 2h: 30 %, colorless oil. Chromatography eluent EtOAc:petrol ether 1:4. ^{1}H NMR ($CDCl_3$) δ 7.386-7.314 (12H, m), 6.529 (1H, ddd, J=13.51 Hz, 5.85 Hz and $^{3}J_{HP}$=6.51 Hz), 5.083 (4H, d, $^{3}J_{HP}$=8.23), 4.862 (1H, ddd, J=13.51 Hz, 2.16 Hz and $^{4}J_{HP}$=1.23 Hz), 4.544 (1H, ddd, J=5.85 Hz, 2.16 Hz and $^{4}J_{HP}$=2.70 Hz); ^{13}C NMR ($CDCl_3$) δ 141.96 (d, $^{2}J_{CP}$ = 5.9 Hz), 135.40 (d, $^{3}J_{CP}$ = 6.9 Hz), 128.69, 128.62, 128.04, 100.23 (d, $^{3}J_{CP}$ = 10.4 Hz), 69.77 (d, $^{2}J_{CP}$ = 5.6 Hz); ^{31}P NMR ($CDCl_3$) δ 3.93. GC-MS *m/z* 305 (M + 1).

N,N-diethylphosphoramidic acid methyl ester vinyl ester 2i: 88 %, colorless oil. Chromatography eluent EtOAc:petrol ether 1:1. ^{1}H NMR ($CDCl_3$) δ 6.576 (1H, ddd, J=13.60 Hz, 5.93 Hz and $^{3}J_{HP}$=6.73 Hz), 4.827 (1H, ddd, J=13.60 Hz, 1.76 Hz and $^{4}J_{HP}$=1.33 Hz), 4.505 (1H, ddd, J=5.93 Hz, 1.76 Hz and $^{4}J_{HP}$=2.21 Hz), 3.722 (3H, d, $^{3}J_{HP}$=11.32 Hz), 3.104 (4H, dq, J=7.11 Hz, $^{3}J_{HP}$=11.87 Hz), 1.122 (6H, t, J=7.11 Hz; ^{13}C NMR ($CDCl_3$) δ 142.39 (d, $^{2}J_{CP}$ = 5.3 Hz), 98.88 (d, $^{3}J_{CP}$ = 10.2 Hz), 53.05 (d, $^{2}J_{CP}$ = 5.7 Hz), 39.79 (d, $^{2}J_{CP}$ = 4.5 Hz), 14.17 (d, $^{3}J_{CP}$ = 1.5 Hz); ^{31}P NMR ($CDCl_3$) δ -9.14. GC-MS *m/z* 193 (M).

Phosphoric acid 1-chloro-ethyl ester diethyl ester 3b: 91 % (without purification), yellow viscose oil. Chromatography eluent hexane:EtOAc 1:1. ^{1}H NMR ($CDCl_3$) δ 6.247 (1H, dq, J=5.61 Hz, $^{3}J_{HP}$=7.79 Hz), 4.201* (1H, ddq, $^{2}J_{HH}$= -10.07 Hz, J=7.10 Hz, $^{3}J_{HP}$= 7.79 Hz), 4.184* (1H, ddq, $^{2}J_{HH}$= -

10.07 Hz, J=7.05 Hz $^{3}J_{HP}$=8.05 Hz), 4.159* (1H, ddq, $^{2}J_{HH}$= -10.13 Hz, J=7.08 Hz, $^{3}J_{HP}$= 8.08 Hz), 4.136* (1H, ddq, $^{2}J_{HH}$= -10.13 Hz, J=7.06 Hz, $^{3}J_{HP}$= 7.99 Hz), 1.845 (3H, dd, J=5.61 Hz, $^{4}J_{HP}$= 1.03 Hz), 1.368 (3H, ddd, J=7.10 Hz, 7.05 Hz, $^{4}J_{HP}$=1.13 Hz), 1.358 (3H, ddd, J=7.08 Hz, 7.06 Hz, $^{4}J_{HP}$=1.09 Hz); ^{13}C NMR ($CDCl_3$) δ 85.72 (d, $^{2}J_{CP}$ = 6.3 Hz), 64.58* (d, $^{2}J_{CP}$ = 6.1 Hz), 64.33* (d, $^{2}J_{CP}$ = 5.8 Hz), 27.65 (d, $^{3}J_{CP}$ = 8.2 Hz), 16.02 (d, $^{3}J_{CP}$ = 6.9 Hz); ^{31}P NMR ($CDCl_3$) δ -3.11. GC-MS *m/z* 217 (M + 1), 181 (M - Cl). Anal. Calcd for $C_6H_{14}ClO_4P \cdot 0.6$ HCl: C, 30.22; H, 6.17. Found: C, 29.98; H, 5.94.

*Due to chiral center and prochirality there is four ^{1}H and two ^{13}C chemical shifts for OCH_2-groups

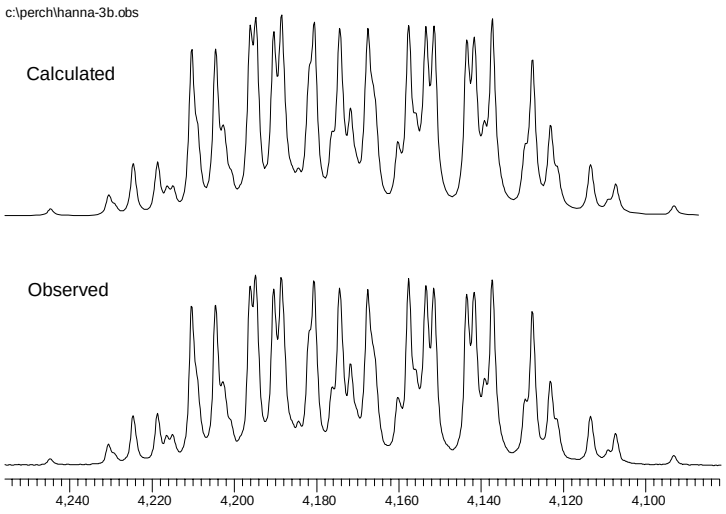

Figure 1. As an example of the complicate structure of the spectra the calculated and observed ^{1}H NMR spectrum for OCH_2-protons signals of **3b**[24]

Phosphoric acid 1-chloro-ethyl ester bis-(2,2,2-trichloro-ethyl) ester 3c: 66 % (without purification), colorless viscose oil. Chromatography eluent CH_2Cl_2:hexane:EtOAc (gradient). ^{1}H NMR ($CDCl_3$) ^{1}H NMR ($CDCl_3$) δ 6.332 (1H, dq, J=5.63 Hz, $^{3}J_{HP}$=7.40 Hz), 4.716* (1H, dd, $^{2}J_{HH}$= -10.97 Hz, $^{3}J_{HP}$=6.82 Hz), 4.667* (1H, dd, $^{2}J_{HH}$= -7.03 Hz, $^{3}J_{HP}$=6.88 Hz), 4.666* (1H, dd, $^{2}J_{HH}$= -10.97 Hz, $^{3}J_{HP}$=6.59 Hz), 4.661* (1H, dd, $^{2}J_{HH}$= -7.03 Hz, $^{3}J_{HP}$=6.44 Hz), 1.919 (3H, dd, J=5.63 Hz, $^{4}J_{HP}$= 1.35 Hz); ^{13}C NMR ($CDCl_3$) δ 94.28, 86.27 (d, $^{2}J_{CP}$ = 6.8 Hz), 77.44* (d, $^{2}J_{CP}$ = 4.4 Hz), 77.27* (d, $^{2}J_{CP}$ = 4.2 Hz), 27.35 (d, $^{3}J_{CP}$ = 8.8 Hz); ^{31}P NMR ($CDCl_3$) δ -6.18. GC-MS *m/z* 423 (M), 389 (M - Cl). Anal. Calcd for $C_6H_8Cl_7O_4P \cdot 0.3$ EtOAc: C, 19.23; H, 2.33. Found: C, 19.15; H, 2.21.

*Due to chiral center and prochirality there is four ^{1}H and two ^{13}C chemical shifts for OCH_2-groups

Phosphoric acid 1-chloro-ethyl ester methyl ester phenyl ester 3d: 87 % (without purification), white solid. Chromatography eluent CH_2Cl_2. Major isomer ca. 80%: ^{1}H NMR ($CDCl_3$) δ 7.380-7.325 (2H, m), 7.260-7.179 (3H, m), 6.328-6.271 (1H,m), 3.929 (3H, d, $^{3}J_{HP}$=11.69 Hz), 1.796 (3H, d, J=5.60 Hz); ^{13}C NMR ($CDCl_3$) δ 150.13 (d, $^{2}J_{CP}$ = 7.0 Hz), 129.82, 125.54, 120.06 (d, $^{3}J_{CP}$ = 4.7 Hz), 86.08 (d, $^{2}J_{CP}$ = 6.2 Hz), 55.30 (d, $^{2}J_{CP}$ = 6.3 Hz), 27.34 (d, $^{3}J_{CP}$ = 8.6 Hz); ^{31}P NMR ($CDCl_3$) δ -6.94; Minor isomer ca 20%: δ 7.380-7.325 (2H, m), 7.260.7.179 (3H, m), 6.342-6.280 (1H,m), 3.887 (3H, d, $^{3}J_{HP}$=11.59 Hz), 1.888 (3H, d, J=5.64 Hz). ^{13}C NMR ($CDCl_3$) δ 150.13 (d, $^{2}J_{CP}$ = 7.0 Hz), 129.77, 125.46, 120.06 (d, $^{3}J_{CP}$ = 4.7 Hz), 85.99 (d, $^{2}J_{CP}$ = 7.2 Hz), 55.30 (d, $^{2}J_{CP}$ = 6.3 Hz), 27.55 (d, $^{3}J_{CP}$ = 8.6 Hz); ^{31}P NMR ($CDCl_3$) δ -7.46. GC-MS *m/z* 251 (M + 1), 215 (M - Cl). Anal. Calcd for $C_9H_{12}ClO_4P$: C, 43.13; H, 4.83. Found: C, 43.21; H, 5.05.

Phosphoric acid 1-chloro-ethyl ester bis-(2,6-dimethyl-phenyl) ester 3e: 92 % (without purification), colorless viscose oil. Chromatography eluent CH_2Cl_2. ^{1}H NMR ($CDCl_3$) ^{1}H NMR ($CDCl_3$) δ 7.050-6.969 (6H, m), 6.285 (1H, dq, J=5.52 Hz, $^{3}J_{HP}$=7.62 Hz), 2.403* (6H, s), 2.303* (6H, s), 1.694 (3H, dd, J=5.52 Hz); ^{13}C NMR ($CDCl_3$) δ 147.95 (d, $^{3}J_{CP}$ = 8.7 Hz), 147.76 (d, $^{3}J_{CP}$ = 8.7 Hz), 130.42 (d, $^{2}J_{CP}$ = 3.4 Hz), 130.34 (d, $^{2}J_{CP}$ = 3.4 Hz), 129.17 (d, $^{4}J_{CP}$ = 1.7 Hz), 129.09 (d, $^{4}J_{CP}$ = 1.7 Hz), 125.60 (d, $^{5}J_{CP}$ = 2.0 Hz), 125.55 (d, $^{5}J_{CP}$ = 2.0 Hz), 86.66 (d, $^{2}J_{CP}$ = 6.4 Hz), 27.22 (d, $^{3}J_{CP}$ = 8.1 Hz), 17.22, 16.99; ^{31}P NMR ($CDCl_3$) δ -12.99. GC-MS *m/z* 369 (M + 1), 333 (M - Cl). Anal. Calcd for $C_{18}H_{22}ClO_4P$: C, 58.62; H, 6.01. Found: C, 59.02; H, 6.27.

2-(1-Chloro-ethoxy)-[1,3,2]dioxaphosphinane 2-oxide 3f: 98 % (without purification), colorless oil. Chromatography eluent hexane:EtOAc 1:4. ^{1}H NMR ($CDCl_3$) ^{1}H NMR ($CDCl_3$) δ 6.309 (1H, dq, J=5.59 Hz, $^{3}J_{HP}$=8.05 Hz), 4.560-4.399 (4H, m), 2.390-2.810 (1H, m), 1.879 (3H, dd, J=5.59 Hz, $^{4}J_{HP}$= 0.85 Hz), 1.833-1.773 (1H, m); ^{13}C NMR ($CDCl_3$) δ 85.44 (d, $^{2}J_{CP}$ = 6.2 Hz), 69.63 (d, $^{2}J_{CP}$ = 7.4 Hz), 69.00 (d, $^{2}J_{CP}$ = 7.2 Hz), 27.74 (d, $^{3}J_{CP}$ = 7.7 Hz), 25.75 (d, $^{3}J_{CP}$ = 7.4 Hz); ^{31}P NMR ($CDCl_3$) δ -9.64.

GC-MS *m/z* 201 (M + 1), 165 (M - Cl). Anal. Calcd for $C_5H_{10}ClO_4P$: C, 29.94; H, 5.03. Found: C, 30.06; H, 5.15.

Phosphoric acid 1-chloro-ethyl ester dibenzyl ester 3h: 68 % (without purification), colorless viscose oil.[22] ^{1}H NMR ($CDCl_3$) ^{1}H NMR ($CDCl_3$) δ 7.397-7.298 (10H, m), 6.150 (1H, dq, J=5.49 Hz, $^3J_{HP}$=7.58 Hz), 5.120-5.051* (4H, m), 1.782 (3H, dd, J=5.49 Hz); ^{13}C NMR$^{\#}$ ($CDCl_3$) δ 135.18, 128.75, 128.59, 128.28, 85.84, 69.91, 27.54; ^{31}P NMR ($CDCl_3$) δ -1.55.

*Due to chiral center and prochirality all four OCH_2-signals have different chemical shifts. $^{\#}$ Due to decomposition peaks are broad and J_{CP}-coupling constants can not be calculated.

Diethyl-phosphoramidic acid 1-chloro-ethyl ester methyl ester 3i: 91 % (without purification), slightly yellow solid. Chromatography eluent 0.5 % MeOH in CH_2Cl_2. Major isomer ca. 60%: ^{1}H NMR ($CDCl_3$) δ 6.247-6.189 (1H, m), 3.682 (3H, d, $^3J_{HP}$=11.38 Hz), 3.178-3.021 (4H, m), 1.828 (3H, dd, J=5.69 Hz, $^4J_{HP}$=0.72 Hz), 1.141 (6H, t, J=7.14 Hz); ^{13}C NMR ($CDCl_3$) δ 85.04 (d, $^2J_{CP}$ = 5.7 Hz), 52.92 (d, $^2J_{CP}$ = 5.8 Hz), 39.90 (d, $^2J_{CP}$ = 4.8 Hz), 27.87 (d, $^3J_{CP}$ = 7.6 Hz), 14.04 (d, $^3J_{CP}$ = 2.2 Hz); ^{31}P NMR ($CDCl_3$) δ 10.14. Minor isomer ca. 40%: ^{1}H NMR ($CDCl_3$) δ 6.247-6.189 (1H, m), 3.737 (3H, d, $^3J_{HP}$=11.45 Hz), 3. 178-3.021 (4H, m), 1.819 (3H, dd, J=5.49 Hz, $^4J_{HP}$=0.71 Hz), 1.116 (6H, t, J=7.08 Hz); ^{13}C NMR ($CDCl_3$) δ 85.30 (d, $^2J_{CP}$ = 7.0 Hz), 53.12 (d, $^2J_{CP}$ = 5.8 Hz), 39.70 (d, $^2J_{CP}$ = 4.4 Hz), 28.01 (d, $^3J_{CP}$ = 7.2 Hz), 14.06 (d, $^3J_{CP}$ = 2.2 Hz); ^{31}P NMR ($CDCl_3$) δ 10.34. GC-MS *m/z* 230 (M + 1), 194 (M - Cl). Anal. Calcd for $C_7H_{17}ClNO_3P$: C, 29.94; H, 5.03. Found: C, 30.06; H, 5.15.