Supporting Information

For

An investigation of the reactions between azido alcohols and phosphorimidites

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Table of Contents

I. Experimental section ---------------------------------------------------------- S2-S6
II. \textsuperscript{1}H NMR spectra of products ------------------------------------- S7-S22
I. Experimental Section

**General procedure for the synthesis of azido phosphates.** To the solution of an azido alcohol (1 mmol) and 1.2 equiv of dibenzyl $N,N$-diisopropylphosphorimidite 4 in 5 mL of anhydrous dichloromethane (DCM) was added 1.2 equiv of tetrazole (0.47 M solution in acetonitrile). After the solution was stirred at room temperature (rt) for 30 min, the temperature was lowered to -40 °C and 1.3 equiv of $m$-CPBA in 2 mL of DCM was added in one portion. This solution was stirred for at the temperature 30 minutes, diluted with DCM, and washed with two 20 mL-portions of 10% sodium bicarbonate solution and 20 mL of brine water, dried with Na$_2$SO$_4$, and concentrated under vacuum. Column chromatography of the residue gave the product as described below.

**2-(Azidomethyl)benzyl dibenzyl phosphate (6)** as colorless syrup, 75%. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.42-7.25 (m, 14 H), 5.06 (d, 2 H), 5.03 (s, 2 H), 5.00 (s, 2 H), 4.35 (s, 2 H). HR-FABMS: calcd for C$_{22}$H$_{23}$N$_3$O$_4$P (M + H)$^+$ 424.1426, found 242.1414.

![2-(Azidomethyl)benzyl dibenzyl phosphate (6)](image)

**3-Azido-2,2-dimethylpropyl dibenzyl phosphate (8)** as colorless syrup, 70%. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.37-7.26 (m, 12 H), 5.06 (dd, J = 2.19, 8.56 Hz, 4 H), 3.71 (d, J = 4.65 Hz, 2 H), 3.11 (s, 2 H), 0.88 (s, 6 H). HR-FABMS: calcd for C$_{19}$H$_{25}$N$_3$O$_4$P (M + H)$^+$ 390.1589, found 390.1579.

![3-Azido-2,2-dimethylpropyl dibenzyl phosphate (8)](image)

**(1R,2S)/(1S,2R)-2-Azidocyclohexyl dibenzyl phosphate (10)** as colorless syrup, 70%. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.48-7.25 (m, 10 H), 5.16-4.94 (m, 4 H), 4.56-4.46 (m, 1 H), 3.67-3.59 (m, 1 H), 2.23-1.20 (m, 8 H). HR-FABMS: calcd for C$_{20}$H$_{25}$N$_3$O$_4$P (M + H)$^+$ 402.1582, found 402.1589.

![**(1R,2S)/(1S,2R)-2-Azidocyclohexyl dibenzyl phosphate (10)**](image)

**(1R,2R)/(1S,2S)-2-Azidocyclohexyl dibenzyl phosphate (12)** as colorless syrup, 92%. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.46-7.29 (m, 10 H), 5.14-5.00 (m, 4 H), 4.22-4.10 (m, 1 H), 3.42-3.32 (m, 1 H), 2.24-2.00 (m, 2H), 1.75-1.20 (m, 6H). HR-FABMS: calcd for C$_{20}$H$_{25}$N$_3$O$_4$P (M + H)$^+$ 402.1582, found 402.1594.
2-Azido-1-phenylethyl dibenzyl phosphate (25) as colorless syrup, 78%. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.48-7.23 (m, 15 H), 5.43 (td, \(J = 7.5, 4.4\) Hz, 1 H), 5.12-4.85 (m, 4 H), 3.59 (dd, \(J = 13.0, 4.4\) Hz, 1 H), 3.46 (dd, J = 13.0, 4.4, 2.3 Hz 1 H). HR-FABMS: calcd for C\(_{22}\)H\(_{23}\)N\(_3\)O\(_4\)P (M + H\(^+\)) 424.1426, found 424.1419.

2-Azido-2-phenylethyl dibenzyl phosphate (28) as colorless syrup, 72%. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.47-7.22 (m, 15 H), 5.06 (s, 2 H), 5.02 (s, 2 H), 4.67 (dd, \(J = 4.7, 8.3\) Hz, 1 H), 4.14-4.02 (m, 2 H). HR-FABMS: calcd for C\(_{22}\)H\(_{23}\)N\(_3\)O\(_4\)P (M + H\(^+\)) 424.1426, found 424.1427.

(1R,2R)/(1S,2S)-2-Azidocyclohexyl dimethyl phosphate (20) as colorless syrup, 91%. It was obtained by the same procedure as described above with dimethyl N,N-diisopropylphosphorimidite 15 replacing 4. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 4.05-4.22 (m, 1H), \(\delta\) 3.82 (d, \(J = 14.2\) Hz 3H), \(\delta\) 3.77 (m, \(J = 14.2\) Hz 3H), \(\delta\) 3.44-3.30 (m, 1H), \(\delta\) 2.30-1.95 (m, 2H), \(\delta\) 1.80-1.60 (m, 2H), \(\delta\) 1.58-1.15 (m, 4H). HR-FABMS: calcd for C\(_8\)H\(_{17}\)N\(_3\)O\(_4\)P (M+H\(^+\)) 250.0957, found 250.0943.

Synthesis of 3-benzxyloxy-3-oxo-1,4,5-trihydrobenzo[7]-2,4,3-oxazaphosphepine (13). To a solution of azido alcohol 5 (100 mg, 0.663 mmol) and phosphorimidite 4 (0.33 mL, 0.995 mmol, 1.5 equiv) in 8 mL of anhydrous toluene was added 1.5 equiv of tetrazole (2.1 mL 0.47 M solution in acetonitrile, 0.929 mmol). The solution was stirred at 80 °C for 2 h and then diluted with DCM, washed with 20 mL of 10% sodium bicarbonate solution and two 20 mL-portions of brine water, dried with Na\(_2\)SO\(_4\), and concentrated under vacuum. Column chromatography of the residue gave 13 as a white powder (110 mg, 60%). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.48-7.12 (m, 9 H), 5.22-
5.05 (m, 4 H), 4.27 (ddd, J = 17.2, 10.4, 8.0 Hz, 1 H), 3.92 (ddd, J = 28.3, 17.2, 5.6 Hz, 1 H), 3.48-3.36 (m, 1 H). HR-FABMS: calcd for C_{15}H_{17}NO_{3}P (M + H)^{+} 290.0946, found 290.0931.

Synthesis of 2-benzyloxy-2-oxo-5,5-dimethyl-1,3,2-oxazaphosphinane (14). To a solution of azido alcohol 7 (100 mg, 0.774 mmol) and phosphorimidite 4 (0.32 mL, 0.929 mmol, 1.2 equiv) in 8 mL of anhydrous toluene was added 1.2 equiv of tetrazole (2.1 mL 0.47 M solution in acetonitrile, 0.929 mmol). The solution was stirred at 80 °C for 2 h and then diluted with DCM, washed with 20 mL of 10% sodium bicarbonate solution and two 20 mL-portions of brine water, dried with Na$_2$SO$_4$, and concentrated under vacuum. Column chromatography of the residue gave 14 as a white powder (90 mg, 45%). $^1$H NMR (CDCl$_3$, 200 MHz): $\delta$ 7.45-7.33 (m, 5 H), 5.04 (d, J = 10.0 Hz, 2 H), 3.98 (dd, J = 2.8, 14.0 Hz, 1 H), 3.84 (dd, J = 2.2, 11.2 Hz, ½ H), 3.73 (dd, J = 2.5, 11.4 Hz, ½ H), 3.26-3.10 (m, 1 H), 3.00 (dd, J = 4.6, 15.2 Hz, 1 H), 2.84 (ddd, J = 3.0, 7.0, 12.7 Hz, ½ H), 2.70 (ddd, J = 2.78, 7.5, 12.5 Hz, ½ H), 1.22 (s, 3 H), 0.79 (s, 3 H). HR-FABMS: calcd for C$_{12}$H$_{19}$NO$_3$P (M + H)$^+$ 256.1103, found 256.1105.

Synthesis of 3-methyloxy-3-oxo-1,4,5-trihydrobenzo[7]-2,4,3-oxazaphosphopine (16) and 3-methyloxy-3-oxo-1,4,7-trihydrobenzo[9]-2,4,5,6,3-oxtiazaphosphonine (17). To a solution of azido alcohol 5 (100 mg, 0.662 mmol) and phosphorimidite 15 (0.19 mL, 0.993 mmol, 1.5 equiv) in 4 mL of anhydrous DCM was added 1.5 equiv of tetrazole (2.1 mL 0.47 M solution in acetonitrile, 0.993 mmol). After the solution was stirred at rt for 7h, it was then diluted with DCM, washed with 20 mL of 10% sodium bicarbonate solution and two 20 mL-portions of brine water, dried with Na$_2$SO$_4$, and concentrated under vacuum. Column chromatography of the residue gave 16 as a white solid (55 mg, 40%) and 17 as colorless syrup (15 mg, 10%).

16. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.39-7.14 (m, 4 H), 5.24-5.08 (m, 2 H), 4.33 (ddd, J = 24.1, 15.7, 12.1 Hz, 1 H), 3.99 (ddd, J = 43.0, 24.1, 8.3 Hz, 1 H), 3.85 (d, J =16.5 Hz, 3 H), 3.50-3.30 (m, 1 H). HR-FABMS: calcd for C$_9$H$_{13}$NO$_3$P (M + H)$^+$ 214.0633, found 214.0649.
17. ¹H NMR (CDCl₃, 300 MHz): δ 8.03 (s, ½ H), 7.52-7.35 (m, 4 H), 5.68 (s, ½ H), 5.24-5.14(dd, 2 H), 4.48 (s, 2 H), δ 3.75 (d, J = 4.1 Hz, 3/2 H), 3.71 (d, J = 4.1 Hz, 3/2 H). HR-FABMS: calcd for C₉H₁₃N₃O₃P (M + H)⁺ 242.0694, found 242.0712.

**General procedure for the synthesis of phosphazides.** To the solution of an azido alcohol (0.853 mmol) and phosphorimidite 15 (1.279 mmol, 1.5 equiv) in 4 mL of anhydrous DCM was added 1.5 equiv of tetrazole (2.8 mL, 0.47 M solution in acetonitrile, 0.993 mmol). The solution was stirred at rt for 1~16 h and then diluted with DCM, washed with 20 mL of 10% sodium bicarbonate solution and two 20 Ml-portions of brine water, dried with Na₂SO₄, and finally concentrated under vacuum. Column chromatography of the residue gave the following products.

**2-Methyloxy-2-oxo-7,7-dimethyl-3,6,7,8-tetrahydro-1,3,4,5,2-oxatrazaphosphocine** (18) as colorless syrup, 21%. ¹H NMR (CDCl₃, 200 MHz): δ 8.56 (s, ½ H), 5.06 (s, ½ H), 3.84-3.76 (m, 5 H), 3.23 (s, 2 H), 0.97 (s, 6 H). HR-FABMS: calcd for C₆H₁₅N₃O₃P (M⁺ + H) 208.0851, found 208.0865.

(5aR,9aR)/(5aS,9aS)-2-Methyloxy-2-oxo-3,5a,6,7,8,9,9a-heptahydrobenzo[7]-1,3,4,5,2-oxatrazaphosphocine (19) as colorless syrup, 41%. ¹H NMR (CDCl₃, 300 MHz): δ 8.68 (d, J = 5.2 Hz, ½ H), δ 5.13 (d, J = 5.2 Hz, ½ H), δ 4.74-4.59 (m, 1 H), δ 3.82 (d, J = 7.0 Hz, 3/2 H), δ 3.76 (d, J = 7.0 Hz, 3/2 H), δ 3.72-3.58 (m, 1H), δ 2.10-1.20 (m, 8H). HR-FABMS: calcd for C₇H₁₅N₃O₃P (M⁺ + H) 220.0851, found 220.0844.

**2-Methyloxy-2-oxo-6-phenyl-3,6,7-trihydro-1,3,4,5,2-oxatrazaphosphocine** (29) as colorless syrup, 10%. ¹H NMR (CDCl₃, 300 MHz): δ 8.03 (d, J = 12.2 Hz, ½ H), 7.48-7.30 (m, 5 H), 5.65
(d, J = 12.2 Hz, ½ H), 4.85-4.78 (m, 1 H), 4.26-4.14 (m, 1 H), 3.81-3.74 (d, 3 H). HR-FABMS: calcd for C₉H₁₃N₃O₃P (M⁺ + H) 242.0695, found 242.0694.

Synthesis of 2-methyloxy-2-oxo-7-phenyl-3,6,7-trihydro-1,3,4,5,2-oxatriazaphosphopine (26) and dimethyl (2-phenylaziridin-1-yl) phosphate (27). To a solution of azido alcohol 23 (100 mg, 0.662 mmol) and phosphorimidite 15 (0.19 mL, 0.993 mmol, 1.5 equiv) in 4 mL of anhydrous DCM was added 1.5 equiv of tetrazole (2.1 mL, 0.47 M solution in acetonitrile, 0.993 mmol). The solution was stirred at rt for 10 h and was then diluted with DCM, washed with 20 mL 10% sodium bicarbonate solution and two 20 mL-portions of brine water, dried with Na₂SO₄, and concentrated under vacuum. Column chromatography of the residue produced 26 (48 mg, 30%) and 27 (32 mg, 21%), both as colorless syrup.

26. ¹H NMR (CDCl₃, 300 MHz): δ 8.07 (d, J = 34.1 Hz, ½ H), 7.50-7.32 (m, 5 H), 5.68 (d, J = 34.1 Hz, ½ H), 5.60-5.47 (m, 1 H), 3.79 (d, J = 11.0 Hz, 3/2 H), 3.72-3.47 (m, 2 H), 3.58 (d, J = 11.0 Hz, 3/2 H). HR-FABMS: calcd for C₉H₁₃N₃O₃P (M⁺ + H) 242.0695, found 242.0702.

27. ¹H NMR (CDCl₃, 300 MHz): δ 7.43-7.24 (m, 5 H), 3.84 (d, J = 10.8 Hz, 3 H), 3.79 (d, J = 10.8 Hz, 3 H), 3.53 (ddd, J = 15.8, 6.1, 3.4 Hz, 1 H), 2.72 (ddd, J = 18.3, 6.1, 1.6 Hz, 1 H), 2.20 (ddd, J = 14.8, 3.4, 1.6 Hz, 1 H). HR-FABMS: calcd for C₁₀H₁₅NO₃P (M⁺ + H) 228.0790, found 228.0794.
II. $^1$H NMR spectra of products