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1,4-Unsubstituted 2-phosphorylated vinylacetylenes as valuable phosphorus-containing dipolarophiles

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2-(Diethoxyphosphoryl)but-2-en-3-yne 2a: light yellow liquid, yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, 6H, J_{HP} 8.0 Hz, 2 $POCH_2CH_3$), 3.19 (d, 1H, J_{HP} 8.0 Hz, ≡CH), 4.11–4.20 (m, 4H, 2 $POCH_2$), 6.36 (d, 1H, J_{HP} 44.0 Hz, $=CH_{trans}$), 6.53 (d, 1H, J_{HP} 20.0 Hz $=CH_{cis}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.17 (d, J_{PC} 6.0 Hz, $POCH_2CH_3$), 62.88 (two d, J_{PC} 5.8 Hz, $POCH_2$), 78.73 (d, J_{PC} 11.0 Hz, ≡C), 82.04 (d, J_{PC} 9.0 Hz, ≡CH), 122.07 (d, J_{PC} 189.2 Hz, P-C=), 140.7 (d, J_{PC} 5.2 Hz, H_2C=). ^{31}P NMR (162 MHz, $CDCl_3$): δ 12.35. Found (%): C, 51.15; H, 6.87; P, 16.38. Calc. for $C_8H_{13}O_3P$ (%): C, 51.07; H, 6.96; P, 16.46.

2-(Diphenylphosphoryl)but-2-en-3-yne 2b: light yellow liquid, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (d, 1H, J_{HP} 8.0 Hz, ≡CH), 6.58 (d, 1H, J_{HP} 32.0 Hz, $=CH_{trans}$), 6.72 (d, 1H, J_{HP} 16.0 Hz $=CH_{cis}$), 7.42–7.47 (m, 4H, Ph), 7.51–7.55 (m, 2H, Ph), 7.76–7.81 (m, 4H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 79.91 (d, J_{PC} 13.1 Hz, ≡C), 85.28 (d, J_{PC} 7.0 Hz, ≡CH), 126.39 (d, J_{PC} 99.6 Hz, P-C=), 128.44 (d, J_{PC} 12.0 Hz, Ph), 130.6 (d, J_{PC} 106.7 Hz, Ph), 132.12 (d, J_{PC} 9.1 Hz, Ph), 132.32 (d, J_{PC} 2.0 Hz, Ph), 140.81 (d, J_{PC} 4.0 Hz, H_2C=). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.29. Found (%): C, 75.02; H, 5.23; P, 12.34. Calc. for $C_{16}H_{13}OP$ (%): C, 75.18; H, 5.19; P, 12.28.

5-Diethoxyphosphoryl-5-ethynyl-3-phenyl-4,5-dihydroisoxazole 3a: viscous liquid, yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 and 1.37 (two t, 3H, J_{HH} 8.0 Hz, $POCH_2CH_3$), 2.81 (d, 1H, J_{HH} 8.0 Hz, ≡CH), 3.74 (dd, 1H, J_{HH} 18.0 Hz, J_{PH} 16.0 Hz, CH*H*), 3.99 (dd, 1H, J_{HH} 24.0 Hz, J_{PH} 16.0 Hz, C*H*H), 4.26–4.41 (m, 4H, 2 $POCH_2$), 7.39–7.42 (m, 3H, Ph), 7.63–7.66 (m, 2H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.44 and 16.46 (two d, J_{PH} 6.0 Hz, $POCH_2CH_3$), 46.06 (d, J_{PC} 1.0 Hz, CH_2), 64.93 and 65.07 (two d, J_{PC} 7.0 Hz, $POCH_2$), 77.24 (d, J_{PC} 9.0 Hz, ≡CH), 77.39 (d, J_{PC} 177.0 Hz, P-C), 79.42 (d, J_{PC} 4.0 Hz, ≡C-), 127.04 (s, Ph), 128.15 (s, Ph), 128. 86 (s, Ph), 130.75 (s, Ph), 155.8 (d, J_{PC} 6.0 Hz, N =C). ^{31}P NMR (162 MHz, $CDCl_3$): δ 13.71. Found (%): C, 59.55; H, 4.32; P, 10.20. Calc. for $C_{13}H_{18}NO_4P$ (%): C, 59.61; H, 4.34; P, 10.25.

5-Diphenylphosphoryl-5-ethynyl-3-phenyl-4,5-dihydroisoxazole 3b: viscous liquid, yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.81 (d, 1H, J_{PH} 4.0 Hz, ≡CH), 3.83 (dd, 1H, J_{HH} 12.0 Hz, J_{PH} 16.0 Hz, CH*H*), 4.03.83 (dd, 1H, J_{HH} 16.0 Hz, J_{PH} 16.0 Hz, CH*H*), 7.34–7.63 (m, Ph), 8.01–8.21 (m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.73 (d, J_{PC} 2.0 Hz, CH_2), 79.53 (d, J_{PC} 7.0 Hz, ≡CH), 80.15 (d, J_{PC} 6.0 Hz, ≡C-), 80.82 (d, J_{PC} 86.0 Hz, P-C), 126.03 (s, Ph), 127.90 (s, Ph), 127.91 (s, Ph), 128.43 (d, J_{PC} 3.0 Hz, Ph), 128.6 (d, J_{PC} 3.0 Hz, Ph), 128.78 (s, Ph), 130.75 (s, Ph), 132.21 (s, Ph), 132.3 (s, Ph), 132.79 (s, Ph), 132.88 (s, Ph), 156.24 (d, J_{PC} 5.0 Hz, N =C).

^{31}P NMR (162 MHz, $CDCl_3$): δ 29.34. Found (%): C, 74.60; H, 4.85; P, 8.38. Calc. for $C_{13}H_{18}NO_4P$ (%): C, 74.39; H, 4.89; P, 8.34.

5-Diethoxyphosphoryl-3,3'-diphenyl-4,5-dihydro-5,5'-biisoxazole 4a: viscous liquid, yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 and 1.35 (two t, 3H, J_{HH} 8.0 Hz, $POCH_2C\mathit{H}_3$), 4.15 (d, 2H, J_{HH} 20.0 Hz, CH_2), 4.24–4.35 (m, 4H, 2 $POCH_2$), 6.95 (d, 1H, J_{HH} 4.0 Hz, =CH), 7.41–7.46 (m, 6H, Ph), 7.69–7.83 (m, 4H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.43 and 16.48 (two d, J_{PH} 5.0 Hz, $POCH_2\mathit{C}H_3$), 43.01 (s, CH_2), 64.68 and 64.83 (two d, J_{PC} 10.0 Hz, $PO\mathit{C}H_2$), 81.52 (d, J_{PC} 173.0 Hz, P-C), 102.33 (d, J_{PC} 4.0 Hz, =CH), 126.89 (s, Ph), 127.14 (s, Ph), 127.9 (s, Ph), 128.47 (s, Ph), 128.91 (s, Ph), 128.96 (s, Ph), 130.28 (s, Ph), 130.95 (s, Ph), 156.25 (d, J_{PC} 7.0 Hz, O-*C*=CH), 162.82 (d, J_{PC} 2.0 Hz, N=*C*-Ph), 168.37 (d, J_{PC} 7.0 Hz, N=*C*-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ 14.26. Found (%): C, 61.82; H, 5.32; P, 7.18. Calc. for $C_{22}H_{23}N_2O_5P$ (%): C, 61.97; H, 5.44; P, 7.26.

5-Diphenylphosphoryl-3,3'-diphenyl-4,5-dihydro-5,5'-biisoxazole 4b: viscous liquid, yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$): 4.04–4.20 (m, 2H, CH_2), 6.51 (d, 1H, J_{HH} 4.0 Hz, =CH), 7.34–8.15 (m, 20H, 4 Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.87 (d, J_{PC} 4.0 Hz, CH_2), 85.33 (d, J_{PC} 81.0 Hz, P–C), 102.35 (d, J_{PC} 3.0 Hz, =CH), 126.83 (s, Ph), 127.15 (s, Ph), 127.54 (s, Ph), 128.44 (s, Ph), 128.63 (d, J_{PC} 12.0 Hz, Ph), (s, Ph), 128.85 (s, Ph), 128.90 (s, Ph), 130.19 (s, Ph), 130.60 (d, J_{PC} 108.0 Hz, Ph), 131.02 (s, Ph), 132.10 (d, J_{PC} 9.0 Hz, Ph), 132.75 (d, J_{PC} 5.0 Hz, Ph), 156.71 (d, J_{PC} 4.0 Hz, O-*C*=CH), 162.45 (d, J_{PC} 1.0 Hz, N=*C*-Ph), 168.59 (d, J_{PC} 8.0 Hz, N=*C*-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.70. Found (%): C, 73.72; H, 4.77; P, 6.42. Calc. for $C_{30}H_{23}N_2O_3P$ (%): C, 73.46; H, 4.73; P, 6.31.

4-[1-(Diethoxyphosphoryl)ethenyl]-1-(2-hydroxyethyl)-1*H*-1,2,3-triazole 5a: viscous liquid, yield 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, 6H, J_{HH} 8.0 Hz, 2 $POCH_2C\mathit{H}_3$), 2.95 (br.s, 1H, OH), 3.93 (t, 2H, J_{HH} 4.0 Hz, CH_2N), 4.01–4.07 (m, 4H, 2 $POCH_2$), 4.44 (t, 2H, J_{PC} 8.0 Hz, $C\mathit{H}_2OH$), 6.14 (d, 1H, J_{PC} 20.0 Hz, *cic*-HC=C-P), 6.76 (d, 1H, J_{PC} 36.0 Hz, *trans*-HC=C–P), 7.92 (s, 1H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.17 (d, J_{PH} 6.0 Hz, $POCH_2\mathit{C}H_3$), 52.69 (s, N-CH_2), 60.72 (s, O–CH_2), 62.71 (d, J_{PC} 6.0 Hz, $PO\mathit{C}H_2$), 123.91 (s, =CH), 127.92 (d, J_{PC} 189.2 Hz, P–C), 129.77 (d, J_{PC} 4.0 Hz, =CH_2), 141.89 (d, J_{PC} 17.2 Hz, P-C=N). ^{31}P NMR (162 MHz, $CDCl_3$): δ 15.68. Found (%): C, 43.50; H, 6.51; P, 11.12. Calc. for $C_{10}H_{18}N_3O_4P$ (%): C, 43.64; H, 6.59; P, 11.25.

4-[1-(Diphenylphosphoryl)ethenyl]-1-(2-hydroxyethyl)-1*H*-1,2,3-triazole 5b: viscous liquid, yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (br.s, 1H, OH), 3.98 (t, 2H, J_{PH} 8.0 Hz, CH_2N), 4.41 (t, 2H, J_{PH} 8.0 Hz, $C\mathit{H}_2OH$), 5.49 (d, 1H, J_{PH} 24.0 Hz, HC=C-P_{cis}), 6.94 (d, 1H, J_{PH} 40.0 Hz, HC=C-P_{trans}), 7.50–7.74 (m, 10 H, 2 Ph), 8.01 (s, 1H, =CH-N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.75 (s, NCH_2), 60.91 (s, CH_2OH), 124.24 (s, N-C=), 128.73 (d, J_{PC} 13.0 Hz, Ph), 130.13 (d, J_{PC} 7.2 Hz, =CH_2), 130.37 (d, J_{PC} 106.3 Hz, Ph), 131.93 (s, Ph), 132.03 (s, Ph), 132.41 (d, J_{PC} 2.0 Hz, HC=), 132.67 (d, J_{PC} 97.0 Hz, P-C=),. ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.07. Found (%): C, 63.83; H, 5.02; P, 9.21. Calc. for $C_{18}H_{18}N_3O_2P$ (%): C, 63.92; H, 5.07; P, 9.16.