A Stable Enol In Small Ring Systems: Clear Differentiation Between Penta- and Tri-valency Of Phosphorus Atoms.


Supporting Information

Syntheses of compounds: 2,3-Di-tert-butyl-1-trimethylsilyl-4-trimethylsilyllox-1,2-dihydro-phosphate (3). Lithium bis(trimethyl-silyl)phosphide as a bis(ethylenediamine) complex (1) (7.55 g (0.0262 mol) and 4.59 g (0.0262 mol) of trans-2-tert-butyl-4,4-dimethyl-pent-2-enoyl chloride (2) were mixed in 40 ml of pentane at the room temperature. After 3 days, the mixture was filtered and purified by the kugelrohr distillation collecting the fraction between 32 and 38°C at 0.1 mm of Hg. Yield of 2,3-di-tert-butyl-1-trimethylsilyl-4-trimethylsilyllox-1,2-dihydro-phosphate (3) was 4.53 g (58%) as a viscous oil. 1H NMR (500 MHz, CD2Cl2, TMS): δ: 0.10 (s, 9H, Me-Si), 0.20 (s, 9H, Me-Si), 1.00 (s, 9H, Me), 1.10 (s, 9H, Me), 2.20 (s, 1H, CH-P). 13C NMR (500 MHz, CD2Cl2, TMS): δ: 1.36 (s, Me-Si), 0.00 (s, Me-Si), 29.92 (s, Me), 30.02 (s, Me), 32.88 (s, C-Me), 35.04 (s, C-Me), 43.52 (d, JPC = 10.1 Hz, C-H), 134.34 (d, JPC = 13.9 Hz, C-C), 144.54 (d, JPC = 5.1 Hz, C=C). 31P NMR (500 MHz, CD2Cl2): δ: 0.40 (s, 1AP). 2,3-Di-tert-butyl-1-trimethylsilyl-4-trimethylsilyllox-1,2-dihydro-phosphate (3) were identified by the mass-spectrometry (ASAP method), which gave M+ ioni at 345.21 corresponding to C15H28OPSi.

3,4-Di-tert-butyl-1-oxo-1,4-dihydro-1,3-phosphole (6). 0.3 g of (0.00087 mol) of 2,3-di-tert-butyl-1-trimethylsilyl-4-trimethylsilyllox-1,2-dihydro-phosphate (3) was dissolved in 5 ml of methylene chloride and left on air for 3 weeks. The resultant crystals of 3,4-di-tert-butyl-1-oxo-1,4-dihydro-1,3-phosphole (6) were formed quantitatively with m.p. 100°C. 1H NMR (500 MHz, CD2Cl2, TMS): δ: 1.15 (s, 9H, Me), 1.19 (s, 9H, Me), 2.95 (dd, JPC = 14.7 Hz, JPC = 0.8 Hz, 1H, CH-P), 7.15 (dd, JPC = 495.6 Hz, JPC = 0.8 Hz, 1H, PH). O-H proton was not observed. 13C NMR (500 MHz, CD2Cl2, TMS): δ: 30.90 (d, JPC = 19.9 Hz, Me), 30.00 (d, JPC = 8.5 Hz, Me), 33.90 (d, JPC = 20.3 Hz, C-Me), 34.20 (d, JPC = 16.8 Hz, C-Me), 57.20 (d, JPC = 56.1 Hz, C-P), 134.30 (d, JPC = 14.1 Hz, C-C), 154.60 (d, JPC = 80.9 Hz, C-C). 31P NMR (500 MHz, CD2Cl2): δ: 4.17 (d, JPC = 495.6 Hz, 1P). The structure was proven by X-ray analysis.

Pyrolysis of 2,3-di-tert-butyl-1-trimethylsilyl-4-trimethylsilyllox-1,2-dihydro-phosphate (3): Tris(trimethylsilyl)phosphine (8), 1,2,5,6-Tetra-tert-butyl-1,3-bis-trimethylsilyllox-1H,5H-1,2-dihydro phosphole [1,2-e][1,2-f]dihydrophophole and 3,4-Di-tert-butyl-1-(2,4-dimethyl-pent-2-enoyl)-phosphetan-2-one (9) was 0.27 g (16%) as colorless crystals with m.p. 169-172°C. 1H NMR (500 MHz, CD2Cl2): δ: 0.98 (s, 9H, Me), 1.05 (s, 9H, Me), 2.60 (br, 2H, CH-P), 3.80 (t, JPC = 8.9 Hz, Me-Si), 3.85 (t, JPC = 8.9 Hz, Me), 34.40 (s, C-Me), 38.06 (t, JPC = 8.9 Hz, C-Me), 53.25 (t, JPC = 15.3 Hz, C-P), 137.69 (t, JPC = 3.4 Hz, C-C), 158.70 (t, JPC = 16.5 Hz, C-C). 31P NMR (500 MHz, CD2Cl2): δ: 10.60 (s, 1P). The structure was proven by X-ray analysis. 3,4-Di-tert-butyl-1-(2,4-dimethyl-pent-2-enoyl)-phosphetan-2-one (9) was isolated after the chromatography of the residue from the above pyrolysis. The chromatography was done on silica gel with eluent with eluent 20% of ethyl ether and 80% of hexane. Compound 9 was additionally purified by the sublimation of the combined chromatographic fractions at 50 °C and 5 mm of Hg. The yield of 3,4-di-tert-butyl-1-(2,4-dimethyl-pent-2-enoyl)-phosphetan-2-one (9) was 0.49 g (60%). The sample starts to sublime at 41-43°C and completely melts at 100-106°C. 1H NMR (500 MHz, CD2Cl2, TMS): δ: 0.98 (s, 9H, Me), 1.05 (s, 9H, Me), 1.10 (s, 9H, Me), 1.13 (s, 9H, Me), 2.85 (dd, JPC = 6.8 Hz, JPC = 7.0 Hz, 1H, CH-P), 3.44 (dd, JPC = 2.4 Hz, JPC = 7.0 Hz, 1H, CH), 5.50 (d, JPC = 1.2 Hz, 1H, C=C-H). 13C NMR (500 MHz, CD2Cl2): δ: 29.90 (d, JPC = 8.9 Hz, Me), 31.20 (d, JPC = 1.7 Hz, Me), 31.40 (d, JPC = 4.8 Hz, Me), 32.30 (d, JPC = 17.4 Hz, C-C), 33.90 (s, C-Me), 35.05 (d, JPC = 6.9 Hz, C-Me), 36.30 (d, JPC = 1.5 Hz, C-Me), 38.90. (d, JPC = 5.0 Hz, C-Me), 77.90 (d, JPC = 21.2 Hz, C-C), 139.10 (d, JPC = 1.7 Hz, C-C), 149.50 (d, JPC = 32.5 Hz, C-C), 211.10 (d, JPC = 29.5 Hz, C=C). 31P NMR (500 MHz, CD2Cl2): δ: 14.10 (s, 1P).