A stable enol in small ring systems: clear differentiation between penta- and tri-valency of phosphorus atoms†

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The first stable enols in 1,2-dihydrophosphetes 6 and 10 were synthesized and structurally characterized with intermolecular hydrogen bonds to phosphoryl groups in 10-membered dimeric structures; in contrast, trivalent analogue 9 exists in keto-form, where such stabilization by hydrogen bonds is not feasible.

Enols of carbonyl compounds have an important and historical role in organic chemistry and especially in biochemical processes.[1] Since Fuson *et al.*'s original discovery of sterically hindered stable enols, particular attention has been paid to the search for enols in strained carbonyl molecules.[2] In this communication, we describe a new enolization in sterically hindered four-membered carbonyl compounds that is promoted by phosphorus atoms. Enolization enthalpy of the parent cyclobutanone in the gas phase was found to be 16.0 kcal mol^{-1}, which points to the difficulty of forming unsaturated cyclic enols in all-carbon four-membered rings.[3]

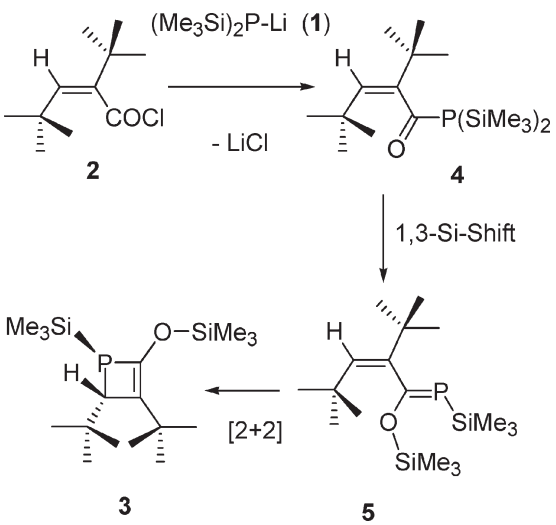
The coupling reaction between lithium bis(trimethylsilyl)-phosphide (**1**) and *Z*-2-*tert*-butyl-4,4-dimethyl-pent-2-enoyl chloride (**2**) led to the formation of 2,3-di-*tert*-butyl-1-trimethylsilanyl-4-trimethylsilanyloxy-1,2-dihydrophosphete (**3**) stereoselectively. The presumptive mechanism of formation of **3** involves a 1,3-shift of a trimethylsilyl group from phosphorus to oxygen in intermediate **4**, affording transient 1-phosphabutadiene (**5**), which then undergoes electrocyclic ring closure affording **3** (Scheme 1).

1-Phosphabutadienes are among the least stable phosphabutadienes, although a few stable examples have been described.[4] Generated *in situ*, 1-phosphabutadienes undergo intermolecular [2 + 2]- and [4 + 2]-cycloadditions.[4b] The ring closure paths (disrotatory or conrotatory) in the parent butadiene have great importance to organic chemistry and numerous studies have been devoted to this field.[5] So far, there are few theoretical studies of 1,2-dihydrophosphetes.[6] Compound **3** is a liquid. In order to establish the orientation in this four-membered ring, a sample of **3** was exposed to air to obtain a more crystalline substance. Hydrolysis and oxidation of **3** to **6** should take place without loss of stereochemistry (Scheme 2).[7] The ring closure in **5** took place with minimization of sterical hindrance, affording cisoidal orientation of the *tert*-butyl and trimethylsilyl groups along the P–C bond in **3** (Scheme 1).

Surprisingly X-ray analysis‡ reveals that **6** exists in a stable enolic form. The enol moiety is stabilized by intermolecular hydrogen bonds to phosphoryl groups, affording a ten-membered dimer in the solid state (Fig. 1). According to the ^{13}C NMR spectrum of **6**, it also exists in an enol form in solution. There are two down-field doublets at 134.30 ppm with $^{2}J_{PC}$ = 14.1 Hz, and at 154.60 ppm with $^{1}J_{PC}$ = 80.9 Hz corresponding to the enol form of **6**.

1,2-Dihydrophosphetes were reported to undergo retro-cyclo-opening, and can react as masked 1-phosphabutadienes.[8] Thus, we carried out a flash-pyrolysis of **3** in an attempt to generate **5**. Unexpectedly, the product of ring expansion, **7**, and tris(trimethylsilyl)phosphine **8** were isolated as distillable components. Chromatography of the residue gave 1,2-dihydrophosphete **9**, which contains a trivalent phosphorus atom. According to X-ray analysis,‡ compound **9** exists in the keto-form. Selective oxidation of **9** by pyridine *N*-oxide resulted in penta-valent phosphorus derivative **10**. In contrast to **9**, X-ray analysis‡ of **10** shows that it exists in the enol form (Fig. 2).

Solid state structures of **9** and **10** are consistent with structures observed in solution. The ^{13}C NMR spectrum of **9** has two doublets of carbonyl groups at 211.10 ppm with



Scheme 1

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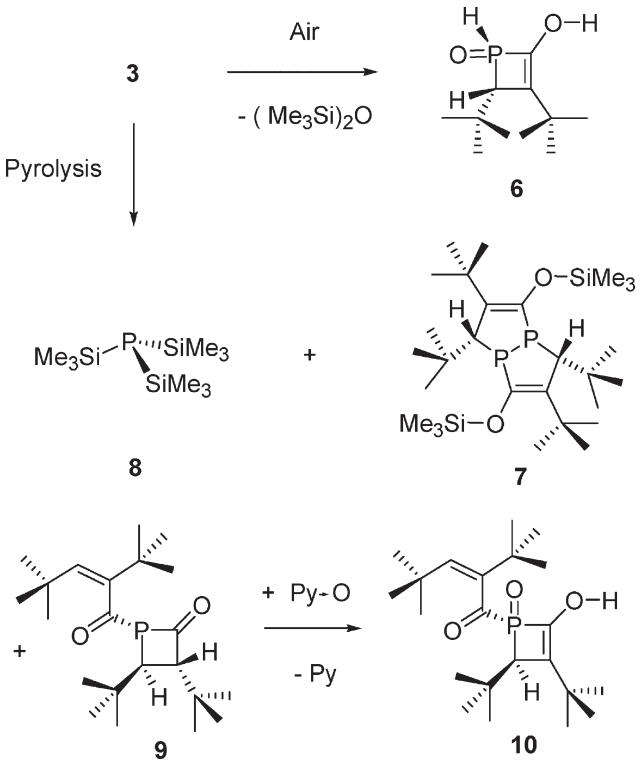
† Electronic supplementary information (ESI) available: Crystallographic cif-files of **6**, **7**, **9**, **10**, and synthesis of compounds **3**, **6**, **7**, **8**, **9**, and **10**. CCDC 691153–691156. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b809877h



Scheme 2

$^{1}J_{PC}$ = 29.5 Hz, and at 211.50 ppm with $^{1}J_{PC}$ = 76.3 Hz. The ^{13}C NMR spectrum of **10** has one doublet of a carbonyl group at 218.00 ppm with $^{1}J_{PC}$ = 53.9 Hz. The ^{31}P NMR spectra of 1,2-dihydrophosphetes are influenced by the type of substituent at the phosphorus atom, not by ring-size. Compounds **6** and **10** contain a phosphoryl group and have typical chemical shifts for phosphine oxides at 4.17 ppm (d, $^{1}J_{PH}$ = 495.6 Hz) and 17.9 ppm correspondingly. Trivalent compound **9** has a chemical shift of 104.00 ppm, which is often associated with acylphosphines. Trivalent compound **3**, with a direct bond between phosphorus and silicon, has an upfield signal at −40.16 ppm, attributed to mono-silylphosphines.

The 1,2-dihydrophosphete rings in **6**, **9** and **10** are nearly planar, with deviation of the phosphorus atom from the C–C–C plane at 0.365 Å for **6**, 0.156 Å for **9**, and 0.501 and

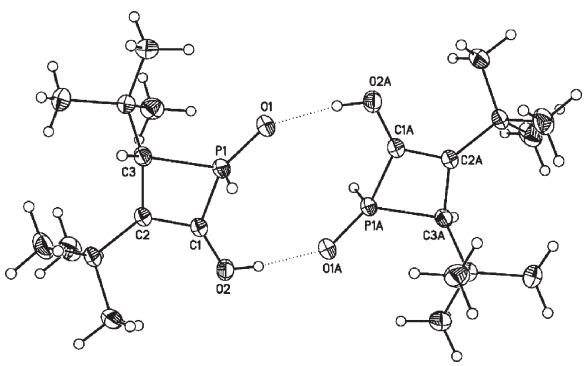


Fig. 1 Stabilization of enol **6** through P═O···H bonds.

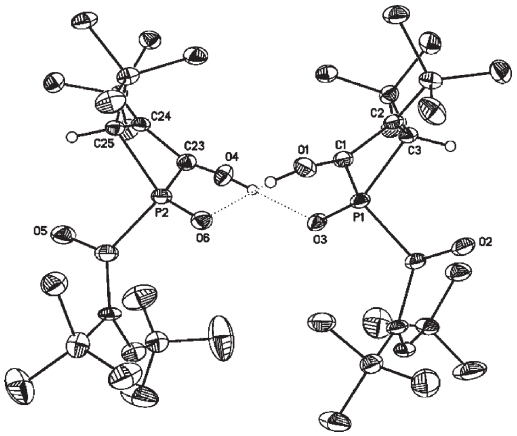


Fig. 2 Stabilization of enol **10** through P═O···H bonds. Structural data of the independent molecule on the right are listed in Table 1.

0.479 Å for **10**. C1–P–C3 internal angles are between 75.15° and 78.03°, which are close to the theoretically calculated number of 74° for such heterocycles.[8] Enol derivatives **6** and **10** have single C–O bond lengths at 1.3401(10) Å and 1.344(6) Å. Ketone derivative **9** clearly has a double bond between oxygen and carbon at 1.1951(19) Å. Enols **6** and **10** have double C–C bonds at 1.3624(10) Å and 1.361(7) Å. Ketone **9** has only single C–C bonds in the ring at 1.531(2) Å and 1.563(2) Å. Intermolecular P═O···O distances in the enol derivatives are 2.590(3) Å for **6** and 2.65(1) Å for **10**, which are typical distances for hydrogen bonds, consistent with the average value of 2.68 Å in the CCDC database (Table 1).

Table 1 Selected bond lengths (Å) and angles (°) for **6**, **9** and **10**

	6	**9**	**10**
P–C1	1.7741(8)	1.8982(17)	1.774(5)
C1–C2	1.3624(10)	1.531(2)	1.361(7)
C2–C3	1.5441(11)	1.563(2)	1.524(7)
C3–P	1.8379(8)	1.8794(16)	1.851(5)
C1–O	1.3401(10)	1.1951(19)	1.344(6)
P–O	1.4966(7)	N/A	1.490(4)
P···C2	2.2862(8)	2.526	2.282(5)
Transannular interaction			
C1–P–C3	78.03(4)	75.15(7)	76.8(2)
P–C1–C2	92.65(5)	94.28(10)	92.5(4)
C1–C2–C3	102.81(6)	96.26(12)	102.5(4)
C2–C3–P	84.59(5)	93.98(9)	84.5(3)
P═O···O–C	2.590(3)	N/A	2.64(1) and 2.65(1)

The formation of intramolecular hydrogen bonds to nitrogen in Mannich/Schiffs bases and to phosphoryl/thiophosphoryl groups in five-membered rings are known to increase the enol form in keto–enol tautomerism.[9] In contrast, C–O–H···P hydrogen bonds to trivalent phosphorus are weak, although not unprecedented, and have been described in a few cases (3.03–3.50 Å).[10] In our case the strong intermolecular hydrogen bonding in the sequences C–O–H···O═P of **6** and **10** is responsible for stabilizing the enol forms, thus revealing the dramatic differences between the effects of pentavalent and trivalent phosphorus atoms in four-membered rings.

Notes and references

‡ Crystal data for all compounds were collected using a Bruker ApexII CCD system using Mo radiation equipped with a graphite monochromator and low temperature apparatus. The structures were solved and refined using the Shelxtl suite of programs.[11]

Crystal data for **6**: $C_{11}H_{21}O_2P$, M = 216.25, triclinic, a = 6.1970(4) Å, b = 8.5935(5) Å, c = 11.9624(7) Å, α = 79.0472(10)°, β = 85.1087(11)°, γ = 80.2040(10)°, V = 615.40(6) Å^3, T = −100 °C, space group = $P\bar{1}$, Z = 2, 26 437 reflections measured, 3801 unique (R_{int} = 0.025) which were used in all calculations, R indices(all data) $R1$ = 0.032, w$R2$ = 0.086.

Crystal data for **7**: $C_{28}H_{56}O_2P_2Si_2$, M = 542.85, trigonal, a = 17.1720(18) Å, c = 60.643(7) Å, V = 15 486(3) Å^3, T = −100 °C, space group $R\bar{3}c$, Z = 18, 55 549 reflections measured, 3863 unique (R_{int} = 0.048) which were used in all calculations, R indices(all data) $R1$ = 0.062, w$R2$ = 0.142.

Crystal data for **9**: $C_{22}H_{39}O_2P$, M = 366.50, orthorhombic, a = 11.3952(6) Å, b = 11.9039(6) Å, c = 33.5993(17) Å, V = 4557.7(4) Å^3, T = −100 °C, space group $Pbca$, Z = 8, 78 472 reflections measured, 5626 unique (R_{int} = 0.042) which were used in all calculations, R indices(all data) $R1$ = 0.064, w$R2$ = 0.143.

Crystal data for **10**: $C_{22}H_{39}O_3P$, M = 382.50, orthorhombic, a = 44.018(15) Å, b = 9.170(3) Å, c = 23.309(8) Å, V = 9409(5) Å^3, T = −100 °C, space group $Pbcn$, Z = 16, 61 459 reflections measured, 7841 unique (R_{int} = 0.22) which were used in all calculations, R indices (all data) $R1$ = 0.173, w$R2$ = 0.235. The overall quality of the structure was limited by the thin data crystal (~0.58 × 0.24 × 0.03 mm) which gave a weak smeared diffraction pattern especially at high angles. The structure also suffers from disorder in the ethylene groups although they were well resolved using a system of restraints for the locations of ethylene and *tert*-butyl atoms (SADI) as well as thermal parameters (EADP). Other thermal parameter restraints (SIMU, ISOR, DELU) were tried but gave unreasonable thermal parameters. Because of the disorder, bond lengths around the ethylene groups should be interpreted cautiously.[12]

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12 This is DuPont contribution # 8869.