

Synthesis, Structure, and Thermolysis of a 1,5-Dioxo-4 λ^5 -phosphaspiro[3.3]heptane: A Novel Pentacoordinate 1,2-Oxaphosphetane

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Received February 24, 1994

In the course of our study on oxetanes bearing highly coordinated main group elements at the neighboring position, we have reported the syntheses and isolation of intermediates of the Wittig and Peterson-type reactions.¹ Recently we also achieved the synthesis of tetracoordinate 1,2-oxaselenetanes as a group-16-element analogue.² Except for tin^{1c} and germanium^{1e} compounds they always have a five-membered Martin ligand which can stabilize such hypervalent species.³ On the other hand, there have been reported a few examples of spiro phosphoranes having two four-membered rings, but they are mostly limited to nitrogen-containing compounds.⁴ From our interest in the influence of ring size on the stability of 1,2-oxaphosphetane⁵ and its potentiality as a double-olefin-extrusion reagent, we have studied the synthesis of a novel spiro pentacoordinate 1,2-oxaphosphetane with one more oxaphosphetane ring. We now report its first synthesis, crystal structure, and thermolysis.

Sequential treatment of dimethylphenylphosphine oxide (**1**) with 5 equiv of *n*-BuLi (THF, -72 °C, 5 h; -30 to -20 °C, 4 h), with 8 equiv of freshly generated hexafluoroacetone (THF, -72 °C; -30 to -20 °C, 1 h; room temperature, 2 h), and then with aqueous NH₄Cl gave bis- β -hydroxy phosphine oxide **2** (53%).

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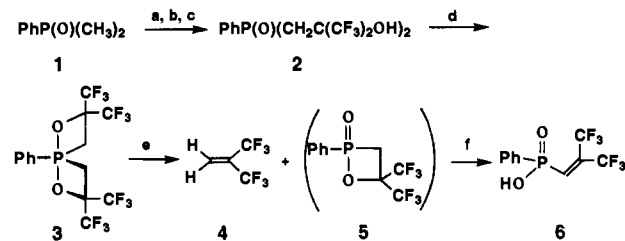
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Scheme 1^a

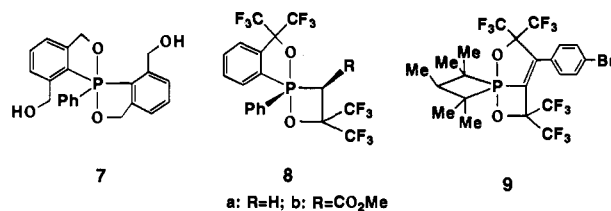


^a (a) *n*-BuLi (5 equiv), THF, -72 °C, 5 h; -30 to -20 °C, 4 h; (b) 8 equiv of (CF₃)₂C=O, THF, -72 °C; -30 to -20 °C, 1 h, room temperature, 2 h; (c) aqueous NH₄Cl; (d) Ph₃P-CCl₄, Et₃N, room temperature, overnight, 50 °C, 5 h; (e) *d*₈-toluene, 190 °C, 24 h; (f) isomerization.

Intramolecular dehydration of **2** by Appel's method⁶ provided a target molecule **3** (79%) (Scheme 1).⁷

Recrystallization of **3** from hexane gave colorless blocks, which melted at 141–143 °C without decomposition. In the ¹H NMR spectrum of **3**, signals due to the methylene protons were observed at δ 3.77 (dd, ²J_{HH} = 17.0 Hz, ²J_{HP} = 16.7 Hz) and 4.09 (dd, ²J_{HH} = 17.0 Hz, ²J_{HP} = 22.6 Hz). In the ¹⁹F and ³¹P NMR spectra of **3** were observed two quartets due to chirality at the P atom with centers of δ_F -78.6, -77.2 (⁴J_{FF} = 9.2 Hz) and a broad singlet (δ_P -31.3) due to the long-range coupling with ¹⁹F nuclei, respectively. These spectral data show equivalency of the two four-membered rings and strongly support the trigonal bipyramid (TBP) structure.

The X-ray crystallographic analysis of **3** indicated that it has a distorted TBP structure with C₂ symmetry (Figure 1).⁸ This is the first example of a phosphorane containing two oxaphosphetane rings. As expected, two oxygen atoms occupy apical positions, while three carbon atoms occupy equatorial positions. The bond angle O(1)–P(1)–O(2) between the two apical bonds deviates by 14.3(1)° from linearity. This deviation increases in the order **7** (1.9°)⁹ < **8b** (14.1°)^{1d} < **3** < **9** (20.3°),^{4b} reflecting the four-membered-ring strain. The bonds P(1)–O(1) (1.757(2)



Å) and P(1)–O(2) (1.758(2) Å) are almost the same, but equatorial bonds P(1)–C(1) (1.818(3) Å) and P(1)–C(3) (1.814(4) Å) are longer than P(1)–C(9) (1.781(3) Å). The dihedral angles P(1)–C(1)–C(2)–O(1) and P(1)–C(3)–C(4)–O(2) are -2.5(2)°

(6) For a review, see: Appel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 801–811.

(7) **3**: colorless crystals (CH₂Cl₂–hexane), mp 141.0–142.7 °C; ¹H NMR (CDCl₃, 270 MHz) δ 3.77 (dd, ²J_{HH} = 17.0 Hz, ²J_{HP} = 16.7 Hz, 2H, PCHH'), 4.09 (dd, ²J_{HH} = 17.0 Hz, ²J_{HP} = 22.6 Hz, 2H, PCHH'), 7.44–7.54 (m, 3H, meta and para H of Ph), 7.90–8.00 (m, 2H, ortho H of Ph); ¹³C{¹H} NMR (CDCl₃, 67.8 MHz) δ 48.1 (d, ¹J_{CP} = 102.5 Hz, PCH₂), 73.1 (d sept, ²J_{CF} = 33.1 Hz, ²J_{CP} = 17.9 Hz, C(CF₃)₂), 122.3 (d q, ¹J_{CF} = 285.1 Hz, ³J_{CP} = 6.7 Hz, C(CF₃)(CF₃')), 123.0 (d q, ¹J_{CF} = 284.4 Hz, ³J_{CP} = 8.5 Hz, C(CF₃)(CF₃')), 129.1 (d, ³J_{CP} = 15.9 Hz, meta C of Ph), 130.5 (d, ¹J_{CP} = 130.6 Hz, ipso C of Ph), 133.5 (d, ⁴J_{CP} = 3.7 Hz, para C of Ph), 134.5 (d, ²J_{CP} = 13.5 Hz, ortho C of Ph); ¹⁹F NMR (CDCl₃, 84.3 MHz) δ -78.6 and -77.2 (A₃B₃ pattern, ⁴J_{FF} = 9.2 Hz); ³¹P{¹H} NMR (CDCl₃, 108 MHz): δ -31.3 (br s). Anal. Calcd for C₁₄H₉F₁₂O₂P: C, 35.92; H, 1.94. Found: C, 35.72; H, 2.05. HRMS: *m/z* calcd for C₁₄H₉F₁₂O₂P: 468.0149, found 468.0153.

(8) C₁₄H₉F₁₂O₂P: FW = 468.18, crystal dimensions (mm) 0.500 × 0.400 × 0.200, triclinic, space group P $\bar{1}$, *a* = 10.484(2) Å, *b* = 10.835(6) Å, *c* = 9.655(3) Å, α = 110.68(3)°, β = 144.76(2)°, γ = 99.80(4)°, *V* = 864.0(7) Å³, *Z* = 2, D_{calc} = 1.799 g/cm³, *R* = 0.058 (*R*_w = 0.069). Full details of the crystallographic structure analysis are described in the supplementary material.

(9) Hellwinkel, D.; Krapp, W.; Schomburg, D.; Sheldrick, W. S. *Z. Naturforsch.* **1976**, *31b*, 948–952.

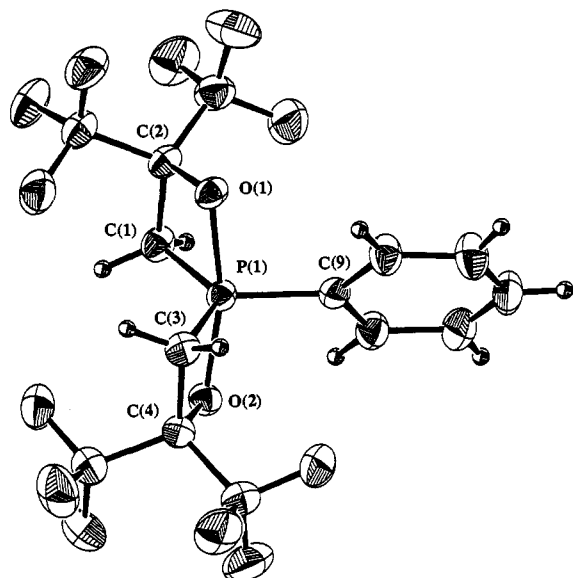


Figure 1. ORTEP drawing of **3**. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): P(1)–O(1), 1.757(2); P(1)–O(2), 1.758(2); P(1)–C(1), 1.818(3); P(1)–C(3), 1.814(4); P(1)–C(9), 1.781(3); O(1)–P(1)–O(2), 165.7(1); C(1)–P(1)–C(9), 117.3(2); C(1)–P(1)–C(3), 126.7(2); C(3)–P(1)–C(9), 116.0(2); P(1)–C(1)–C(2), 89.2(2); C(1)–C(2)–O(1), 98.3(2); C(2)–O(1)–P(1), 95.2(2); P(1)–C(1)–C(2)–O(1), –2.5(2); P(1)–C(3)–C(4)–C(2), –2.2(2).

and –2.2(2)°, respectively, indicating that the four-membered ring is almost planar.

The thermolysis of **3** (*d*₈-toluene, 190 °C) was carried out in a sealed tube and monitored by ¹⁹F NMR spectroscopy. The

reaction was complete after 24 h to give quantitatively olefin **4** and vinylphosphinic acid **6** instead of a double olefin extrusion. The phosphinic acid **6** was most likely formed by isomerization of intermediary tetracoordinate 1,2-oxaphosphetane **5** under the reaction conditions. Although a detailed kinetic study of the thermolysis has not been carried out yet, the thermolysis of compound **8a** under the same conditions gave the olefin **4** with 38% of **8a** unreacted, indicating that a spiro[3.3] compound is more reactive than a spiro[4.3] compound, because of the four-membered-ring strain.

In conclusion we have synthesized a novel spiro pentacoordinate 1,2-oxaphosphetane, 1,5-dioxo-4λ⁵-phosphaspiro[3.3]-heptane, and elucidated thermal behavior giving the olefin more readily than a spiro 1,2-oxaphosphetane bearing the Martin ligand. Further investigations including the synthesis of unsymmetrical compounds are in progress.

Acknowledgment. This work was partially supported by a Kurata Research Grant (T.K.) and a Grant-in-Aid for Scientific Research (B) No. 04553062 (T.K.) from the Ministry of Education, Science and Culture. We are grateful to Dr. N. Tokitoh of the University of Tokyo for the determination of the X-ray structure of **3**. We also thank Central Glass and Tosoh Akzo Co. Ltd. for gifts of hexafluoroacetone trihydrate and alkyllithiums, respectively.

Supplementary Material Available: An experimental procedure for the synthesis of **3**, physical and spectral data for **2** and **6**, and X-ray crystallographic data with tables of thermal and positional parameters, bond lengths, and bond angles of **3** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.