

The Phosphorus Version of the Oxaspiropentene-Cyclobutenone Rearrangement

Ngoc Hoa Tran Huy,*^{,†,‡} Bruno Donnadieu,[†] Guy Bertrand,*^{,†} and François Mathey*^{,‡}

[†]UCR-CNRS Joint Research Chemistry Laboratory, Department of Chemistry, University of California Riverside, Riverside, California 92521-0403, and [‡]Nanyang Technological University, Division of Chemistry & Biological Chemistry, 21 Nanyang Link, Singapore 637371

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Summary: The phosphatriafulvene complex 1 is sulfurized at phosphorus by reaction with propylene sulfide at room temperature. The X-ray crystal structure of 2 shows a long P-S bond (2.0039(5) Å) compatible with a zwitterionic formulation. The reaction of 1 with propylene oxide takes place at 110 °C and leads to the ring-expanded 1-phosphacyclobutenone 3. DFT calculations support the intermediacy of a phosphatriafulvene epoxide and its rearrangement to a four-membered ring, paralleling the oxaspiropentene-cyclobutenone conversion.

In spite of their low stability, it has proven possible to characterize a few oxaspiropentenes¹ and to demonstrate that they rearrange easily into the corresponding cyclobute-nones (eq 1).^{1a,b}



While studying the chemistry of phosphatriafulvenes obtained by condensation of stable nucleophilic carbenes with electrophilic terminal phosphinidene complexes,² we have discovered a rearrangement that appears to be the phosphorus version of this oxaspiropentene rearrangement. As for any phosphaalkenes with inverse electron density,³ the negatively charged phosphorus of phosphatriafulvenes is easily oxidized. We have found that a controlled oxidation takes place upon reaction with epoxides or episulfides. In the case of episulfides, the reaction stops at the primary sulfurization product (eq 2).



Compound **2** was characterized by X-ray crystal structure analysis (Figure 1). The most significant features of the structure concern its zwitterionic formulation. At 2.0039(5) Å, the P1–S1 bond has clearly a single-bond character, there

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is no bond between C1 and S1 (distance 3.138 Å), the threemembered ring remains essentially aromatic, and the P1–C1 bond is just slightly elongated by the sulfurization (1.8293(14) Å in 2 vs 1.806(8) Å in 1). More drastic conditions are needed to perform the reaction with the corresponding epoxide. At 110 °C, the primary product rearranges to give the four-membered-ring species 3 (eq 3), whose structure was established by X-ray analysis (Figure 2).



Similar compounds have already been obtained by insertion of carbon monoxide into phosphirenes (e.g., **4**).⁴ However, the presence of the amino substituents in **3** induces a significant change in the structure of the four-membered ring. Indeed, the C2–C3 bond has no significant doublebond character at 1.417(6) Å (vs. 1.36(1) Å in **4**) and one of the nitrogens (N2) is planar (\sum (angles) = 359.7°), hence the zwitterionic formulation. A related rearrangement has been found by Regitz on studying the reaction of azides with noncomplexed phosphatriafulvenes.⁵ Taking into account the carbon case and the fact that the controlled oxidation of phosphaalkene complexes is known to produce oxaphosphiranes,⁶ we were obliged to consider the possible formation of a spirooxaphosphirane as a precursor for **3** instead of

^{*}To whom correspondence should be addressed. E-mail: fmathey@ ntu.edu.sg (F.M.).

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Figure 1. X-ray crystal structure of sulfide 2. Main distances (Å) and angles (deg): P1-S1 = 2.0039(5), P1-C1 = 1.8293(14), P1-C4 = 1.8385(14), P1-W1 = 2.5282(4), C1-C2 = 1.3865(18), C1-C3 = 1.3857(19), C2-C3 = 1.4096(18); C1-P1-S1 = 109.80(5), C4-P1-S1 = 105.42(5), S1-P1-W1 = 115.873(18), C1-P1-C4 = 96.60(6), C1-P1-W1 = 108.54(5), C4-P1-W1 = 118.79(5).



Figure 2. X-ray crystal structure of phosphetene 3. Main distances (Å) and angles (deg): P1-C1 = 1.886(4), P1-C3 = 1.838(5), P1-C4 = 1.817(4), P1-W1 = 2.5004(12), C1-C2 = 1.431(7), C2-C3 = 1.417(6), C2-N1 = 1.416(5), C3-N2 = 1.321(6), C1-O1 = 1.220(5); C1-P1-C3 = 71.82(19), P1-C1-C2 = 92.4(3), C1-C2-C3 = 100.2(3), P1-C3-C2 = 95.0(3), C2-N1-C10 = 116.0(4), C2-N1-C13 = 112.8(4), C10-N1-C13 = 119.8(4), C3-N2-C16 = 119.2(4), C3-N2-C19 = 117.8(4), C16-N2-C19 = 122.7(4).

the oxygen analogue of the zwitterionic sulfide **2**. In order to check this hypothesis, we decided to perform DFT calculations at the B3LYP/6-31G(d)-Lanl2dz (W) level⁷ on the model compound **5**. We were delighted to find that it corresponds to a genuine minimum (no negative frequency). Its computed structure is shown in Figure 3. As expected, the three-membered ring is highly localized. The parameters of the *O*-cyclopropene unit are very close to those computed for the parent oxaspiropentene. ^{1c} Similarly, the computed parameters for **6** are in good agreement with those reported



Figure 3. Computed structure of oxaphosphirane 5. Main distances (Å) and angles (deg): P11-W12 = 2.4944, P11-C1 = 1.7843, P11-O2 = 1.7148, C1-O2 = 1.4525, C1-C7 = 1.4591, C1-C9 = 1.4584, C7-C9 = 1.3151; C1-O2-P11 = 67.99, C1-P11-O2 = 49.00, C7-C1-C9 = 53.58, C2-C1-C7-C9 = 113.94.

earlier for the triphenyl-substituted species 4^4 but are rather different from those of **3**.



In terms of energy, **5** is higher than **6** by 46.0 kcal mol⁻¹ but the transition state for a concerted rearrangement is higher than **5** by 36.2 kcal mol⁻¹ (ZPE included). This last value is too high for a ready rearrangement at 110 °C. Our conclusion is that the rearrangement probably proceeds in a stepwise manner. Thus, the introduction of phosphorus in the cycle does not block the oxaspiropentene-cyclobutenone rearrangement but seems to significantly alter its mechanism.

Experimental Section

Synthesis of the Sulfurization Product 2. A solution of 1 (70 mg, 1 mmol) in THF (5 mL) and propylene sulfide (0.1 mL) was stirred overnight at room temperature and then evaporated under vacuum. The light yellow precipitate was washed with pentane and dried under vacuum. Light yellow microcrystals were isolated (50 mg, 70% yield). ¹P NMR (CDCl₃): δ 32.7 ppm (¹J_{PW} = 249.5 Hz). ¹H NMR (CDCl₃): δ 1.32, 1.34 (2s, 24 H, Me), 4.04 (m, 4 H, CH), 7.43, 8.03 (2 m, 5H, Ph). The ¹³C NMR spectrum in CDCl₃ appears to be very complex: all the resonances corresponding to phenyl and carbonyl carbons are doubled, suggesting blocked rotations of the phenyl and W(CO)₅ groups around their bonds with phosphorus. Exact mass: *m*/*z* calcd for C₂₆H₃₃N₂O₅PSW [M + H] 701.1431, found 701.1431. Single crystals suitable for X-ray study were obtained from CH₂Cl₂ at -20 °C.

Synthesis of the Phosphacyclobutenone 3. A solution of 1 (prepared from 245 mg (0.4 mmol) of the 7-phosphanorbornadiene precursor² and 110 mg (0.4 mmol) of diisopropylcyclopropenylidene carbene² in diglyme (2 mL)) and an excess of propylene oxide (2 mL) were heated in a pressure tube at 110 °C for 4 h. The product

was purified by chromatography on silica gel with 1/4 hexane/ dichloromethane as the eluent; 170 mg of light yellow crystals was obtained (62% yield). ³¹P NMR (CDCl₃): δ 37.24 (¹J_{P-W} = 226.2 Hz). ¹H NMR (CDCl₃): δ 1.16, 1.18 (2s, 12 H, Me), 1.38 (br, 12 H, Me), 3.54 (m, 4H, CH), 7.50, 7.79 (2 m, 5H, Ph). ¹³C NMR (CDCl₃): δ 22.59, 23.24 (s br, CH₃); 51.43, 62.01 (s br, CH), 126.19 (d, ¹J_{CP} = 66.5 Hz, *ipso* C(Ph)), 128.99 (d, ³J_{CP} = 9.2 Hz *meta* CH Ph), 130.99 (d, ²J_{CP} = 12.7 Hz, N-C=), 131.65 (s, *para* CH Ph), 133.16 (d, ²J_{CP} = 11.4 Hz, *ortho* CH Ph), 176.27 (s, ¹J_{CP} = 43.6 Hz, N-C=), 184.49 (d, ¹J_{PC} = 25.2 Hz, C=O), 195.60 (d, ¹J_{PC} = 5.8 Hz, *cis* CO), 198.24 (d, ²J_{PC} = 24.1 Hz, *trans* CO). Exact mass: *m*/z calcd for C₂₆H₃₄N₂O₆PW (M + H) 685.1664, found 685.1668. Single crystals suitable for X-ray study were obtained from $CH_2Cl_2/$ hexane at $-20\ ^{\circ}C.$

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Supporting Information Available: CIF files giving details of the X-ray crystal structure analysis of compounds **2** and **3**. This material is available free of charge via the Internet at http:// pubs.acs.org.