

In summary, the isotope effects, the differences in the energies of activation, and the  $A^H/A^D$  ratios in the ene reaction of PTAD with alkenes **1** and **2** have been determined. These results are in agreement with substantial hydrogen tunneling in the title reaction.

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### The First Direct Observation of a Phosphenite: IR, UV, and $^{31}\text{P}$ NMR Spectra of 2,6-Di-*tert*-butyl-4-methylphenyl Phosphenite

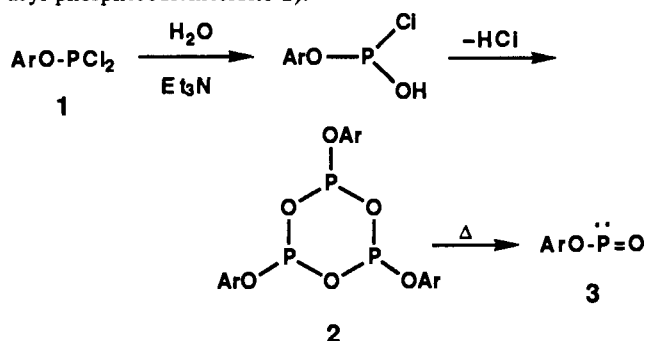
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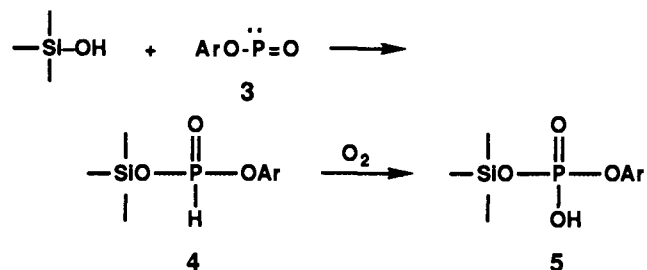
Even after the intense effort of recent years in the field of low-coordination phosphorus compounds, two-coordinate species with a p-p  $\pi$ -bond between phosphorus and oxygen remain a rarity;<sup>1</sup> except for the observation of some positive ions in mass spectra ( $\text{PhO-PO}^+$ ,<sup>2</sup>  $\text{Ph-PO}^+$ ,<sup>3</sup>  $3^4$ ), there is no record of an organic derivative bearing this feature that has been directly detected by spectroscopic techniques or that has been isolated. Evidence for the existence of such an organic compound is derived solely from trapping experiments.<sup>1</sup> In this communication, we report the infrared, ultraviolet, and  $^{31}\text{P}$  NMR spectra of 2,6-di-*tert*-butyl-4-methylphenyl phosphenite (**3**), generated by the thermolysis of the cyclic trimer **2** ( $\text{Ar} = 2,6\text{-di-}i\text{-tert-butyl-4-methylphenyl}$ ; prepared as reported<sup>5</sup> by partial hydrolysis of the sterically hindered aryl phosphorodichloridite **1**).



Chasar et al.<sup>4</sup> had previously sublimed **2** (220 °C, 1–1.2 kPa) and obtained a sublimate from which the dimer of the phosphenite was isolated. This suggested that the monomeric phosphenite was present in the gaseous products from the pyrolysis, possibly deriving a measure of stabilization from the space demand of the O-substituent.

To prove the intermediacy of phosphenite **3** in the gas phase, we employed a technique that we have developed for detecting alkyl metaphosphates ( $\text{RO-PO}_2$ ) in solution;<sup>6</sup> we exposed silica gel to the gaseous products with the expectation that the powerfully

electrophilic<sup>1</sup>  $\text{P=O}$  group would attack the surface hydroxy groups as it attacks alcohols in solution and create the H-phosphonate group on the surface (**4**). We employed an evacuated (0.15 mm)



Kugelrohr apparatus with the first bulb serving as the reactor for decomposing the solid trimer (0.29 g), the second as the reactor containing solid silica gel (1.2 g, Aldrich 70–230 mesh), the whole assembly being rotated inside the oven (250 °C) to keep fresh silica surface exposed to **3**. After 1 h, the silica gel was removed, washed three times with 2-propanol, and the CP-MAS  $^{31}\text{P}$  NMR spectrum then recorded (Bruker 200 MHz,  $\text{CaHPO}_4$  as reference). The major signal at  $\delta -4$  is consistent with the expected H-phosphonate **4**; the ethyl ester of the same H-phosphonate has  $\delta +4$ , but as is typical of phosphates, it can be expected that the silyl group will cause an upfield shift of 8–10 ppm.<sup>7</sup> A small signal at  $\delta -16$  is attributed to the corresponding phosphate (**5**), since exposing the silica to oxygen enhanced this signal and reduced that for **4**. A small signal at  $\delta +7$  may be due to adsorbed  $\text{ArOPH(O)OH}$  from hydrolysis. We conclude that the gas phase did indeed contain the phosphenite **3**.

Trimer **2** was then thermolyzed at 250 °C and  $10^{-5}$  mm in such a way as to allow deposition of **3** on a KBr window at 12 K in an APD Cryogenics Displex closed-cycle helium cryostat.<sup>9</sup> The infrared spectrum was recorded at 12 K and then at several temperatures up to 272 K. A strong band at  $1235\text{ cm}^{-1}$  at 12 K is attributed to stretching of  $\text{P=O}$  in phosphenite **3**; values summarized<sup>1</sup> for phosphorous acid and its halo derivatives in argon matrices show a range from  $1252.6$  to  $1292.2\text{ cm}^{-1}$ . The signal was noticeably diminished on reaching 150–200 K and essentially disappeared by 270 K. As it disappeared, a new strong signal appeared at  $820\text{ cm}^{-1}$  assignable to  $\text{P-O-P}$  bending<sup>9</sup> as would be present in either the dimeric or trimeric condensation product of phosphenite **3**. That the low temperature was not in some way responsible for the observed spectral changes was shown by re-cooling the sample on the KBr window to 12 K, without effect on the IR spectrum.

A film of **3** was similarly deposited on a quartz plate in the Displex apparatus at 12 K, and the ultraviolet spectrum was recorded.<sup>8</sup> The spectrum consisted only of two equal-intensity bands at 271 and 278 nm. These signals disappeared by the time the temperature was raised to 272 K; the spectrum then resembled that of the pure trimer **2** in possessing only end absorption at 200

(7) A typical example is given: Quin, L. D.; Hughes, A. N.; Wu, X.-P.; Dickinson, C. L. *J. Chem. Soc., Chem. Commun.* **1988**, 555.

(8) The Displex is equipped with a standard DMX-15 optical spectroscopy vacuum shroud. Suprasil windows were used on the shroud for UV-vis spectroscopy, KBr windows for IR spectroscopy. The pyrolysis reaction chamber consisted of a 15 cm long  $\times$  4 mm (i.d.) Pyrex tube with a bulb at one end, attached with epoxy resin to a stainless steel plate with a hole drilled in it to allow effusion of pyrolysis volatiles from the bulb through the plate. The reaction chamber, charged with about 30–50 mg of **2**, was attached in an orientation perpendicular to the optical windows of the DMX-15 shroud, placed over the Displex cooling stage and its attached spectroscopic sample holder, and the Displex cooling assembly then evacuated to  $<0.01$  mTorr. The sample holder was then precooled to 11–12 K, the DMX-15 shroud was rotated so that the shroud plate holding the pyrolysis chamber faced the sample holder inside, and the chamber was suddenly heated to 250 °C by placement inside a preheated Kugelrohr oven. Heating was continued for about 60 s, then the heat source was removed, and the outer shroud rotated to align the sample holder optical disk with the shroud optical windows. A visually transparent film of neat material was deposited as a matrix on the cold sample window. Spectra (UV-vis by Shimadzu UV-260, IR by Perkin Elmer 1420) were subsequently acquired at 12 K and then at 50, 100, 200, and 270 K.

(9) For the dimer,  $\text{P-O-P}$  bending has been noted at  $853\text{ cm}^{-1}$  (Nujol).<sup>4</sup>

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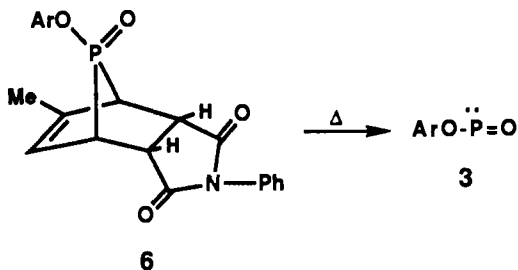
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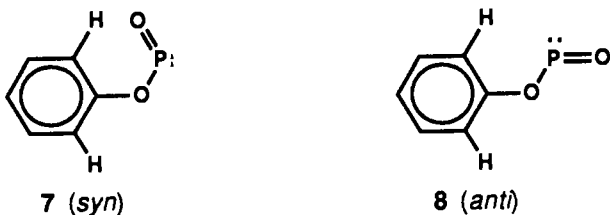
(6) Quin, L. D.; Wu, X.-P.; Breuer, E.; Mahajna, M. *Tetrahedron Lett.* **1990**, *31*, 6281.

nm (acetonitrile) and was not further changed on recooling to 12 K. This is the first UV spectrum to be recorded for a two-coordinate phosphoryl compound. INDO/S-CI computations<sup>10</sup> suggest that the transient bands are due to transitions of  $\pi \rightarrow \pi^*$  nature; a more detailed analysis of the spectrum is in progress.

We have also observed the <sup>31</sup>P NMR spectrum of phosphinite 3. This was accomplished by condensing the gases from the pyrolysis of trimer 2 on a vacuum line (300–350 °C, 0.1 mm) into an NMR tube sealed on the line and chilled by liquid nitrogen, into which ethylene dichloride had been condensed to serve later as the solvent. The sample was thawed (about –30 °C), and the tube was rapidly inserted in the probe of a Varian 300 MHz NMR spectrometer. The spectrum consisted mainly of signals for the dimer ( $\delta$  176.5) and trimer ( $\delta$  120.0 (d,  $J$  = 10 Hz), 127.9 (t,  $J$  = 10 Hz), whose parameters matched those reported.<sup>4,5</sup> However, a small signal (about 4–5% of total intensities) was present at  $\delta$  238. It disappeared after a few hours, behavior that suggested it could arise from the monomeric phosphinite 3. Nearly the same <sup>31</sup>P NMR spectrum, containing the weak transient signal at  $\delta$  238, was obtained when phosphinite 3 was generated by a different method, the thermal fragmentation (250 °C, 0.03 mm) of the 7-phosphanorbornene derivative 6.<sup>11</sup> Since this is the first report



of the <sup>31</sup>P NMR shift of any two-coordinate phosphoryl compound, we felt it necessary to validate our assignment by computational methods. The simpler model PhO—P=O was held in fixed rotational conformations for these calculations.<sup>12</sup> Values ( $\pm 30$ ) calculated for the fully coplanar conformations 7 (syn) and 8 (anti) were  $\delta$  247.9 and  $\delta$  265.0, respectively. With phenyl perpendicular



to the plane of the O—P=O moiety, the anti conformer had  $\delta$  280.2, the syn  $\delta$  258.1. If an equal contribution from all conformers is arbitrarily assumed, an averaged shift for phenyl phosphinite is  $\delta$  263  $\pm$  30. The experimental value of  $\delta$  238 is within this range, and we believe the assignment of this shift to the more highly substituted derivative 3 is supported by the theoretical computations.

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## Thermal Interconversion of a Pair of Diastereomeric Cyclopropanones. An Upper Limit for a Cyclopropanone–Oxyallyl Energy Separation

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The racemization of enantiomerically enriched *trans*-2,3-di-*tert*-butylcyclopropanone 1a,b in various solvents at 80 °C, described in a pioneering paper by Greene and co-workers,<sup>1</sup> is the only prior case in which a thermal stereomutation experiment has been used to estimate the energy separation between a cyclopropanone and its corresponding oxyallyl. The authors<sup>1</sup> postulated a disrotatory<sup>2</sup> ring opening of the cyclopropanone to a planar oxyallyl intermediate or transition state 2, in which one *tert*-butyl group would occupy a hindered position on the allylic moiety (Scheme I).

To evaluate the stereomutation barrier in a less hindered case and thereby provide a bridge to the simple cyclopropanones amenable to computational study,<sup>3,4</sup> we have investigated the diastereomeric spirocyclopropanones 3 and 4. Because of the decreased hindrance in the cognate oxyallyls 5 and 6 (Scheme II) relative to that in 2, we expected  $\Delta G^\ddagger$  values for 3 and 4 to be much lower than those for 1a,b.

Compounds 3a and 4a were obtained<sup>5</sup> in a 1.65:1 ratio from the addition of diazomethane to the corresponding ketene, 2-(oxomethylene)bicyclo[2.2.1]heptane. Aliquots of diethyl ether solutions of this mixture of 3a and 4a were stored for a series of times at several temperatures over the range 235–256 K. As monitored by direct capillary gas chromatography, quenching with methanol–ether gave two hemiketal products from each cyclopropanone, in addition to negligible amounts of Favorski esters. The hemiketal ratio changed with time, and at 283.5 K, for example, reached an equilibrium 3a:4a value ( $1/K_{eq}$ ) of 0.82. By this technique (GC method), the rate constant  $k_{obsd}$  for approach to the equilibrium composition could be obtained. It corresponds to the sum of the forward and reverse rate constants,  $k_f$  and  $k_r$  (eq 1).

$$k_{obsd} = \frac{1}{t} \ln \frac{[4]_{eq} - [4]_0}{[4]_{eq} - [4]} = k_f + k_r = \left(1 + \frac{1}{K_{eq}}\right) k_f \quad (1)$$

The reaction also could be monitored (229–247 K) by direct <sup>2</sup>H NMR observation (Figure 1) of 3b and 4b in a high-field spectrometer (11.74 T, rf 500 MHz for protons), which for each diastereomer showed only the two CD<sub>2</sub> signals. The isotopically labeled compounds were synthesized from 2-(oxomethylene)bicyclo[2.2.1]heptane and *dry*<sup>6</sup> diazomethane-*d*<sub>2</sub>.<sup>7,8</sup> Rate and equilibrium constants determined by the GC and NMR methods were in agreement to within 20% and 5%, respectively.

Scheme II illustrates a hypothetical mechanism for stereomutation via oxyallyls 5 and 6. The phenomenological rate

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