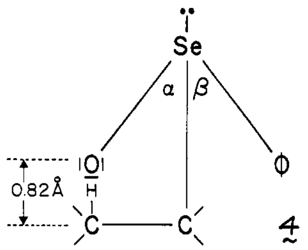
as represented in the cyclic array, **4**, of the centers involved in



4

CYLIC ARRANGEMENT LEADING
TO TUNNELING H-TRANSFER
IN SELENOXIDE THERMOLYSIS

H transfer. Using the VSEPR model[11] as the basis for interpretation, tunneling can be said to be fostered in ethyl-*tert*-butyl sulfoxide[9] mainly because of the alkyl group repulsions. Such circumstances tend to widen the C–S–Et angle as well as diminish the O–S–C angle from what is realized in a normal sulfoxide, where the angle is sufficiently great to accommodate a concerted, linear, H-transfer transition state.[4] Due to the longer bonds (compared to sulfur), even the bulkiest substituents on selenium would be mutually less repulsive. In addition, the more electropositive selenium releasing electrons to the oxygen and phenyl substituents must experience much weaker repulsive forces between its bonding electron pairs. Such factors make for considerably smaller angles α and β (in **4**) as compared to normal sulfoxides. The observation of tunneling and the low-activation demand in the thermal β-elimination reaction of selenoxides is thus made understandable.

Acknowledgment. Support of this research by the National Science Foundation, Grant CHE 79-11110, is gratefully acknowledged.

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(11) (a) Gillespie, R. J. "Molecular Geometry"; Van Nostrand Reinhold, New York, 1972. (b) *J. Chem. Educ.* **1963**, *40*, 295; *Ibid.* **1967**, *47* 118.

A Stable Monocyclic Triarylalkoxy P-H Phosphorane, a 10-P-5 Species with an Apical P-H Bond, and Its Conjugate Base, a Phosphoranide

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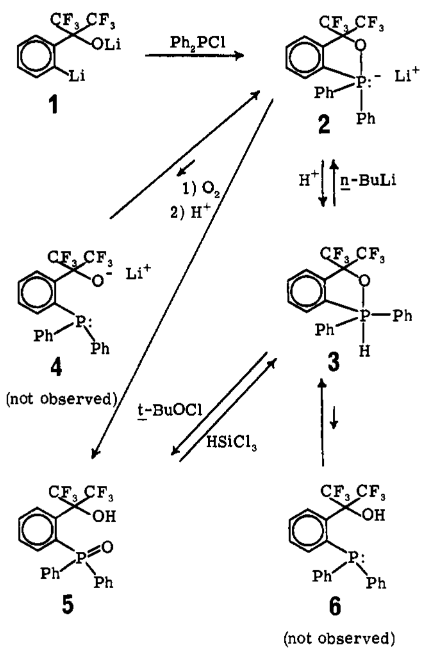
We wish to report the isolation of a monocyclic triarylalkoxy phosphorane possessing an apical P–H bond, 10-P-5 species[1] **3**, and the anion formed from it by deprotonation, the 10-P-4 species phosphoranide **2**. Although other monocyclic P–H phosphoranes have been reported,[2] none have been reported as having an apical P–H bond. We are not aware of other reports of a monocyclic phosphoranide anion.

Scheme I



Phosphorane **3** was prepared from the reaction of dilithium reagent **1**[3] and Ph_2PCl in 50% isolated yield[4] and purified by column chromatography (silica gel, $CHCl_3$) (Scheme I). The ^{31}P NMR of **3** (all ^{31}P NMR chemical shifts are expressed as ppm downfield of external 85% H_3PO_4) with a doublet at −49.30 ppm ($CDCl_3$, $^1J_{PH} = 266$ Hz) clearly indicates a 10-P-5 species with direct P–H bonding.[5] No evidence for 8-P-3 species **4** or **6** is seen in the NMR spectra at temperatures as low as −100 °C.[6] Phosphoranide **2** gives phosphine oxide **5**[7] upon exposure to oxygen. Compound **5**, prepared (in 100% yield) from **3** and *tert*-butyl hypochlorite,[7] was converted to **3** in high yield (80%) upon treatment with $HSiCl_3$.

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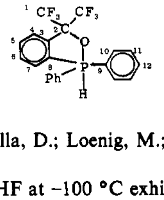
(1) The designation 10-P-5 refers to the fact that 10 electrons are formally involved in bonding 5 ligands to phosphorus. (See: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753).

(2) (a) Malavaud, C.; Barrans, J. *Tetrahedron Lett.* **1975**, 3077. (b) Wieber, M.; Hoos, W. R. *Monatsh. Chem.* **1970**, *101*, 776. (c) Laurenco, C.; Burgada, R. *Tetrahedron* **1976**, *32*, 2253. (d) Lafaille, L.; Mathis, F.; Barrans, J. *C. R. Hebd. Seances Acad. Sci., Ser. C Ser. C* **1977**, *285c*, 575. (e) Boisdon, M. T.; Malavaud, C.; Mathis, F.; Barrans, J. *Tetrahedron Lett.* **1977**, 3501. (f) Malavaud, C.; Charbonnel, Y.; Barrans, J. *Ibid.* **1975**, 497. (g) Lopez, L.; Fabas, C.; Barrans, J. *Phosphorus Sulfur* **1979**, *7*, 81.

(3) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591.

(4) Elemental analyses of all new compounds are within 0.4% of calculated values. **3**: mp 149–150 °C; ^1H NMR ($CDCl_3$) δ 6.82 (d, 1, $^1J_{PH} = 266$ Hz, P-H), 7.34–7.43 (m, 6), 7.65–7.71 (m, 3), 8.06–8.21 (m, 5, H ortho to P on PPh_2; H ortho to P on disubstituted phenyl); ^{19}F NMR ($CDCl_3$) ϕ 74.80 (s); ^{31}P NMR ($CDCl_3$) δ −49.30 (d, $^1J_{PH} = 266$ Hz); ^{31}P NMR (THF) δ −49.45 (d, $^1J_{PH} = 273$ Hz); IR (CCl_4) 2256 cm^{-1} (ν_{P-H}); IR (Nujol) 2150 cm^{-1} (ν_{P-H}); ^{13}C NMR (CD_2Cl_2, 62.908 MHz, ^1H decoupled) δ 79.76 (septet, $^2J_{CF} = 30.0$ Hz, C-2), 123.48 (q, $^1J_{CF} = 290.4$ Hz, C-1), 125.91 (d, $^2J_{CP} = 13.4$ Hz, C-7), 128.66 (s, C-11), 128.92 (s, C-12), 131.40 (d, $^1J_{CP} = 16.5$ Hz, C-9), 131.86 (s, C-4), 132.51 (d, $^2J_{CP} = 10.6$ Hz, C-3), 133.86 (d, $^1J_{CP} = 18.5$ Hz, C-8), 134.81 (s, C-5), 135.11 (d, $^2J_{CP} = 13.4$ Hz, C-10), 131.92 (s, C-6). The following carbons exhibited doublet structure from coupling to protons in the off-resonance proton-decoupled spectrum: C-4, C-5, C-6, C-7, C-10, C-11, and C-12. MS (70 eV) *m/e* (relative intensity) 428 (24.0, $M^{+\cdot}$), 427 (100.0, $M^{+\cdot}-H$). Anal. ($C_{21}H_{15}F_6OP$) C, H, P.



(5) Brazier, J. F.; Houalla, D.; Loenig, M.; Wolf, R. *Top. Phosphorus Chem.* **1976**, *8*, 99.

(6) Phosphorane **3** in THF at −100 °C exhibited a ^{31}P NMR resonance at −47.9 ppm (doublet of sharp lines, $^1J_{PH} = 279$ Hz). No downfield resonance (expected for **4**) was detected. Phosphoranide **2** revealed no change in its ^{31}P NMR at −100 °C in THF.

(7) mp 168.5–170 °C; ^1H NMR ($CDCl_3$) δ 7.27–7.73 (m, 13), 7.90–8.13 (m, 1); ^{19}F NMR ($CDCl_3$) ϕ 74.47 (s); ^{31}P NMR ($CDCl_3$) δ 43.0 (s); MS (70 eV) *m/e* (relative intensity) 444 (1.04, $M^{+\cdot}$), 443 (3.31, $M^{+\cdot}-H$), 376 (26.5, $M^{+\cdot}-CF_3$), 375 (100.0, $M^{+\cdot}-CF_3-H$). Anal. ($C_{21}H_{15}F_6O_2P$) C, H, P.

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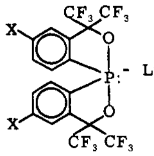
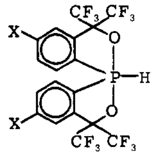
That **2** is a 10-P-4 species and not an 8-P-3 phosphino alkoxide (**4**) is evidenced by its ^{31}P NMR chemical shift of −11.1 ppm (THF), similar to that observed for a closely analogous case previously described,[8a] **7a**, and for the analogous compound reported herein, **7b**,[8b] formed by deprotonation of the trigonal-bipyramidal[8c] (TBP) conjugate acids **8a** and **8b**. The slow proton exchange between **2** and **3** allowed a simple ^{31}P NMR determination of an approximate pK_a of **3**. Upon addition of 1 equiv of ethyl acetoacetate (pK_a = 10.68[9]), **2** was 74% protonated to give **3**. From this we calculate a pK_a of 11.6.[10a] A Hammett correlation of pK_a and substituent σ values for a series of substituted hexafluoro-2-phenyl-2-propanols (R_FOH) gave $\rho = 1.49 \pm 0.13$ from which we calculate pK_a = 9.53 for **6** (*o*-PPh_2, $\sigma = 0.16$).[10b] The ΔG for the process equilibrating isomeric acids **3** and **6** cannot be determined directly or from the difference in their pK_a as they do not share a common conjugate base. However, since **2** is more stable than **4** (**4** is not observed), we calculate a lower limit to the ΔG for the equilibrium **3** ⇄ **6** to be 3.0 kcal/mol ($\Delta G_{30^\circ C} = -RT \ln [(K_a)_6/(K_a)_3]$).



7a, X = CH_3, δ^{31}P -17.9 ppm
7b, X = H, δ^{31}P -18.5 ppm



8a, X = CH_3, δ^{31}P -47.6 ppm (d, J = 730 Hz)
8b, X = H, δ^{31}P -48.2 ppm (d, J = 733 Hz)

We have recently solved the X-ray crystal structure of **3**. The preliminary results at the current level of refinement (R = 0.06) clearly reveal the apical disposition of the P–H bond with an approximate TBP geometry about phosphorus.[11]

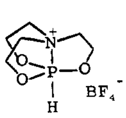
Phosphoranes with P–H bonds normally exhibit $^1J_{PH}$ in the range 650–900 Hz.[5] Verkade's tricyclic phosphorane **9** with an apical proton[13] has $^1J_{PH}$ = 791 Hz, much larger than that of **3** (266 Hz). This observation must be reconciled with the hypothesis that both substances indeed have apical P–H bonds.

It has been noted[5,14] that $^1J_{PH}$ increases linearly, in a series of tetracoordinate (8-P-4) P–H species, as the sum of the electronegativities of the other three atoms bound to phosphorus.[14] The extension of this correlation to P–H phosphoranes is complicated by the probability that in a TBP molecule the effect on $^1J_{PH}$ of a substituent in an equatorial position is different from the effect of that same substituent in an apical position. Most reported P–H phosphoranes are thought to have slightly distorted TBP geometry with the proton occupying an equatorial position. We have found that 52 such equatorial P–H phosphoranes, for which relatively unambiguous structural assignments can be made, show a variation of spin–spin coupling constants with substituent (from 621 to 1115 Hz) and this is described[15] by

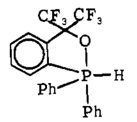
$$^1J_{PH} = 306[\textstyle\sum\sigma_I(\text{equatorial}) + 0.505\sum\sigma_I(\text{apical})] + 595 \quad (1)$$

where $\sum\sigma_I$ is the sum of Taft σ_I parameters.[16] The point for each of these compounds falls within two standard deviations[16] of the regression line. An equatorial substituent is thus shown to be about twice as effective as an apical substituent in influencing $^1J_{PH}$ for an equatorial proton.

Phosphorane **9** (whose X-ray crystallographic structure has an apical proton) and **3** (which we here postulate to have an apical proton) lie below the line of eq 1 by 174 Hz (4.9 standard deviations) and 478 Hz (13.4 standard deviations), respectively.[17] The approximate hypervalent bonding scheme[19] suggests that apical bonds will have less central atom s-orbital contribution than will the equatorial bonds, in keeping with the observation that these compounds show much smaller values of $^1J_{PH}$ than predicted by eq 1. This is consistent with the postulated structure for **3**.



9



10

Infrared P–H stretching frequencies for these 10-P-5 compounds usually fall in the range 2360–2430 cm^{-1}.[5] Both **3** (2256 cm^{-1}, CCl_4; 2150 cm^{-1}, Nujol) and **9** (2240 and 2286 cm^{-1}, KBr)[13] exhibit lower P–H stretching frequencies than usual, in accord with the postulated apical disposition of their P–H bonds.

Another line of evidence for the structure assigned to **3**, with an apical proton, is the observation that the ^{19}F NMR of **3** shows[20] a single sharp line (74.80 ppm upfield of $CFCl_3$) at temperatures as low as −100 °C. The CF_3 groups of the isomer of **3** with an apical phenyl and an equatorial proton, **10**, are nonequivalent and might be expected to give rise to two ^{19}F multiplets.[21] If a very rapid equilibrium of **10** and its enantiomer is responsible for the equivalence of the CF_3 groups, the energy barrier must be a very small one.

The 63-MHz ^{13}C NMR spectrum[4] provides further evidence for structure **3** in solution at ambient temperature. Seven carbons show doublet structure from coupling to protons in the off-resonance proton-decoupled spectrum, as expected for structure **3** but not for structure **10**.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (CHE-79-07-7905692). We are grateful to Dr. Itshak Granoth of the Israel Institute for Biological Research, Ness Ziona, for many enlightening discussions and Dr. Steve Ulrich of the Molecular Spectroscopy Laboratory, Roger Adams Laboratory, for obtaining the ^{31}P NMR spectra.

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(8) (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4623. (b) **8b** (from 2 equiv of **1** and 1 equiv of PCl_3): yield 21.7%; mp 156–157 °C; ^{1}H NMR ($CDCl_3$) δ 8.37 (d, 1, $^1J_{PH}$ = 733 Hz), 7.60–7.93 (m, 6), 8.17–8.53 (m, 2, H ortho to P); ^{19}F NMR ($CDCl_3$) ϕ 75.03 (q, 6, $^4J_{FF}$ = 9.0 Hz), 76.30 (dq, $^4J_{FF}$ = 9.0 Hz, $^4J_{PF}$ = 4.5 Hz); ^{31}P NMR (Et_2O) −48.2 ppm (d, $^1J_{PH}$ = 733 Hz); MS (10 eV) *m/e* (relative intensity) 516 (12.1, $M^{+\cdot}$), 515 (55.6, $M^{+\cdot}$–H), 448 (17.3, $M^{+\cdot}$–CF_3), 447 (100.0 M^{+}–CF_3). Anal. ($C_{18}H_9F_{12}O_2P$) C, H, P. (c) Full results of a crystal structure determination of **8b**, confirming a TBP structure with an equatorial P–H disposition will be reported in a later paper.

(9) Eidinoff, M. L. *J. Am. Chem. Soc.* **1945**, *67*, 2072.

(10) (a) Application of this method using CH_3NO_2 as the weak acid (pK_a = 10.24)[12] gave a pK_a of 11.8 for **3**. (b) Using the σ value determined for the para isomer by Johnson, A. W.; Jones, H. L. *J. Am. Chem. Soc.* **1968**, *90*, 5232.

(11) Full results of the X-ray crystal-structure determination for **3**, carried out in collaboration with Dr. Scott Wilson, will be reported in a later paper. The TBP structure is only slightly distorted, with angles between apical and equatorial bonds in the range 85.2 (2)–92.5 (11)°.

(12) Wheland, G. W.; Farr, J. *J. Am. Chem. Soc.* **1943**, *65*, 1433.

(13) Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 6607. A crystal structure of **9** has been described: Clardy, J. C.; Milbrath, D. S.; Springer, J. P.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 623.

(14) (a) Wolf, R.; Houalla, D.; Mathis, F. in "Composés Organiques du Phosphore"; CNRS: Paris, 1966; pp 84–98. (b) Mavel, G. *Ibid.*, pp 49–70.

(15) Correlation coefficient = 0.9042, number of data points = 52, standard deviations: slope, 20.43; *y* intercept, 15.86; *y* residuals, 35.77; largest *y* residual = 66.31 (1.85 standard deviations off the line).

(16) Values used were for model substituents in the tables of Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323. The P–H phosphoranes used included examples of every structural variety in ref 5, except for two for which no suitable models for σ_I could be found. This study will be described in detail in a later paper.

(17) Hellwinkel's spirobicyclic P–H phosphorane[18] with four aryl ligands ($^1J_{PH}$ (calcd) = 699 Hz, $^1J_{PH}$ (obsd) = 482 Hz) and a number of other P–H phosphoranes that are monocyclic[2c–e] all fall off and below the line, by about 4–5 standard deviations. These data suggest either static apical P–H structures for these compounds or equilibria interconverting apical and equatorial P–H sites. The fact that **3** is so far off the line (13.4 standard deviations) is consistent with a static apical P–H structure for **3**.

(18) Hellwinkel, D. *Chem. Ber.* **1969**, *102*, 528.

(19) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.

(20) ^{19}F NMR ($CDCl_3$); ambient temperature, ϕ 74.80 (sh s); ^{19}F NMR (THF-d_8): ambient temperature, ϕ 74.14 (sh s); −102 °C, 72.0 (sh s).

(21) For example, phosphorane **8a**[8a] reveals nonisochronous and nonisogamous CF_3 groups, one type endo, the other exo to the two phenyl rings: ^{19}F NMR (THF) ϕ 74.32 (6 F, q, $^4J_{FF}$ = 9 Hz), 75.58 ppm (6 F, dq, $^4J_{FF}$ = 9 Hz, $^4J_{FP}$ = 3 Hz). Phosphorane **8b**[8b] also exhibits this behavior.