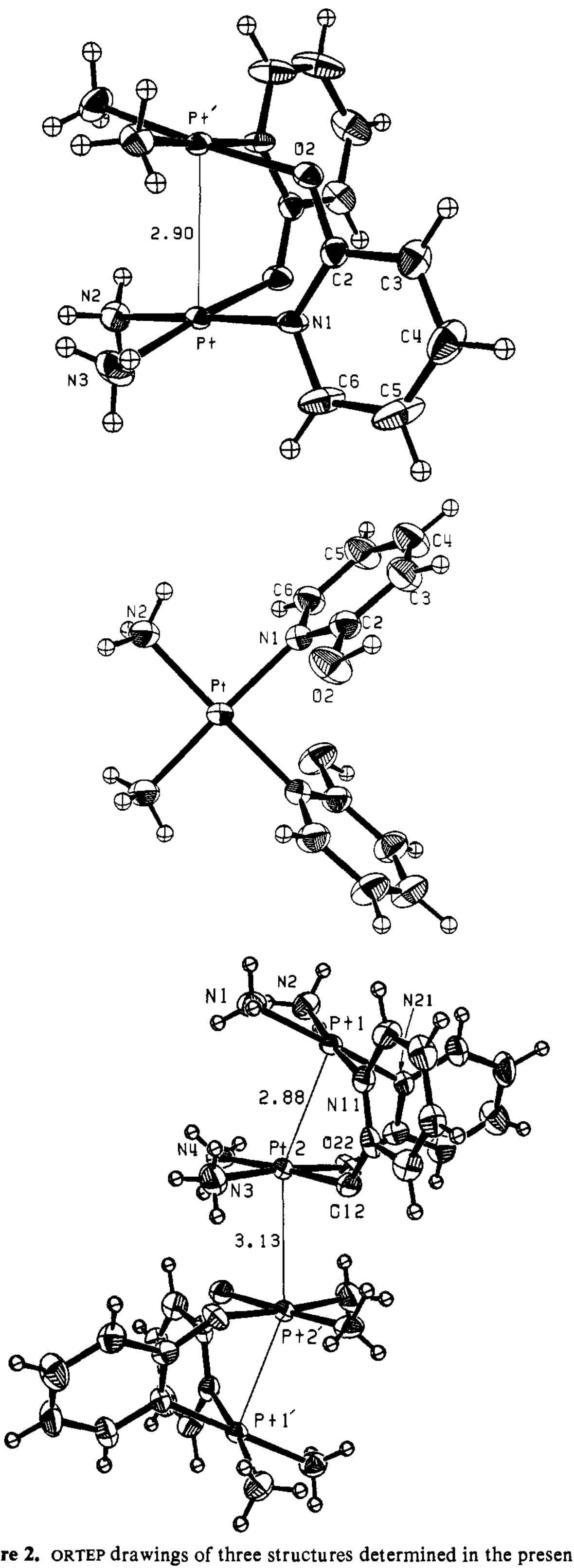

Figure 2. ORTEP drawings of three structures determined in the present study, head-to-tail bis(μ-α-pyridonato-*N*,*O*)bis(*cis*-diammineplatinum(II)) nitrate dihydrate (**5**), bis(2-hydroxypyridine)diammineplatinum(II) chloride (**6**), and head-to-head bis(μ-α-pyridonato-*N*,*O*)bis(*cis*-diammineplatinum(II)) nitrate (**7**). For clarity, hydrogen atoms are depicted as arbitrary spheres with $B = 1$ Å^2. In **5** there is a crystallographic twofold axis relating the two halves of the cation; in **6**, the platinum atom lies on a crystallographic twofold axis; in **7**, the two halves of the tetramer are related by a crystallographic inversion center.

adduct (**8**).

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Supplementary Material Available: Atomic positional and thermal parameters for compounds **5**–**7** (2 pages). Ordering information is given on any current masthead page.

Structure of the Reaction Barrier in the Selenoxide-Mediated Formation of Olefins

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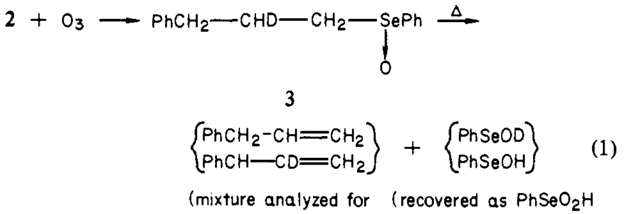
The use of selenoxide-forming procedures has become very popular as a means of introducing the double bond into complex organic structures via a stereospecific, syn elimination.[1] These methods appear to have been almost indispensible in the synthesis of many natural products[2] where reaction of compounds with low-activation requirements have their greatest utility. The mechanistic course of the analogous reaction of sulfoxides, which have somewhat higher activation demands, has been studied in these laboratories by application of kinetic deuterium isotope effect criteria.[3] Through measurement of the temperature dependence of k_H/k_D it was shown that the normal thermolysis of sulfoxides takes place via a planar, 5-membered, pericyclic transition state.[4] This investigation of the course of thermolysis of selenoxides was undertaken with the objective of ascertaining the origins of the diminished activation requirements[1d,f] when selenium replaces sulfur in corresponding reaction transition states.

Cinnamyl alcohol was converted to 3-phenyl-2-deuteriopropanol (**1**) in near quantitative yield by the procedure of Hochstein and Brown.[5] This was converted to the tosylate and thence to the phenyl selenide (**2**) utilizing a method described by Clark and Heathcock.[6] When **2** was ozonized to its selenoxide **3** and this in turn decomposed unimolecularly[1d,f] in an inert solvent at temperatures within the range 40–85 °C, the product composition of allybenzenes (in accord with eq 1) could be directly related



$$2 + O_3 \longrightarrow \underset{\textstyle 3}{PhCH_2{-}CHD{-}CH_2{-}\underset{\textstyle O}{\overset{}{\underset{|}{Se}}}Ph} \xrightarrow{\Delta} \left\{\begin{matrix} PhCH_2{-}CH{=}CH_2 \\ PhCH{-}CD{=}CH_2 \end{matrix}\right\} + \left\{\begin{matrix} PhSeOD \\ PhSeOH \end{matrix}\right\} \quad (1)$$

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Table I. Temperature Dependence of k_H/k_D in Thermolysis[a] of Selenoxide 3

solvent[b]	reaction temp, °C	measured ratio[c,b] M_{119}/M_{118}	corrected ratio[d] $M_D/M_H = k_H/k_D$	no. of determinations
CH_2Cl_2	40.5	0.749 ± 0.002	5.23 ± 0.01	20 000
$CHCl_3$	61.7	0.722 ± 0.002	4.00 ± 0.01	20 000
CCl_4	77.2	0.704 ± 0.001	3.443 ± 0.005	20 000
$C_2H_4Cl_2$	84.4	0.694 ± 0.001	3.165 ± 0.005	20 000

Calculated Parameters

$A_H/A_D = 0.092 \pm 0.003$, $[\Delta E_a]^H_D = 2.52 \pm 0.06$ kcal/mol

[a] The kinetic runs were carried out by the slow, dropwise addition of ca. 150 mg of reactant in dilute solution to the stirred solvent (>100 mL) maintained at the desired temperature to better than ±0.1 °C, as observed on a Bureau of Standards calibrated thermometer immersed in the liquid being heated in a flask surrounded by thermoregulated, insulated mantle. After all the reactant solution was added, heating was continued until all of the decomposition reaction had been completed, as determined by a preliminary rate measurement. This procedure was rigorously followed in order to preclude any significant part of the thermal decomposition reaction from occurring during a "heating-up" period, i.e., the period required for the very dilute solution of reactant to come to the stipulated reaction temperature. [b] We have concluded that, within the range of water-free (very dry) chlorinated solvents and reaction media employed, no significant solvent effect or comproportionation effect[1d] could have been exerted on the rate ratio k_H/k_D, determined at each of the temperatures, for the following reasons. (a) Solvent effects observed for the syn elimination of selenoxides have only been noted for protic solvent.[1d] All the solvents used (Table I) were inert, chlorinated solvents which have virtually the same dielectric strength and no H-bonding properties to accommodate those of the selenoxides. Thus there was no basis for anticipating an effect on relative rate, k_H/k_D, arising from the medium changes in Table I even if a very slight solvent effect on the absolute rate of selenoxide decomposition had occurred. Preliminary studies, in fact, had supported this conclusion before undertaking the actual k_H/k_D measurements. (b) The possibility of a reverse bimolecular addition of benzeneselenic acid to the olefin product was made extremely minimal by working at concentrations of less than 0.005 molar. The (bimolecular) comproportionation side reaction leading to β-hydroxy selenides[1d] was similarly suppressed at these reaction concentrations, as evidenced by failure to observe any such side products in the course of thin-layer and other chromatographic procedures applied in the workup and purification of the olefinic product prior to mass ratio analysis.[7] These reaction conditions were selected to avoid the use of the amines usually recommended[1d] to inhibit reverse and side reactions when working at "preparative" reaction concentrations. The addition of amine inhibitors was avoided for fear of an influence on k_H/k_D through possible catalytic effects deviating the essential cyclic mechanism of syn elimination. (c) Finally, we believe, if any significant secondary D-isotope effect had been involved, due to even the small likelihood of reversibility of the cyclic, unimolecular syn elimination mechanism of selenoxide thermolysis, we should have seen this revealed (1) either as a departure from the linear Arrhenius relation of the log k_H/k_D vs. $1/T$ (correlation coefficient $r = 0.999$), or (2) the sizes of such secondary D-isotope effects, as might have resulted from reversibility ($k_H/k_D \sim 1.1$), would be negligible compared to the much greater magnitudes of the tunnel effect observed ($k_H/k_D \sim 3.2$–5.2) and thus have no impact on the mechanistic conclusions drawn from the results reported in Table I. That is to say, the quality of the results and the considerations taken above appear to exclude even the remote possibilities of experimental artifact and coincidence. [c] The molecular ions of allylbenzene and 2-deuterioallylbenzene were measured at 118 and 119 amu, respectively, with an ionizing potential of 70 eV. [d] M_D/M_H was derived from M_{119}/M_{118} by subtracting out the contributions of the M_{D-1} peak and the M_{D+1} peak. Analyses of pure allylbenzene and 2-deuterioallylbenzene gave the ratios $M_{H+1}/M_H = 0.0923 \pm 0.0002$ and $M_{D-1}/M_D = 1.167 \pm 0.001$, respectively. The following correction factor was used:

$$\frac{M_D}{M_H} = \frac{M_{119} - M_{H+1}}{M_{118} - M_{D-1}} = \frac{M_{119}/M_{118} - 0.0923}{1 - 1.167(M_{119}/M_{118})}$$

to the kinetic deuterium isotope effect as a function of temperature. The high precision method employed to determine isotope ratios[7] readily yielded k_H/k_D values of the necessary precision and accuracy for applying this criterion of reaction mechanism.

The results compiled in Table I are deemed to be indicative of a tunneling pathway of β elimination, since A_H/A_D is found to be considerably less than 0.7[3,8] and $[\Delta E_a]^H_D$ is much greated than the carbon–hydrogen zero-point energy difference, $[\Delta E_0]^H_D$. These experimental values, $A_H/A_D = 0.092$ and $[\Delta E_a]^H_D = 2.52$ kcal/mol, are to be referenced to the parameters determined in normal sulfoxide thermolysis[4] where $A_H/A_D = 0.76$ and $[\Delta E_a]^H_D$ was equal to $[\Delta E_0]^H_D = 1.15$ kcal/mol. They must also be compared to the isotope effect found for highly hindered sulfoxides ($[\Delta E_a]^H_D = 3.2$ kcal/mol and $A_H/A_D = 0.07$).[9] In this case (and elsewhere)[3d] tunneling has been identified as the consequence of steric deformation of a 5-membered cyclic arrangement, bringing into close proximity the centers between which the H transfer is to occur.

In order to perceive the distance of separation of the reaction centers implicated in the tunneling event, calculations were carried out by using the Bell–Caldin[8,10] assumptions of a truncated, unsymmetrical, parabolic barrier. A discussion of the iterative procedures applied, by using a computer program previously devised, and the results obtained are given in Table II. The barrier width at the level of tunneling is thus found to be less (0.82 Å) than a normal C–H bond length (~1.1 Å).

Table II. Data Used and/or Derived in Calculations[10] of the Reaction Barrier Dimensions of the (3) Selenoxide β Elimination

temp, °C	ln (k_H/k_D), Arrhenius	ln (k_H/k_D), quantum mechanical	difference	difference, %
40.5	1.654	1.651	0.003	0.181
61.7	1.386	1.390	0.004	0.289
77.2	1.236	1.226	0.010	0.809
84.4	1.152	1.163	0.011	0.955

Semiclassical Energy Quantities Calculated[10]

$\Delta H^\circ_{rxn} = -9412 \pm 2000$ cal/mol
$E^H_{classical} = 10\,588 \pm 100$ cal/mol
$E^D_{classical} = 10\,888 \pm 100$ cal/mol,
barrier width = 0.820 ± 0.001 Å
$E^D_{classical} - E^H_{classical} = 300$ cal/mol[a]

[a] This quantity could be regarded as an approximation of the zero-point energy difference for the vibration that would be converted to a translation in the classical TS‡. It seems to suggest that a bending vibration is involved and that the classical cyclic translation state would be too distorted to permit a linear H transfer; i.e., the elongated bonds to selenium could only accommodate a bent TS‡ of H transfer if the reaction could have occurred classically, in contradistinction to the sulfur analogue.

It can be concluded, therefore, that the lowering of the activation energy for thermal elimination attending the substitution of sulfoxide by selenoxide is to be correlated with a severe shortening of the distance of separation of the oxygen and carbon centers

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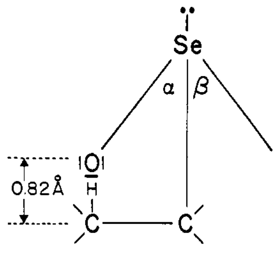
as represented in the cyclic array, **4**, of the centers involved in



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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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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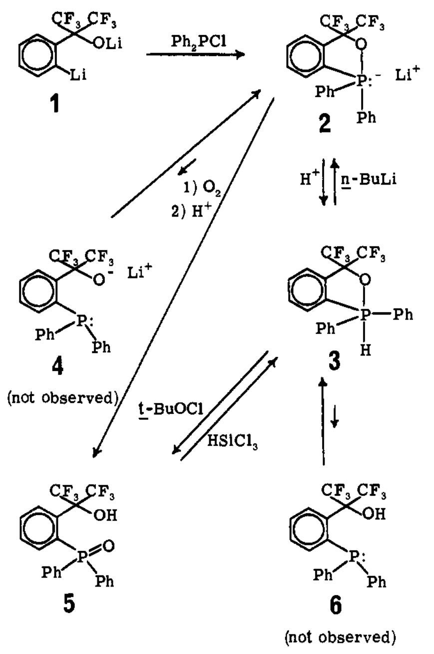
We wish to report the isolation of a monocyclic triarylalkoxy phosphorane possessing an apical P–H bond, 10-P-5 species[1] **3**, and the anion formed from it by deprotonation, the 10-P-4 species phosphoranide **2**. Although other monocyclic P–H phosphoranes have been reported,[2] none have been reported 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).

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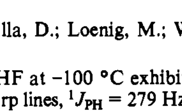
(4) Elemental analyses of all new compounds are within 0.4% of calculated values. **3**: mp 149–150 °C; ^1H NMR ($CDCl_3$) δ 6.82 (d, 1, $^1J_{PH} = 266$ Hz, P-H), 7.34–7.43 (m, 6), 7.65–7.71 (m, 3), 8.06–8.21 (m, 5, H ortho to P on PPh_2; H ortho to P on disubstituted phenyl); ^{19}F NMR ($CDCl_3$) 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^{+}–H). Anal. ($C_{21}H_{15}F_6OP$) C, H, P.



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(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^{+}–H), 376 (26.5, M^{+}–CF_3), 375 (100.0, M^{+}–CF_3–H). Anal. ($C_{21}H_{15}F_6O_2P$) C, H, P.

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