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Synthesis and Thermolysis of a Phosphorus(III) Oxalate. Evidence for the Generation of an Arylphosphinidene Oxide

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Motivated by the discovery of useful reactive synthons in organophosphorus chemistry, the search for suitable precursors to phosphinidene, R−P (phosphanediyls), has become a field of intense investigation.[1] The identities of trapping products from the thermolysis of precursor molecules such as phosphanorbornadienes,[2] phosphaketenes,[3] phosphorus diazides,[3] phospholenes,[4] and phosphiranes[4] are consistent with the intermediacy of phosphinidenes. However, as pointed out by Mathey,[1] such products can be formed by routes other than those that involve free phosphinidenes. It is, in fact, only recently that a phosphinidene has been matrix-isolated and shown to possess a triplet ground state.[5] Considerably less information is available concerning the corresponding phosphinidene oxides, RPO. These two-coordinate species are of interest because, unlike the corresponding phosphinidenes, it has been calculated that they possess a phosphorus atom in a singlet ground state (the HOMO being the nonbonding lone pair at phosphorus)[6] and can therefore be expected to constitute attractive alternative phosphorus synthons. We describe a novel approach to phosphinidene oxide generation based on the thermolysis of the first phosphorus(III) oxalate.

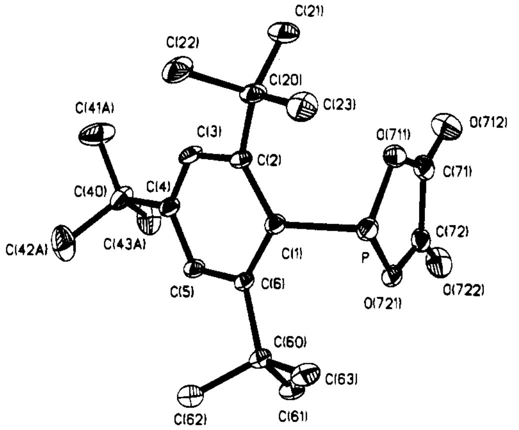

Figure 1. Structure of **1** in the crystal. Selected bond distances (Å) and angles (deg): P−C(1) 1.846(3), P−O(711) 1.689(2), P−O(721) 1.699(2), O(711)−C(71) 1.346(4), C(71)−O(712) 1.191(4), C(71)−C(72) 1.520(4), C(72)−O(722) 1.201(4), O(721)−C(72) 1.341(4), C(1)−P−O(711) 98.67(11), C(1)−P−O(721) 96.41(11), O(711)−P−O(721) 91.28(10).

Treatment of Ar′PCl$_2$ (Ar′ = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) with an excess of Ag$_2$C$_2$O$_4$ in MeCN solution resulted in quantitative production of the corresponding oxalate derivative Ar′PC$_2$O$_4$ (**1**).[7] Compound **1** is moderately air stable; moreover, even though exposure to daylight does not result in significant decomposition, it is advisable to store the product in the dark. Preliminary identification of **1** was based on spectroscopic observations.[8] Of special interest were (i) the detection of IR bands at 1818 and 1780 cm^{-1} which correspond to the C═O stretching frequencies, (ii) the observation of the molecular ion at *m/z* 364

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(7) Compound **1** was prepared by mixing a 2-fold excess of silver oxalate with Ar′PCl$_2$ in MeCN solution at 25 °C. After 30 min of stirring, the solvent was removed from the reaction mixture under reduced pressure and the residue was extracted with Et$_2$O. Filtration, followed by concentration of the filtrate and storage overnight at −20 °C, resulted in a 90% yield of colorless crystalline **1** (mp 90 °C dec). The gas phase pyrolysis experiment was carried out by loading **1** in the bottom of a long evacuated (10^{-2} Torr) Schlenk tube. The lower part of the apparatus was heated to 60 °C to allow **1** to sublime into the middle section, which was heated to 300 °C. The product of the pyrolysis (compound **3**) was condensed on a cold finger placed at the top of the tube.

(8) Analytical data for **1**: ^{31}P NMR (C$_6$D$_6$, 121.5 MHz) δ 180 (s); ^{1}H NMR (C$_6$D$_6$, 300.1 MHz) δ 1.09 (s, 9H, *p*-(CH$_3$)$_3$C), 1.38 (s, 18H, *o*-(CH$_3$)$_3$C), 7.24 (s, 2H, H-aryl); ^{13}C NMR (C$_6$D$_6$, 75.5 MHz) δ 30.9 (*p*-(*C*H$_3$)$_3$C), 33.3 (*o*-(*C*H$_3$)$_3$C), 34.7 (*p*-(CH$_3$)$_3$*C*), 39.4 (*o*-(CH$_3$)$_3$*C*), 123.7 (*m*-C-aryl), 138.9 (d, $^1J_{PC}$ = 72.7 Hz, *ipso*-C-aryl), 151.2 (d, $^2J_{PC}$ = 4.7 Hz, C-oxalate), 152.5 (*p*-C-aryl), 157.0 (d, $^2J_{PC}$ = 6.7 Hz, *o*-C-aryl); MS (EI, 70 eV) *m/z* 364 (M$^+$), 308 (M$^+$ − 2CO), 292 (M$^+$ − CO − CO$_2$), 277 (M$^+$ − CO − CO$_2$ − CH$_3$); HRMS (EI) for C$_{20}$H$_{29}$O$_4$P calcd 364.1803, found 364.1795. Anal. Calcd for **1**·THF: C, 66.05; H, 8.48. Found: C, 65.20; H, 9.05.

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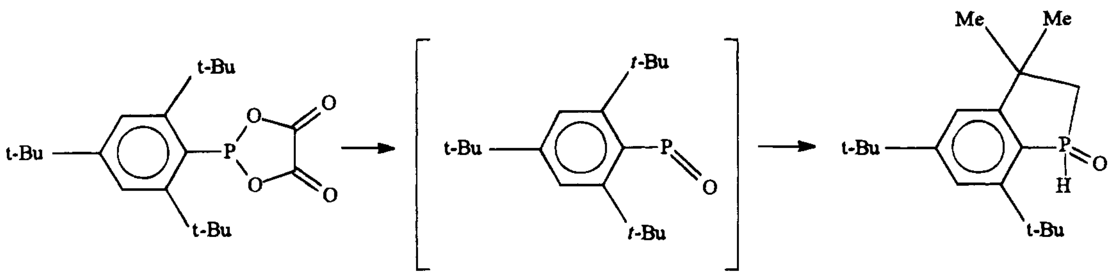
Scheme 1



1 2 3

amu in the EI mass spectrum, and (iii) the presence of a downfield doublet (δ 151.2, $^2J_{PC} = 4.7$ Hz) in the ^{13}C NMR spectrum which is attributable to the oxalate carbon resonances. Similarly, the presence of doublets at δ 138.9 ($^1J_{PC} = 72.7$ Hz, *ipso*-C-aryl) and 157.0 ($^2J_{PC} = 6.7$ Hz, *o*-C-aryl) confirm the attachment of the Ar′ ring to the phosphorus atom. Because **1** constitutes a novel heterocyclic system, an X-ray crystal structure analysis was undertaken.[9] Compound **1** crystallizes with one interstitial molecule of THF. The solid state structure of **1**·THF is composed of individual molecules of the phosphorus(III) oxalate (Figure 1), and there are no unusually short intermolecular distances. As expected, the P−O(711)−C(71)−C(72)−O(721) five-membered ring is planar within experimental error (sum of the endocyclic angles = 539.8(3)°). The existence of steric hindrance in **1** is evident from the nonplanarity of the aryl ring: the *ipso* carbon C(1) resides 0.19 Å above the plane containing C(2), C(3), C(4), C(5), and C(6). This distortion is accompanied by a displacement of the phosphorus atom 0.95 Å above the same plane. The coordination geometry at phosphorus also merits comment. The values for the C(1)−P−O(711), C(1)−P−O(721), and O(711)−P−O(721) angles (respectively equal to 98.67(11), 96.41(11), and 91.28(10)°) indicate significant deviations from the ideal tetrahedral geometry. This feature, rather than resulting from any electronic effect, is more likely to be due to the geometric constraints imposed by the oxalato ligand on the phosphorus center.

Insights into the decomposition chemistry of **1** were provided by the EI mass spectrum, which exhibits an intense peak at *m/z* 292 corresponding to the [Ar′PO]$^+$ fragment. Additional pertinent information was derived from a gas phase vacuum pyrolysis experiment.[7] Heating the vapor of **1** at 300 °C resulted in quantitative conversion to the known phosphinic acid (**3**).[10] Since this thermolytic process took place in a dynamically evacuated system, a mechanism leading to the generation of the transient arylphosphinidene oxide Ar′P=O (**2**) by elimination of one molecule of CO_2 and one molecule of CO from **1**, followed by intramolecular insertion of the phosphorus atom into the C−H bond of an *ortho tert*-butyl group, is very probable (Scheme 1). It is important to note that several approaches to the generation of organophosphinidene oxides have already been proposed, including dehalogenation of phosphonic chlorides[11] and extrusion of RP=O fragments from a phosphanorbornene,[12] a phospholene oxide,[13] and a phosphirane oxide.[14] However, in all of these reactions, the generation of the phosphinidene oxide was inferred from trapping reactions. In each case it is possible to devise alternative trapping mechanisms (e.g. radical or ionic processes) that do not involve the transient formation of the postulated intermediate.[15] As in the conversion of a phosphaketene to a phosphaindane,[3] the present results are best explained on the basis of an intramolecular cyclization reaction. As such, the foregoing observations provide strong evidence for the intermediacy of arylphosphinidene oxide **2**.

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Supporting Information Available: Tables of crystal data, structure refinement details, atomic coordinates, bond lengths and angles, and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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(9) Crystals of **1**·THF suitable for X-ray analysis were obtained by cooling a saturated THF solution of **1** overnight. X-ray data for $C_{24}H_{37}O_5P$ (**1**·THF): triclinic $P\bar{1}$, $a = 9.750(1)$ Å, $b = 11.692(2)$ Å, $c = 12.125(1)$ Å, $\alpha = 68.155(9)°$, $\beta = 89.681(7)°$, $\gamma = 76.779(9)°$, $V = 1244.1(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.165$ g/cm^3. Radiation source: Mo Kα, $\lambda = 0.710\,73$ Å. The structure solution and refinement were based on F^2 using all data (3146 reflections) and converged to wR2 = 15.62% and R1 = 5.45%.

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