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Crystallographic Characterization of a Stable 7-Phosphanorbornadiene-7-Oxide: 2,3-Benzo-1,4,5,6,7-pentaphenyl-7-phosphabicyclo[2.2.1]hepta-2,5-diene-7-oxide

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ABSTRACT: *The stable 7-phosphanorbornadiene derivative, 2,3-benzo-1,4,5,6,7-pentaphenyl-7-phosphabicyclo[2.2.1]hepta-2,5-diene-7-oxide (*1*) was synthesized in 45% yield via the Diels-Alder reaction of pentaphenylphosphole oxide and benzyne. The reaction occurs specifically to give a single isomer, which was characterized by use of X-ray crystallography and* ^{31}*P NMR spectroscopy.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:182–186, 2000

INTRODUCTION

The unusual chemical, spectroscopic, and stereochemical characteristics of 7-phosphanorbornene (7-phosphabicyclo[2.2.1]hept-2-ene) derivatives have long been of interest. The earlier literature has been thoroughly reviewed [1], and there is a wealth of more recent published work. However, reports concerning the closely related, and potentially even more interesting, 7-phosphanorbornadiene (7-phosphabicyclo[2.2.1]hepta-2,5-diene) system have appeared only sporadically. This is because of the ease with which such compounds fragment (to give the corresponding phosphinidene derivative and a benzene or naphthalene derivative) during attempted syntheses, particularly those undertaken early in the development of this area of phosphorus heterocyclic chemistry [2]. More recently, however, successful syntheses of several 7-phosphanorbornadiene derivatives (as P-oxides or metal carbonyl complexes) have been reported in the literature although, in most instances, these compounds have not been fully characterized. It is also noteworthy that although numerous P(III) derivatives of 7-phosphanorbornenes have been reported [1], no such derivative of the 7-phosphanorbornadiene system has yet been reported.

While there are a few known instances of [4 + 2] cycloadditions of alkenes to P(III) phosphole derivatives to give 7-phosphanorbornene derivatives [3], the obvious route to 7-phosphanorbornadienes via a Diels-Alder reaction of an alkyne with a phosphole appears to be thwarted either by reactions involving the phosphorus lone-pair [4] (with strongly electrophilic alkynes) or by a [1,5] sigmatropic rearrangement of the phosphole [5] (with less electrophilic alkynes), which causes the cycloaddition to

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follow a different course. However, two successful approaches have been developed for the preparation of stable compounds containing the 7-phosphanorbornadiene skeleton. These methods are also of the Diels-Alder type and involve use of either a phosphole oxide [6–8] or a metal (Cr, Mo, W) pentacarbonyl complex of a phosphole as the diene in the [4 + 2] cycloaddition [9]. Metal complexation of the 7-phosphanorbornadienes gives rise to quite stable products [9,10], while preparation of the oxides provides short- [7] or long-term [6,8] stability at room temperature; both of these methods effectively circumvent unwanted reactions at the phosphorus center of a P(III) phosphole derivative.

These systems are therefore ripe for further study, and as part of a general examination of the chemical and spectroscopic behavior of 7-phosphanorbornadienes, the synthesis and both the spectroscopic and X-ray crystallographic characterization of 2,3-benzo-1,4,5,6,7-pentaphenyl-7-phosphabicyclo[2.2.1]hepta-2,5-diene-7-oxide (**1**) were undertaken.

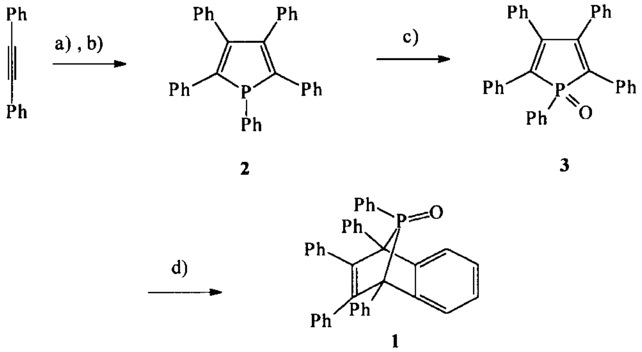
DISCUSSION

Compound **1** was chosen for the initial part of our investigation since, although it was the first stable phosphanorbornadiene derivative to be reported [6], no synthetic or spectroscopic (other than mass spectrometric) details were recorded and characterization was based almost entirely upon its chemical behavior. In fact, the only such compound to be fully characterized (including X-ray crystallographic data) to date [9a] is the $Cr(CO)_5$ complex of 2,3-*bis*(methoxycarbonyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hepta-2,5-diene. The synthesis reported herein is, broadly speaking, similar to that very briefly referred to (without experimental details) in the initial report by Stille et al. [6]. It involves a Diels-Alder reaction between the known [11] pentaphenylphosphole oxide, **3** (prepared [11] from the phosphole, **2**), and benzyne, which is generated in situ [12]. For clarity, the entire synthetic route used is shown in Scheme 1.

Following clean-up of the crude reaction mixture by column chromatography on silica gel, a ^{31}P NMR analysis of the eluted mixture revealed the presence of unreacted **3** ($\delta\ ^{31}P = 42.4$) together with the anticipated product, **1**, which gave rise to a resonance at $\delta\ ^{31}P = 95.7$. A pure sample of **1** was subsequently obtained (45% yield, c.f. 92%, Stille et al. [6]) by recrystallization from a mixture of pentane and benzene.

The ^{31}P shift noted previously is alone a strong indication that **1** has the strained, P-bridged structure present in both 7-phosphanorbornene and 7-phosphanorbornadiene P-oxides. The former have long been known to exhibit extremely large ^{31}P shifts compared with systems in which the internal C-P-C angle is less severely constrained and such shifts typically fall in the range $\delta = 80–100$ [1]. For the few examples of the latter, known ^{31}P shifts fall in the range $\delta = 102–104$ [8]. The single signal observed also indicates that the cycloaddition is stereospecific as has been observed [1] for all other phosphole oxide [4 + 2] dimerizations and Diels-Alder cycloadditions. For epimeric (with respect to the phosphorus center) 7-phosphanorbornene derivatives, the ^{31}P NMR chemical shifts of the epimeric phosphorus nuclei are significantly different [1] (see also Figure 1 [13a]). This is also the case with less strained systems [13b].

Considering stereochemical aspects of the reaction, one would expect the benzyne addition to occur



SCHEME 1 (a) Li(s), Et_2O, rt; (b) $PhPCl_2$, Et_2O, rt, 40% from diphenylacetylene; (c) 30% H_2O_2, benzene 80°C, 75%; (d) *i*-amylnitrite, CH_2Cl_2, anthranilic acid, acetone, 45%.

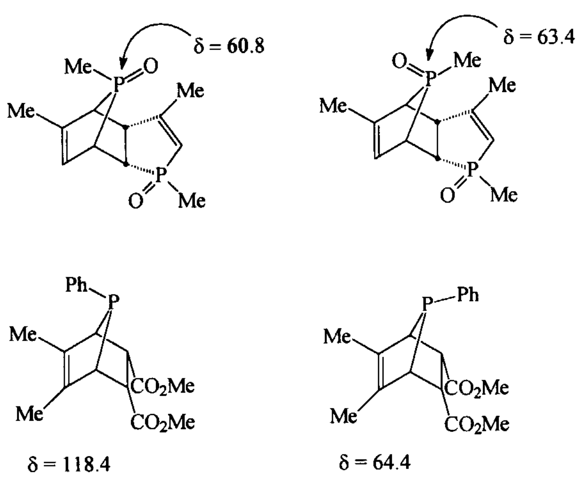


FIGURE 1 Changes in ^{31}P chemical shifts for epimeric phosphorus atoms [13a].

from the less hindered face of the pentaphenylphosphole oxide, to give the stereochemistry shown in Scheme 1, as is the norm [1] in such reactions. However, while in some cases it has been possible to determine the specific stereoisomer obtained by use of either proton-proton [13b] or phosphorus-carbon [14] NMR coupling data, the phosphorus-carbon coupling pattern could not be used to assign the stereochemistry in **1**. Thus, although some ^{13}C NMR spectral assignments could be made (e.g., the two core bridgehead sp^3 carbons are observed at δ ^{13}C = 66.74 with $^1J_{PC}$ = 57.8 Hz and the two pairs of core sp^2 carbons appear at δ ^{13}C 145.0 and 145.4 with two-bond coupling constants of 17.3 and 10.6 Hz, respectively), the large number of aromatic carbon resonances which overlap in the δ = 120–140 ppm region precluded any detailed structural analysis. Therefore, in the absence of definitive spectroscopic data, the structure of **1** was unambiguously ascertained in the solid state by use of single crystal X-ray diffraction techniques; the structure of compound **1** is presented in Figure 2, while crystallographic refinement parameters and selected metrical data are collected in Tables 1 and 2, respectively.

The crystallographic data immediately reveal that the addition of benzyne to **3** occurs, as expected, on the less hindered face of the phosphole oxide, opposite to the phenyl group. In this context, it is interesting to note that in the case of the structurally characterized 7-phosphanorbornadiene complex derived from the Cr(CO)$_5$-protected phosphole reported by Mathey et al. [9a] and referred to previously, the steric demands of the metal fragment dictate that addition occur syn to the P-Ph unit. The salient structural feature evident in both of the independent molecules of **1** (see Experimental section) is the compressed endocyclic bridge angle [C(1)–P(1)–C(4) = 91.4(5)°; C(101)–P(2)–C(104) = 86.1(4)°], a phenomenon that has been observed in related phosphorus- [9a, 15] and germanium-based [16] complexes. Although the P=O distances in **1** parallel those reported in the literature [15,17], the corresponding P-Ph distances in **1** [1.95(1) Å and 1.87(1) Å] appear to be lengthened in comparison to related organometallic [1.822(3) Å] [9a] and phosphine oxide [1.81(1) Å] [15] cycloadducts, possibly owing to the presence of the benzannulated ring in **1**. In general, the carbocyclic framework in **1** exhibits no unusual features, with the exception that the incipient Diels-Alder bonds in one of the independent molecules of **1** [C(1)–C(2) = 1.66(2) Å; C(3)–C(4) = 1.73(2) Å] appear to be elongated relative to

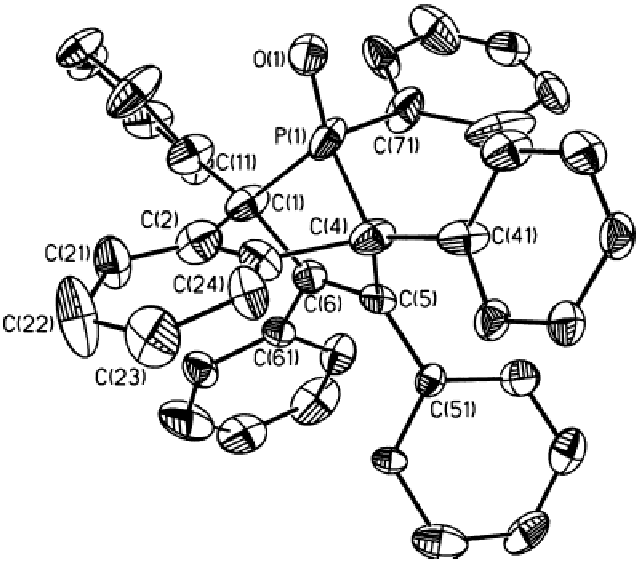


FIGURE 2 The crystallographically determined structure of one of the two independent molecules of **1** with thermal ellipsoids shown at the 20% probability level (benzene solvates and hydrogen atoms have been omitted for clarity).

TABLE 1 Crystallographic Collection and Refinement Parameters for **1·C$_6$H$_6$**.

Empirical formula	$C_{46}H_{35}OP$
Molecular weight	1269.42
Description	yellow prism
Size, mm^3	0.34 × 0.30 × 0.25
Temperature, K	299(2)
Crystal system	monoclinic
Space group	*P*n
a, Å	17.544(1)
b, Å	10.2166(8)
c, Å	19.524(1)
α, deg.	90
β, deg.	90.709(3)
γ, deg.	90
Volume, Å^3	3499.3(4)
Z	2
Calcd Density, g/cm3	1.205
Scan Mode	ω-scans
F(000)	1336
θ-range, deg.	1.57 to 22.50
Index ranges	$-21 \le h \le 21$ $-12 \le k \le 12$ $-23 \le l \le 24$
No. Refl. Collected	20716
No. Indep. Refl.	8231
Rint	0.0678
Data/restr./param.	8220/8/812
GOF on F^2 (all)	0.825
Final R (I > 2σ(I))*	R1 = 0.0714; wR2 = 0.1882
R indices (all data)*	R1 = 0.1541; wR2 = 0.2469
Trans., (max., min.)	0.9734, 0.7752
Largest diff. Peak, e/Å^3	0.490
Largest diff. Hole, e/Å^3	−0.256

TABLE 2 Selected Bond Lengths [Å] and Angles [deg.] for Both of the Independent Molecules of **1**·$\mathbf{C_6H_6}$

P(1)–O(1)	1.440(6)	C(101)–P(2)–C(104)	86.1(4)
P(1)–C(4)	1.75(1)	O(2)–P(2)–C(171)	110.9(4)
P(1)–C(1)	1.78(1)	C(101)–P(2)–C(171)	108.5(5)
P(1)–C(71)	1.95(1)	C(104)–P(2)–C(171)	105.4(5)
P(2)–O(2)	1.496(6)	C(11)–C(1)–C(6)	123.5(9)
P(2)–C(101)	1.82(1)	C(11)–C(1)–C(2)	117.3(11)
P(2)–C(104)	1.87(1)	C(6)–C(1)–C(2)	104.3(8)
P(2)–C(171)	1.87(1)	C(11)–C(1)–P(1)	116.7(7)
C(1)–C(2)	1.66(2)	C(6)–C(1)–P(1)	97.7(7)
C(2)–C(3)	1.28(2)	C(2)–C(1)–P(1)	91.2(8)
C(3)–C(4)	1.73(2)	C(41)–C(4)–C(5)	114.7(8)
C(4)–C(5)	1.61(1)	C(41)–C(4)–C(3)	121.4(9)
C(5)–C(6)	1.35(1)	C(5)–C(4)–C(3)	104.6(7)
C(1)–C(6)	1.55(1)	C(41)–C(4)–P(1)	123.2(7)
C(101)–C(102)	1.57(2)	C(5)–C(4)–P(1)	99.5(6)
C(102)–C(103)	1.359(14)	C(3)–C(4)–P(1)	88.7(6)
C(103)–C(104)	1.57(2)	C(111)–C(101)–C(102)	119.3(8)
C(104)–C(105)	1.54(1)	C(111)–C(101)–C(106)	116.3(8)
C(105)–C(106)	1.33(1)	C(102)–C(101)–C(106)	108.5(8)
C(101)–C(106)	1.60(1)	C(111)–C(101)–P(2)	119.8(7)
O(1)–P(1)-C(4)	121.4(5)	C(102)–C(101)–P(2)	91.9(6)
O(1)–P(1)–C(1)	125.1(4)	C(106)–C(101)–P(2)	96.5(6)
C(4)–P(1)–C(1)	91.4(5)	C(141)–C(104)–C(105)	123.5(8)
O(1)–P(1)–C(71)	108.3(6)	C(141)–C(104)–C(103)	119.7(9)
C(4)–P(1)–C(71)	108.2(6)	C(105)–C(104)–C(103)	106.8(7)
C(1)–P(1)–C(71)	99.5(6)	C(141)–C(104)–P(2)	110.8(6)
O(2)–P(2)–C(101)	119.9(5)	C(105)–C(104)–P(2)	94.1(6)
O(2)–P(2)–C(104)	123.2(4)	C(103)–C(104)–P(2)	95.0(6)

the corresponding bond in the other molecule [C(101)–C(102) = 1.57(2) Å; C(103)–C(104) = 1.57(2) Å]; however, it is unclear whether this difference is statistically significant.

CONCLUSIONS

The title compound was prepared by way of a stereospecific Diels-Alder reaction involving pentaphenylphosphole oxide and benzyne with the dienophile adding at the least hindered face of the phosphole oxide. This reaction thus proceeds stereospecifically to give only one isomer. In addition to characterizing the product by use of ^{31}P NMR spectroscopy, the stereochemistry and other structural parameters of the product were determined by use of X-ray crystallography. Studies on the chemistry of this system are in progress and results will be reported in due course.

EXPERIMENTAL

General Procedures

Preparative details for compounds **2** [11] and **3** [11] have been previously reported in the literature while only brief indications were given for **1**. Solvents (Fisher) and reagents (Aldrich) were used without further purification. NMR spectra were recorded on a Bruker AC-E 200 MHz NMR spectrometer. Positive shifts are assigned to ^{31}P and ^{13}C signals downfield of external 85% H_3PO_4 and internal TMS, respectively, and reported in ppm. The mass spectrum was recorded on a Micromass AutoSpec. Elemental analyses were obtained in our laboratories using a CEC (SCP) 240-XA Analyzer.

2,3-Benzo-1,4,5,6,7-pentaphenyl-7-phosphabicyclo[2.2.1]hept-5-ene-7-oxide **1**

A solution of *i*-amylnitrite (0.9 mL, 0.67 mmol) was heated under reflux in CH_2Cl_2 (1.0 mL) to remove CO_2 and N_2. Anthranilic acid (0.085 g, 0.67 mmol) and **3** (0.30 g, 0.62 mmol) in acetone (0.40 mL) were added dropwise over one hour. The reaction mixture was heated under reflux for five hours and then cooled, followed by stirring overnight. The solvents were removed under reduced pressure and the residue was dissolved in ether (0.93 mL). The ether was washed with saturated $NaHCO_3$ (0.65 mL). The aqueous layer was extracted with ether. The combined organics were washed with saturated $NaHCO_3$ and NaCl, dried over Na_2SO_4, and removed under reduced pressure. Initial purification was completed using column chromatography (hexanes) followed by recrystallization (pentane/benzene). Yield 45%. m.p. 164–166°C; ^{1}H NMR ($CDCl_3$): δ 6.63 (dd, J = 6.46, 1.64 Hz, 4H), 7.51–6.98 (m, 20H), 7.93 (t, J = 8.61 Hz, 5H); ^{13}C NMR ($CDCl_3$): δ 66.74 ($^1J_{PC}$ = 57.8 Hz), 124.2 (J_{PC} = 5.8 Hz), 126.5, 127.3, 128.0 (J_{PC} = 11.8 Hz), 128.4, 129.6, 131.1 (J_{PC} = 7.3 Hz), 131.9, 132.4, 134.1 (J_{PC} = 6.79 Hz), 135.5, 145.0 ($^2J_{PC}$ = 17.3 Hz), 145.4 ($^2J_{PC}$ = 10.6 Hz); ^{31}P NMR ($CDCl_3$): δ 95.7; EI MS (*m/e*) observed, 432 (M^+-POC_6H_5); calcd, 432.1879. Analysis for **1**·C_6H_6: calculated for $C_{40}H_{29}PO \cdot C_6H_6$, C 87.04, H 5.56; found, C 86.90, H 5.85%.

X-Ray Crystallography

Crystallographic data for **1**·$\mathbf{C_6H_6}$ were collected from a suitable sample mounted with epoxy on the end of a thin glass fiber. The instrument used for the collection of diffraction data was a P4 Siemens diffractometer equipped with a Siemens SMART 1K CCD Area Detector (using the program SMART) and a rotating anode using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) [18]. Data processing was carried out by use of the program SAINT, and the program SADABS was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by using the direct methods procedure in the Siemens SHELXTL program library, and refined by full-matrix least squares methods on F^2. All nonhydrogen atoms (with the exception of the carbon atoms in one of the independent benzene solvates in $\mathbf{1 \cdot C_6H_6}$) were refined using anisotropic thermal parameters. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded. Compound **1** crystallizes with two independent molecules per asymmetric unit, and during the course of the refinement process, two benzene solvates were also located within the asymmetric unit and refined. Crystallographic data for $\mathbf{1 \cdot C_6H_6}$ have been deposited (deposition number 136612) with the Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

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