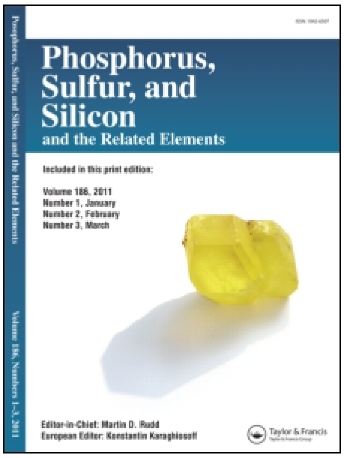

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OPTICALLY ACTIVE PHOSPHINE CHALCOGENIDES. 22.[1] STEREOCHEMISTRY AND X-RAY STRUCTURE OF THE MAJOR ENDO CYCLOADDUCT OF (*S*)-METHYLPHENYLVINYLPHOSPHINE OXIDE TO CYCLOPENTADIENE

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OPTICALLY ACTIVE PHOSPHINE CHALCOGENIDES. 22.[1] STEREOCHEMISTRY AND X-RAY STRUCTURE OF THE MAJOR ENDO CYCLOADDUCT OF (*S*)-METHYLPHENYLVINYLPHOSPHINE OXIDE TO CYCLOPENTADIENE

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The stereochemistry of the major endo adduct obtained in the thermal Diels-Alder reaction of (*S*)-methylphenylvinylphosphine oxide and cyclopentadiene was analyzed by a single-crystal X-ray diffraction technique $C_{14}H_{17}OP$, space group $P2_12_12_1$, $a = 7.042(1)$ Å, $b = 10.522(1)$ Å, $c = 18.039(1)$ Å, $V = 1336.6(3)$ Å^3, $Z = 4$. The structure was solved by direct methods and was refined by full matrix least-square calculations to $R = 0.043$ and $S = 1.033$ using 2635 unique reflections with $I > 3\sigma(I)$. In the crystal packing two intermolecular C—H···O contacts involving phosphoryl oxygen and α and ortho hydrogens were revealed. The studied compound was identified as the endo adduct of the *S* configuration at C2. On the basis of this finding it could be concluded that (*S*)-methylphenylvinylphosphine oxide preferred to enter the studied 4 + 2 cycloaddition in the s-trans conformation.

Key words: Enantiomeric phosphine oxide, X-ray analysis, absolute configuration, vinyl phosphine oxide, 4 + 2 cycloaddition, reactive conformation.

INTRODUCTION

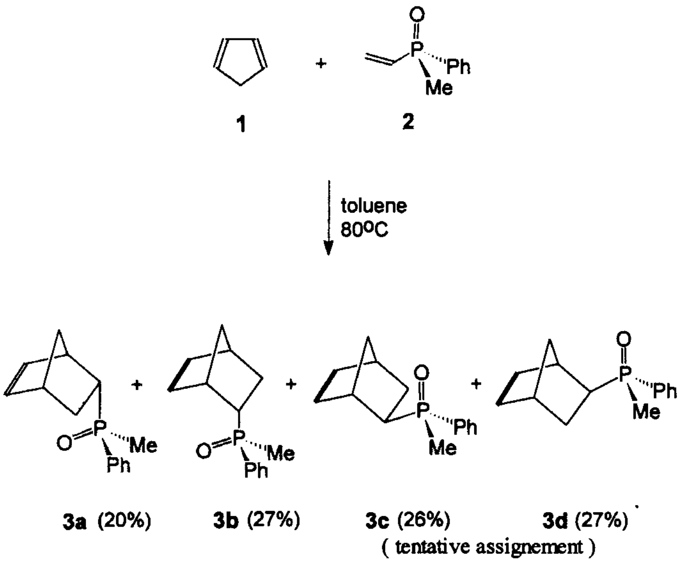
A propensity of simple conjugated olefins bearing strongly activating groups, e.g., C═O[2] or S→O[3], to exist and to react thermally in the s-cis conformation is already well substantiated experimentally and theoretically. Also simple vinyl phosphine oxides,[4,5] as well as sulfides[6,7] and selenides,[7] were recently shown to have similar bias towards the s-cis conformation in the ground state and they were also implied to favor this conformational array in their 1,3-dipolar cycloaddition reactions with nitrile oxides and nitrones.[8] The latter reactions have later been tuned to occur with high stereoselectivity and through the use of properly selected P-chiral vinyl phosphine derivatives have offered a means for efficient chirality transfer from P to C.[9] In contrast with these findings, a closely related thermal Diels-Alder reaction of cyclopentadiene and (*S*)-methylphenylvinylphosphine oxide used as a model P-chiral vinyl phosphine derivative was found to occur with markedly lower diastereofacial selectivity and with no apparent distinction between an exo and an endo approach (Scheme I).[10]

A single-crystal X-ray diffraction study presented in this paper provides an insight into the absolute stereochemistry of the predominant endo cycloadduct **3b** and implies strongly that the formation of this product had to involve s-trans conformation as the reactive conformation of **2**.

RESULTS AND DISCUSSION

An ORTEP drawing of **3b** showing also its absolute configuration is displayed in Figure 1.

The revealed stereochemistry corresponds at P with the S_P configuration of the starting **2** and indicates unequivocally that the configuration of **3b** at C2 is *S*. On the basis of this finding it can be further concluded that the favored reactive conformation of vinyl phosphine oxide **2** during the formation of the endo products was s-trans. Of the two possible cycloaddition stereochemical pathways which could potentially lead to **3b** of the found configuration, i.e., **A** and **B** (Figure 2), the one



SCHEME I

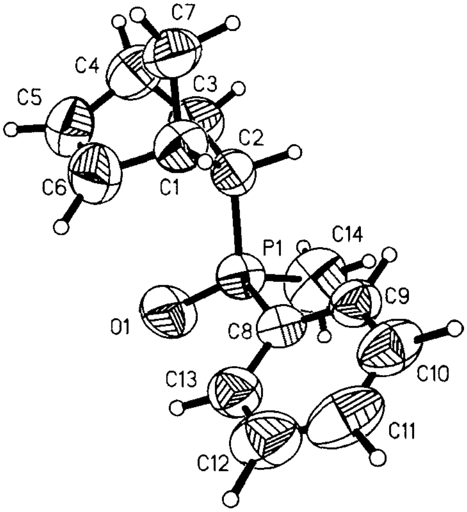


FIGURE 1 ORTEP drawing of **3b** showing 50% probability ellipsoids.

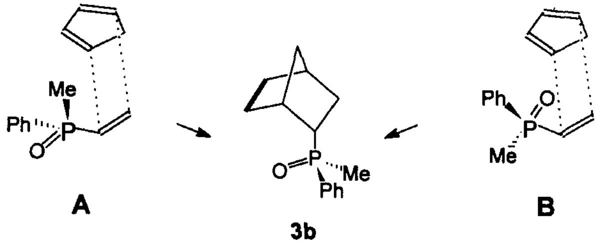


FIGURE 2 Stereodifferentiated cycloaddition paths leading to **3b**.

in which **2** assumes the s-trans conformation entails apparently the less crowded approach of the two reactants. In **A** the incoming cyclopentadiene faces P—Me substitutent whereas in **B**, P—Ph.

The bond lengths and bond angles found for **3b** are listed in Table I. It follows from these data that the phosphorus tetrahedron is deformed in the usual way showing increased O—P—C angles and decreased C—P—C angles with the corresponding values ranging from 111.5(1) to 115.1(1)° and 104.4(2) to 105.6(1)°, respectively. The torsion angle O1—P1—C8—C13 = 2.0(2)° indicates that phosphoryl and phenyl groups in **3b** assume a nearly co-planar arrangement. Such an alignment of Ph—P=X fragments has been previously observed in some phosphine chalcogenides bearing P—Ph substituents,[4,5,7] although several other arrangements of these two groups in the crystals are also on record.[5,12,13] As indicated by the torsion angle O1—P1—C2—C1 = 66.8(2)° the phosphoryl group and norbornene ring are in the skew conformation.

Inspection of the bonds lengths in **3b** reveals that the bridging C4—C7 bond is considerably shorter than C1—C7 bridging bond [1.485(5) vs. 1.543(4) Å]. The found difference falls in the range of analogous differences recorded already for

TABLE I

Bond lengths [Å] and bond angles [deg] for **3b**

P(1)-O(1)	1.484(2)
P(1)-C(14)	1.793(3)
P(1)-C(2)	1.795(2)
P(1)-C(8)	1.800(2)
C(1)-C(6)	1.511(4)
C(1)-C(7)	1.543(4)
C(1)-C(2)	1.543(3)
C(2)-C(3)	1.564(3)
C(3)-C(4)	1.528(5)
C(4)-C(7)	1.485(5)
C(4)-C(5)	1.497(5)
C(5)-C(6)	1.304(5)
C(8)-C(9)	1.378(3)
C(8)-C(13)	1.391(3)
C(9)-C(10)	1.390(4)
C(10)-C(11)	1.364(5)
C(11)-C(12)	1.370(5)
C(12)-C(13)	1.387(4)

O(1)-P(1)-C(14)	114.2(2)
O(1)-P(1)-C(2)	115.09(12)
C(14)-P(1)-C(2)	104.4(2)
O(1)-P(1)-C(8)	111.51(12)
C(14)-P(1)-C(8)	105.60(14)
C(2)-P(1)-C(8)	105.12(10)
C(6)-C(1)-C(7)	99.0(2)
C(6)-C(1)-C(2)	107.4(2)
C(7)-C(1)-C(2)	99.1(3)
C(1)-C(2)-C(3)	101.7(2)
C(1)-C(2)-P(1)	117.1(2)
C(3)-C(2)-P(1)	115.2(2)
C(4)-C(3)-C(2)	102.9(2)
C(7)-C(4)-C(5)	100.1(3)
C(7)-C(4)-C(3)	101.7(2)
C(5)-C(4)-C(3)	106.0(3)
C(6)-C(5)-C(4)	108.0(3)
C(5)-C(6)-C(1)	107.5(3)
C(4)-C(7)-C(1)	94.4(2)
C(9)-C(8)-C(13)	120.0(2)
C(9)-C(8)-P(1)	121.9(2)
C(13)-C(8)-P(1)	118.1(2)
C(8)-C(9)-C(10)	119.8(3)
C(11)-C(10)-C(9)	120.0(3)
C(10)-C(11)-C(12)	120.6(3)
C(11)-C(12)-C(13)	120.3(3)
C(12)-C(13)-C(8)	119.3(3)

69 structures containing the norbornene skeleton (1.432–1.658 Å)[14] and in the studied case do not affect markedly the overall approximate mirror symmetry of the ring system.[15]

Figure 3 shows the stereo packing diagram for **3b** viewed down the x axis. The found two shortened intermolecular C—H···O contacts, i.e., C9—H91···O1 of 2.36 Å and C2—H21···O1 of 2.11 Å, are indicated by the dotted lines.

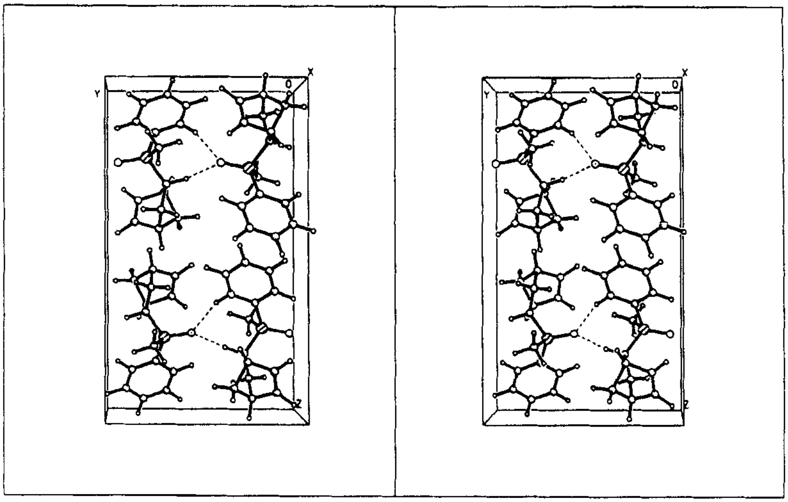


FIGURE 3 Stereoview of cell packing for **3b** showing the C—O···O contacts.

TABLE II

Crystal data and experimental parameters for **3b**

Formula	$C_{14}H_{17}OP$
M	232.261
a(Å)	7.042(1)
b(Å)	10.522(1)
c(Å)	18.039(1)
V_c(Å^3)	1336.6(3)
Z	4
F(000)	496
μ(Cu Kα)(cm^{-1})	16.3
space group	$P2_12_12_1$
D_x(Mg m^{-3})	1.15
Radiation	Cu Kα
Scan mode	$\omega - 2\theta$
θ range(°)	1 - 75
Reflections with $I>2\sigma(I)$	2635
R	0.043
S	1.033

TABLE III

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **3b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
P(1)	376(1)	2972(1)	2653(1)	64(1)
O(1)	470(3)	4360(2)	2510(1)	98(1)
C(1)	3301(4)	2045(3)	1705(1)	75(1)
C(2)	1172(3)	1984(2)	1904(1)	62(1)
C(3)	220(5)	2257(3)	1137(1)	88(1)
C(4)	1917(6)	2337(3)	611(2)	104(1)
C(5)	2937(6)	3539(3)	806(2)	103(1)
C(6)	3725(5)	3386(3)	1454(2)	96(1)
C(7)	3230(6)	1388(3)	941(2)	99(1)
C(8)	1826(3)	2527(2)	3433(1)	58(1)
C(9)	1917(4)	1293(2)	3684(1)	70(1)
C(10)	3055(5)	996(3)	4290(2)	90(1)
C(11)	4078(5)	1926(5)	4633(2)	102(1)
C(12)	4004(5)	3156(4)	4386(2)	101(1)
C(13)	2878(4)	3472(3)	3782(2)	78(1)
C(14)	-1961(4)	2396(4)	2862(2)	108(1)

EXPERIMENTAL

Separation of **3b** from the product mixture detailed in Scheme I was achieved through the combined use of column chromatography and repeated crystallization techniques which led eventually to the isolation of pure product, although in only minute amounts [**3b** mp 135–7°C; $[\alpha]_D = -97°$ (c 0.1, $CDCl_3$); $\delta_P(CDCl_3)$ 39.04 ppm]. A single crystal of approximate dimensions of 0.28, 0.30, 0.25 mm suitable for the X-ray measurement was obtained by slow evaporation of benzene solution.

Accurate unit cell dimensions were obtained by the least-squares fit to the θ values of 25 reflections measured on a Enraf-Nonius CAD4 diffractometer. The intensity data were collected using graphite-monochromated Cu-Kα radiation and the ω-2θ scan technique. The measured intensities were corrected for Lorentz and polarization effects. Crystal and experimental details are listed in Table II.

The structure was solved by direct methods using the SHELX-86 program[16] and was refined by the full-matrix least-squares methods. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized and in the final cycles of refinement a weighting scheme based on counting statistics was used with $w = 1/[\sigma^2F_o^2 + (0.074\,P)^2 + 0.31\,P]$ where $P = [\mathrm{Max}(F_o^2, 0) + 2\,F_c^2]/3$. An empirical isotropic extinction correction was introduced and the parameter x was refined to the value of 0.004(1). During the refinement of the nonhydrogen atoms with anisotropic parameters, the hydrogen atom contributions (with the exception of the methyl hydrogens) were included in the structure factors after calculation of their positions on the basis of idealized geometry; the positions of the methyl hydrogens were found from a difference map. The hydrogen atoms were refined in the riding mode. The refinement was terminated when the maximum shift in any parameter was less than 0.1σ. The final difference Fourier map showed no peaks higher than 0.35 Å^{-3}. Convergence was obtained at R = 0.043 and s = 1.033. The resulting Flack absolute structure parameter[17] was 0.03(3). Table III lists the final atomic positional parameters.

Most of the computations were performed with the SHELXTL-92 crystal structure determination program[18] on an IBM PC 486 minicomputer.[19]

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