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Stereostructure of 8-Chloro-5,6-di(methoxycarbonyl)-4,7-dimethyl-2-ethoxy-2-phosphabicyclo[2.2.2]octa-5,7-diene 2-Oxide

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ABSTRACT

The first X-ray structure of a phosphabicyclooctadiene, together with the NMR and mass spectral characterization of its isomers, is reported. © 1996 John Wiley & Sons, Inc.

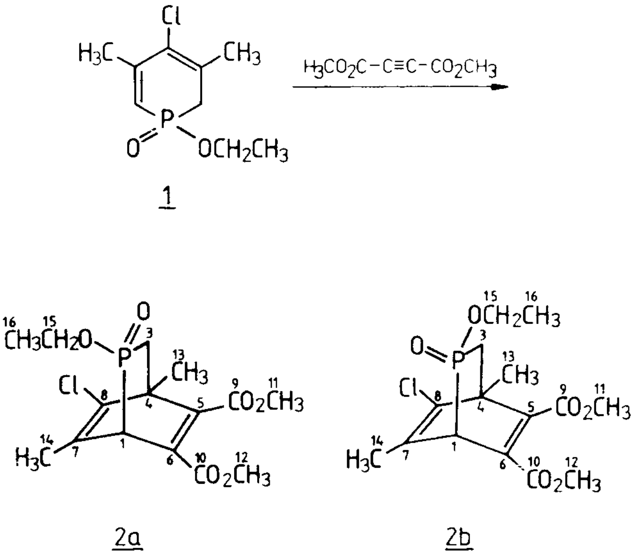
INTRODUCTION

Derivatives of the 2-phosphabicyclo[2.2.2]octadiene oxide ring system are useful, as they are readily fragmented on irradiation with ultraviolet light to give 3-coordinate methylenephosphine oxides [1–3]. Although the phosphabicyclooctadienes were fully characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, the stereostructures of their diastereomers could be assigned only tentatively [4].

Single-crystal X-ray analysis has now allowed us to evaluate the stereostructure of a pure phosphabicyclooctadiene diastereomer and so made possible the exact assignment of ^{31}P, ^{1}H, and ^{13}C NMR spectral data to the isomers.

RESULTS AND DISCUSSION

The diastereoisomeric mixture of title compound 2 [5] was prepared by the cycloaddition of 4-chloro-3,5-dimethyl-1-ethoxy-1,2-dihydrophosphinine 1-oxide (1) to dimethyl acetylenedicarboxylate (Scheme 1). We were successful in obtaining one of



SCHEME 1

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the isomers in pure form from the mixture by column chromatography. After recrystallization, it was subjected to single-crystal X-ray analysis. It turned out that we had isomer **2b** in hand (Figure 1). Positional parameters and selected values of geometrical parameters for one of the enantiomers of **2b** are listed in Tables 1 and 2, respectively.

This is the first case in which the stereostructure of a 2-phosphabicyclo[2.2.2]octa-5,7-diene 2-oxide has been elucidated by X-ray analysis.

The bicyclo[2.2.2]octadiene structure becomes distorted because of the presence of atom P(2). This is shown by the lengthening of the C(3)–C(4) bond by 0.04 Å (expected value: 1.530 Å). This modification is significant in view of the high force constants characterizing these kinds of bond stretching processes. P(2) discriminates between the two C atoms connected: the P(2)–C(1) bond is significantly longer than the P(2)–C(3) bond. The bond angles around P(2) are distorted: those including 0(12) are significantly wider, while the other two are narrower than 109.5°. While the plane of the C(5)–CO_2Me group is almost perpendicular to that determined by sp^2 C atoms C(5) and C(6) and the other C atoms connected to them, the C(6)–CO_2Me group is almost parallel to the plane of the sp^2 C atoms. The difference in the bond lengths for C(6)–C(18) and C(5)–C(14) looks marginal at first glance (0.008 Å); it may suggest, however, a somewhat larger delocalization via C(5)–C(6)–C(18)–O(21) than via C(6)–C(5)–C(14)–O(17), as a survey on the length of the C = C-CO_2C type of bonding in a variety of compounds suggests that small differences may also be characteristic [6]. The length of the C(6)–C(18) bond is very close to the average value (1.488 Å), while bond lengths similar to that of C(5)–C(14) occur in just a few cases.

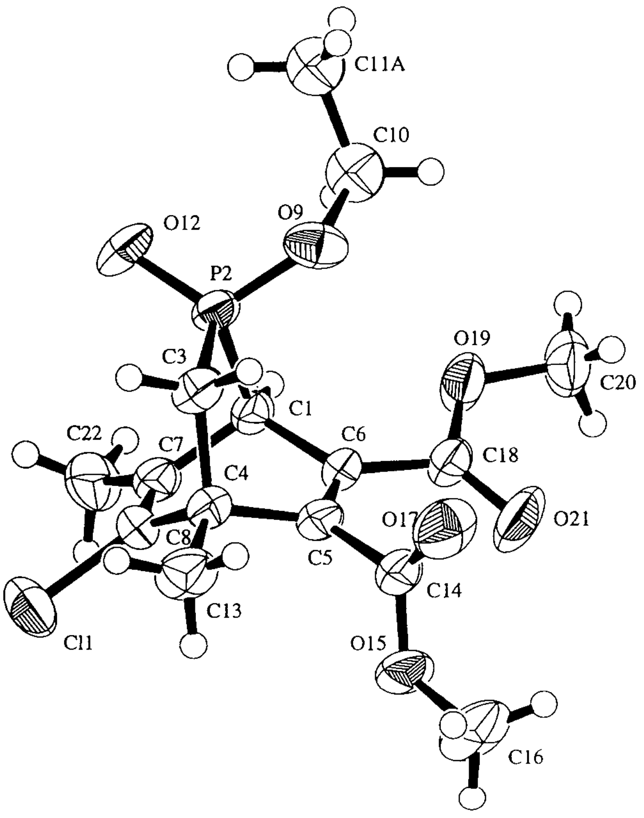

FIGURE 1 Perspective view of **2b**.

TABLE 1 Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **2b** (*U(eq)* Is Defined as One-Third of the Trace of the Orthogonalized U_{ij} Tensor)

	x	*y*	*z*	*U(eq)*
Cl(1)	5096(1)	4157(1)	2209(3)	76(1)
P(2)	3595(1)	3295(1)	1082(2)	38(1)
O(9)	3042(1)	3461(3)	921(5)	51(1)
O(12)	3737(2)	2400(2)	1098(6)	53(1)
O(15)	3999(1)	6612(2)	1307(6)	56(1)
O(17)	3325(2)	6121(3)	2498(7)	69(1)
O(19)	3183(2)	4685(2)	−2656(6)	55(1)
O(21)	3322(2)	5968(3)	−1631(7)	74(2)
C(1)	3893(2)	3907(3)	−612(7)	37(1)
C(3)	3767(2)	3911(3)	2955(8)	45(1)
C(4)	4127(2)	4617(3)	2394(8)	42(1)
C(5)	3851(2)	5167(3)	1121(8)	39(1)
C(6)	3724(2)	4803(3)	−358(7)	36(1)
C(7)	4412(2)	3823(3)	−127(8)	42(1)
C(8)	4519(2)	4191(3)	1355(9)	46(1)
C(10)	2780(2)	3066(3)	−521(6)	60(2)
C(11A)	2562(2)	2265(3)	40(6)	59(4)
C(11B)	2365(2)	2553(3)	213(6)	62(4)
C(13)	4294(2)	5092(3)	4008(6)	60(2)
C(14)	3682(2)	6016(3)	1696(8)	44(1)
C(16)	3885(3)	7454(4)	1900(12)	82(3)
C(18)	3398(2)	5225(3)	−1608(8)	44(1)
C(20)	2826(3)	5030(4)	−3795(10)	69(2)
C(22)	4733(2)	3318(4)	−1261(10)	64(2)

TABLE 2 Selected Bond Lengths (Å) and Angles (°) for Phosphabicyclooctadiene **2b** with the Estimated Standard Deviations

Atoms		Atoms	
P(2)–O(12)	1.479(4)	O(12)–P(2)–O(9)	115.3(2)
P(2)–O(9)	1.574(4)	O(12)–P(2)–C(3)	116.2(3)
P(2)–C(3)	1.816(6)	O(9)–P(2)–C(3)	103.5(2)
P(2)–C(1)	1.835(5)	O(12)–P(2)–C(1)	113.2(2)
C(1)–C(7)	1.503(7)	O(9)–P(2)–C(1)	107.5(2)
C(1)–C(6)	1.515(7)	C(3)–P(2)–C(1)	99.5(2)
C(3)–C(4)	1.570(7)	C(7)–C(1)–C(6)	110.6(4)
C(4)–C(8)	1.520(8)	C(7)–C(1)–P(2)	102.3(4)
C(4)–C(5)	1.529(7)	C(6)–C(1)–P(2)	105.3(3)
C(5)–C(6)	1.333(8)	C(4)–C(3)–P(2)	109.5(4)
C(5)–C(14)	1.499(7)	C(8)–C(4)–C(5)	106.2(5)
C(6)–C(18)	1.491(7)	C(6)–C(5)–C(4)	116.1(4)
C(7)–C(8)	1.323(8)	C(5)–C(6)–C(1)	116.0(5)
		C(8)–C(7)–C(1)	113.4(5)
		C(7)–C(8)–C(4)	119.5(5)

The X-ray structure made possible for the first time the assignment of ^{31}P and ^{13}C NMR spectra of **2a** and **2b** (Table 3); **2b** was also characterized by ^{1}H NMR and mass spectral data (see the Experimental section).

EXPERIMENTAL

FT ^{31}P NMR spectra were recorded with an IBM NR-80 spectrometer using 85% H_3PO_4 as external standard with $CDCl_3$ as solvent and internal lock. Downfield shifts have positive signs. ^{13}C and ^{1}H NMR spectra were recorded with Varian XL-300 and Bruker AW-80 spectrometers, respectively, with Me_4Si as internal standard. Coupling constants are given in hertz. The mass spectrum was obtained on a MS 25-RFA spectrometer at 70 eV.

8-Chloro-4,7-dimethyl-2-ethoxy-5,6-di(methoxycarbonyl)-2-phosphabicyclo[2.2.2]octa-5,6-diene 2-oxide (**2b**)

A solution of 3.3 g (0.0150 mol) of 4-chloro-3,5-dimethyl-1-ethoxy-1,2-dihydrophosphinine 1-oxide [7] and 1.94 mL (0.0158 mol) of dimethyl acetylenedicarboxylate in 10 mL of toluene was refluxed for 5 days. Solvent was removed *in vacuo*. The crude product thus obtained was purified by column chromatography (silica gel, 3% methanol in chloroform eluant) to give 3.3 g (61%) of **2** as the mixture of two isomers. ^{31}P NMR ($CDCl_3$) δ +57.3 (60%) for **2a** and +56.2 (40%) for **2b**. **2b** (0.7 g (21%)) could be obtained from the oily mixture of the isomers by repeated column chromatography; mp 141–142°C (ethyl acetate-*n*-pentane); ^{31}P NMR ($CDCl_3$) δ +56.3; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.3, 3H, CH_2CH_3), 1.52 (d, J = 3.2, C–CH_3), and 1.62 (d, J = 9.3, C_3–H_2) total intensity 5H, 2.08 (d, J = 3.2, 3H, C–CH_3), 3.78 (s), and 3.82 (s) CO_2CH_3, total intensity 6H, 3.95–4.20 (m, OCH_2) overlapped by 4.20 (d, J = 17.3, C_1–H) total intensity 3H; ^{13}C NMR, Table 3; MS, *m/z* (relative intensity): 362 (M^+, 6), 347 (29), 331 (7), 327 (4), 303 (49), 275 (32), 225 (100) (these data are similar to those reported for the mixture of **2a** and **2b** [5]). Anal. calcd. for $C_{15}H_{20}ClO_6P$: C, 49.66; H, 5.57. Found: C, 49.98; H, 5.87.

TABLE 3 ^{31}P and ^{13}C NMR Data for the Isomers of Phosphabicyclooctadiene **2** in $CDCl_3$

	2a	**2b**
$\delta^{31}P$	+57.3	+56.3
$\delta^{13}C$ C1	47.2(73.4)	47.1(71.2)
$(J_{PC})C_3$	28.1(128.7)	28.5(131.3)
C_4	46.8(6.7)	46.9(7.6)
C_7	133.1(10.2)[a]	132.7(9.7)[b]
C_9, C_{10}	162.5(3.7), 166.3(4.0),	163.0(4.0), 166.7(3.8)
C_{11}, C_{12}	52.3 52.8	52.5, 52.7
C_{13}	20.6(12.7)	20.7(12.7)
C_{14}	18.6(2.4)	19.1
C_{15}	62.1(6.4)	62.2(6.5)
C_{16}	16.4(5.7)	16.3(5.6)
other:	131.5(19.8)[a]	132.3(≈20)[b]
	150.1(19.4)	149.3(≈10)

[a,b]Tentative assignment.

X-ray Crystal Structure Determination for **2b**

Crystals of $C_{15}H_{20}ClO_6P$ (Mw = 362.73) are orthorhombic: space group *Pbca*, a = 27.957(4), b = 15.914(3), c = 7.749(3) Å, V = 3448 Å^3, Z = 8, D_c = 1.398 gcm^{-3}. X-ray data were collected from a transparent cubic crystal of approximate dimensions of 1.0 × 1.0 × 1.0 mm^3 with a Rigaku AFC6S diffractometer using graphite monochromated Cu-K_α radiation (lambda = 1.54178 Å with theta range of 3.16 to 75.13°.) Out of the 3555 observations, 3545 were used for the structure analysis and refinement. They were corrected for absorption by the psiscan method. Relative transmission coefficients ranged from 0.492 to 0.998. No decay correction had to be used. The structure was solved by direct methods, and nonhydrogen atoms were refined anisotropically for 197 variables to a final R = 0.0697 (I > 2sigma(I)), R_{tot} = 0.1514. The highest residual peak in the final difference electron density map was 0.786 eÅ^{-3}. Initial calculations have been made with the help of the program teXsan [8], the hydrogen positions being generated and the final structure refinement calculations being carried out with the program SHELXL-93 [9].

ACKNOWLEDGMENTS

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