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Crystal and Molecular Structure of Bis(dimethylphosphatovinyl) Carbonate ($C_9H_{16}P_2O_{11}$)

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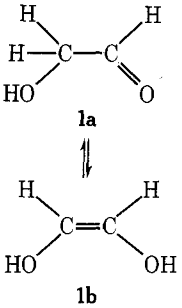
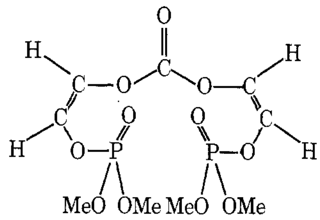
The reaction of 2 mol of 2,2,2-trimethoxy-2,2-dihydro-1,3,2-dioxaphospholene with 1 mol of phosgene ($COCl_2$) gave bis(dimethylphosphatovinyl) carbonate, $C_9H_{16}P_2O_{11}$. The crystal structure of this vinyl phosphate–vinyl carbonate was solved by x-ray diffraction techniques. The crystals grow in an orthorhombic space group *Pbca* with eight molecules per unit cell. The cell dimensions are $a = 7.257$ (2), $b = 21.788$ (8), and $c = 20.267$ (8) Å. Intensities of 1415 reflections were measured on a G.E. XRD-5 diffractometer. The structure was solved by Patterson methods and refined to a final R of 9.5% for 912 observed reflections by least-squares methods. Bond angles around both phosphorus atoms deviate from those of a tetrahedron, ranging from 99.4 to 116.9° and 101.3 to 115.4°, respectively. The formation of a trigonal bipyramidal oxyphosphorane intermediate by the addition of nucleophiles to the phosphorus involves relatively small additional bond angle deformations.

This paper describes the synthesis and the crystal and molecular structure of a carbonate–diphosphate ester, **2**, derived from the enediol tautomer, **1b**, of glycolaldehyde.



1a

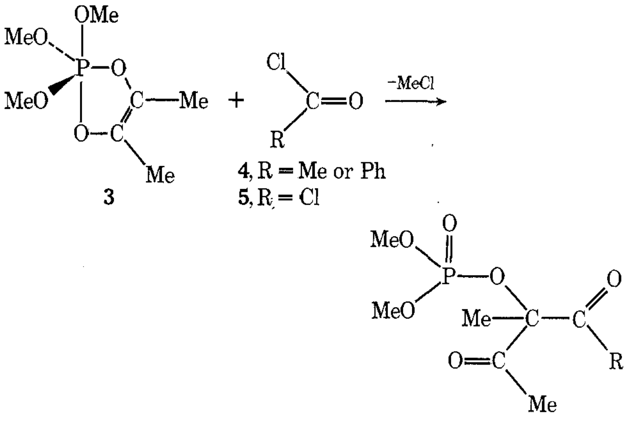
1b



2

There is now considerable information on the molecular structure and the reactivity of five-membered cyclic unsaturated[2] and saturated[3–7] phosphate esters and phosphate esters of hydroxy ketones.[8,9] The x-ray structure of methyl ethylene phosphate[10] and methyl pinacol phosphate[11] have been described.

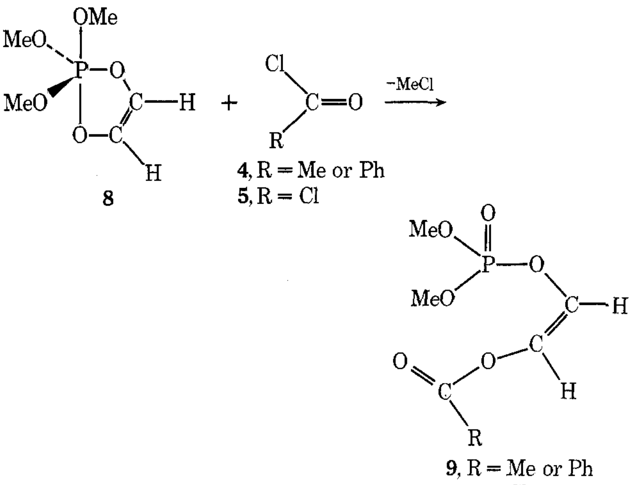
Synthesis of Bis(dimethylphosphatovinyl) Carbonate (2). The synthesis of the carbonate **2** is based on a remarkable property of the 2,2,2-trialkoxy-1,3,2-dioxaphospholene system,[12] **3**, with pentacoordinated phosphorus. According to x-ray crystallographic data, the ring in five-membered[13–17] and four-membered[18] cyclic oxyphosphoranes occupies the apical equatorial skeletal position in a trigonal bipyramid. The oxyphosphorane **3** *with two methyl substituents on the ring* undergoes exclusive C-acylation[19] with acyl halides **4** and with phosgene (**5**) under certain conditions, to give phosphate esters of α-hydroxy-β-diketones, **6**, and of α-hydroxy-β-keto acid chlorides, **7**, respectively. In contrast, the oxyphosphorane **8** *with hydrogens on the ring* undergoes exclusive O-acylation[20] under comparable conditions, to give the carboxylate–phosphate



3

4, R = Me or Ph
5, R = Cl

6, R = Me or Ph
7, R = Cl



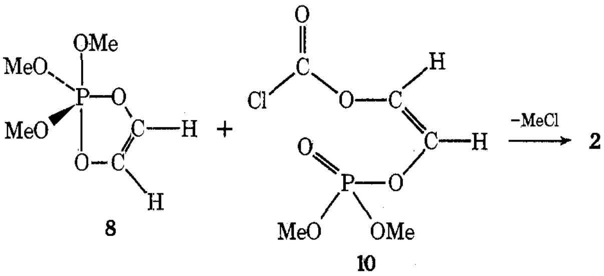
8

4, R = Me or Ph
5, R = Cl

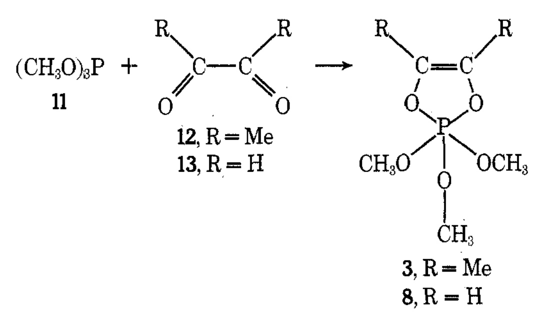
9, R = Me or Ph
10, R = Cl

ester derivatives **9** and **10** of the enediol tautomer of glycolaldehyde.

The chlorocarbonate–phosphate ester **10** reacts with a second mole of the oxyphosphorane, **8**, to give the desired crystalline carbonate **2**. The latter, **2**, can be made directly from the oxyphosphorane, **8**, and phosgene (**5**) without the isolation of the monophosphate **10**.



The oxyphosphoranes[12] **3** and **8** are synthesized from trimethyl phosphite (**11**) and the corresponding α-dicarbonyl compound, biacetyl (**12**) and glyoxal (**13**).



Experimental Section

Bis(dimethylphosphatovinyl) Carbonate (2). Phosgene ($COCl_2$) was passed through anhydrous $CuSO_4$, condensed in a calibrated trap at −70 °C, and distilled into a flask containing CH_2Cl_2 at 0 °C. A solution of 2,2,2-trimethoxy-2,2-dihydro-1,3,2-dioxaphospholene (**8**, 78.4 g, 2 molar equiv) in CH_2Cl_2 (30 ml) was added to the phosgene–CH_2Cl_2 solution at 0 °C. The addition lasted 15 min, and the reaction mixture was kept for 1 h at 0 °C and 2 h at 20 °C, with stirring. The solvent was removed at 30 °C and 20 mm (last traces at 0.2 mm), and the residue was recrystallized from benzene or from chloroform-ether. The bisphosphate **2** had mp 69–70 °C and was obtained in 95% yield: δ^{31}P +2.9; τ_A 3.65; τ_B 3.65; $J^{A}_{HC{=}CHB} = 3.5$; $J^{A}_{HC{=}COP} = 1.2$; $J^{B}_{HCOP} = 5.9$ Hz; τ_C 6.15; $J^{C}_{HCOP} = 11.5$ Hz.[28]

Anal. Calcd for $C_9H_{16}O_{11}P_2$: C, 29.8; H, 4.4; P, 17.1. Found: C, 29.6; H, 4.4; P, 17.0.

The bisphosphate **2** was also made in two stages. (1) The oxyphosphorane **8** (1 mol) in CH_2Cl_2 was added to phosgene ($COCl_2$, 1–2 mol) in CH_2Cl_2 at 0 °C (30 min). After 30 min at 20 °C, the solvent was removed and the dimethyl phosphatovinyl chlorocarbonate[20] (**10**) was purified by short-path distillation: bp 95–97 °C (0.5 mm); δ^{31}P −1.6; τ_A 3.33; τ_B 3.78; $J^{A}_{HC{=}CHB} = 3.5$; $J^{A}_{HC{=}COP} = 1.1$; $J^{B}_{HCOP} = 5.9$ Hz; τ_C 6.15; $J^{C}_{HCOP} = 11.2$ Hz.[28] (2) The oxyphosphorane **8** (1.1 mol) in CH_2Cl_2 was added to the chlorocarbonate **10** (1 mol) in CH_2Cl_2 at 0 °C. After 1 h at 20 °C, the solvent was removed and the bisphosphate **2** was purified as indicated above.

X-Ray Crystallographic Data. Crystals of the carbonate **2** were sealed in Lindemann glass capillaries under a dry argon atmosphere for x-ray examination. Preliminary Weissenberg and precession photographs indicated the orthorhombic space group *Pbca* with systematic absences: $0kl$, $k = 2n + 1$; $hk0$, $h = 2n + 1$; and $h0l$, $l = 2n + 1$. Lattice dimensions were determined from least-squares refinement of 20 2θ values measured on a G.E. XRD-5 diffractometer: $a = 7.257$ (2); $b = 21.788$ (8); and $c = 20.267$ (8) Å. The density was not measured but the calculated density is 1.499 g/cm^3 for eight molecules per unit cell. The linear absorption coefficient is 3.3 cm^{-1} for Mo Kα radiation.

The crystal used for collection of intensity data was 0.12 × 0.14 × 1.3 mm. The intensity data were collected with zirconium-filtered Mo Kα radiation on a G.E. diffractometer equipped with a scintillation counter for detection. The crystal decomposed in the x-ray beam, completely disappearing in about 10 days. Because of this, the data were collected by counting only peak heights. In order to bring the intensity data to a uniform scale, the intensities of three standard reflections were recorded every 2 h and used to scale the data. The background was estimated from a single scan from 3 to 45 °C.

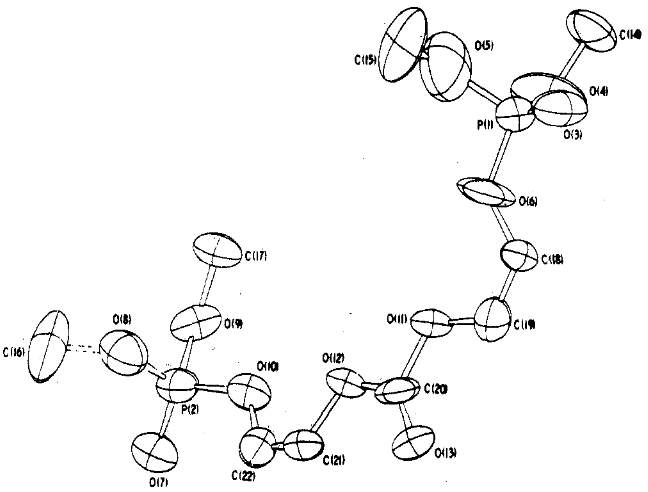


Figure 1. ORTEP drawing of bis(dimethylphosphatovinyl) carbonate ($C_9H_{16}P_2O_{11}$).

The intensities of 1415 reflections were measured in this way and 912 were considered above background by estimating $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization factors.[21] Neither absorption nor extinction corrections were applied; however, both real and imaginary terms were used for the form factor of phosphorus. Form factors were taken from the International Tables for X-Ray Crystallography.[22]

Structure Determination and Refinement. The structure was solved from the three-dimensional Patterson by first locating the phosphorus positions from the Harker section. The Fourier synthesis phased on these atoms showed the oxygen atoms around the phosphorus atoms and the next Fourier synthesis showed the complete structure. Both positional and anisotropic thermal parameters were refined by full-matrix least squares, minimizing $\Sigma w|(F_o - F_c)|^2$. Weights were calculated according to the method of Hughes,[23] since counting statistics were not considered valid, because of data collection difficulties; the final R factor ($R = \Sigma|F_o - F_c|/\Sigma F_o$) was 0.095. A final three-dimensional difference map showed no features >0.5 eA^{-3}. Hydrogen atom locations were not attempted.

Discussion

Figure 1 is an ORTEP drawing of the molecule while Table I lists the bond distances and angles.[24]

The large standard deviations for the bond distances and angles are mainly due to difficulties in the collections of data. The short carbon–oxygen distance of 1.17 Å for the carbonate is definitely shorter than the accepted value for CO_3^{-2} of 1.29 (4) Å.[25] However, it does compare favorably with that of $COCl_2$ (1.17 Å) and CO_2 (1.16 Å). The C=C distances of 1.29 Å are slightly shorter than the average value of 1.34 Å.[26]

The carbon atom, C(20), and three surrounding oxygen atoms of the carbonate group are planar, with deviations from the least-squares plane of 0.001 Å. The angles around C(20) vary from 106.9° to 127.2° even though the sum is 360°. This represents a considerable distortion from the normal 120° in the carbonate ion.[27] Inorganic carbonates show some variations from 120°, but not as large as these.

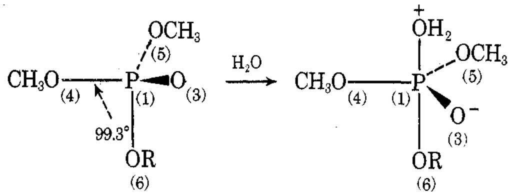
With respect to the phosphate groups, the sets of atoms O(3)–P(1)–O(6)–C(18) and O(7)–P(2)–O(9)–C(17) are nearly planar, with deviations from the least-squares planes of less than 0.1 and 0.02 Å, respectively. The other four O–P–O–C planes show considerably greater deviations.

One of the most interesting features of the structure of **2** pertains to the bond angles about the tetracoordinated

Table I. Bond Distances and Angles

P(1)–O(3)	1.42 (1)	P(2)–O(7)	1.42 (1)
P(1)–O(4)	1.56 (2)	P(2)–O(8)	1.58 (1)
P(1)–O(5)	1.57 (1)	P(2)–O(9)	1.56 (1)
P(1)–O(6)	1.54 (1)	P(2)–O(10)	1.56 (1)
O(4)–C(14)	1.43 (2)	O(8)–C(16)	1.46 (2)
O(5)–C(15)	1.36 (2)	O(9)–C(17)	1.45 (2)
O(6)–C(18)	1.41 (2)	O(10)–C(22)	1.35 (2)
C(18)–C(19)	1.29 (2)	C(21)–C(22)	1.29 (2)
O(11)–C(19)	1.40 (2)	O(12)–C(21)	1.38 (1)
O(11)–C(20)	1.37 (2)	O(12)–C(20)	1.36 (2)
		C(20)–O(13)	1.17 (2)
O(3)–P(1)–O(4)	115.7 (7)	O(7)–P(2)–O(8)	115.4 (6)
O(3)–P(1)–O(5)	116.9 (7)	O(7)–P(2)–O(9)	112.2 (6)
O(3)–P(1)–O(6)	115.0 (7)	O(7)–P(2)–O(10)	115.4 (6)
O(4)–P(1)–O(5)	103.9 (8)	O(8)–P(2)–O(9)	108.4 (5)
O(4)–P(1)–O(6)	99.4 (7)	O(8)–P(2)–O(10)	101.3 (5)
O(5)–P(1)–O(6)	103.7 (7)	O(9)–P(2)–O(10)	102.7 (5)
P(1)–O(4)–C(14)	123.7 (12)	P(2)–O(8)–C(16)	120.6 (10)
P(1)–O(5)–C(15)	127.9 (13)	P(2)–O(9)–C(17)	122.2 (8)
P(1)–O(6)–C(18)	122.8 (9)	P(2)–O(10)–C(22)	119.6 (9)
O(6)–C(18)–C(19)	117.3 (13)	O(10)–C(22)–C(21)	123.4 (13)
C(18)–C(19)–O(11)	121.4 (13)	C(22)–C(21)–O(12)	119.2 (13)
C(19)–O(11)–C(20)	116.7 (11)	C(21)–O(12)–C(20)	115.0 (10)
O(11)–C(20)–O(13)	125.9 (14)	O(12)–C(20)–O(13)	127.2 (14)
		O(11)–C(20)–O(12)	106.9 (11)

phosphorus atoms. These angles show significant departures from the tetrahedral 109° value, notably O(4)–P(1)–O(6) = 99.4°, O(5)–P(1)–O(6) = 103.7°, O(3)–P(1)–O(4) = 115.7°, for one of the phosphate functions and O(8)–P(2)–O(10) = 101.3°, O(9)–P(2)–O(10) = 102.7°, O(7)–P(2)–O(8) = 115.4°, for the other phosphate group. On the assumption that a trigonal bipyramidal oxyphosphorane is formed as an intermediate in nucleophilic displacement on tetracoordinated phosphorus,[2–9] the data show that only relatively small additional distortions of the O–P–O bond angles of 2 can lead to the trigonal bipyramid when water or hydroxide ion is added to the phosphorus.[12d]



14 (= 2) 15

Registry No.—**2**, 57775-18-5; **5**, 75-44-5; **8**, 5871-05-6; **10**, 57918-70-4.

Supplementary Material Available. Observed and calculated structure factors and a table of final positional and thermal parameters along with their standard deviations (1 page). Ordering information is given on any current masthead page.

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