Stereospecificity of alkylation of phosphite anion in electrochemical version of the Michaelis—Becker reaction

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Benzylation of *cis*-2-hydro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane in the electrochemical version of the Michaelis—Becker reaction occurs stereospecifically with retention of the stereochemistry of the hydrophosphoryl center and affords stereochemically pure 2-benzyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (yield 60—70 %). The structure of this compound was determined by X-ray diffraction analysis. The mechanism of the process was discussed.

Key words: cathodic electrolysis, stereoselective alkylation of phosphite anion, 2-benzyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinane.

The generation of dialkyl phosphite anions in cathodic electrolysis of dialkyl phosphites made it possible to accomplish the electrochemical version of the Michaelis—Becker reaction[1] and to develop thus a new approach to the preparation of olefins.[2] To evaluate the synthetic potentialities of the new method for the generation of phosphite anions, it is of interest to determine their stereochemical stability under the experimental conditions. This problem can be solved by the method of stereochemical correlations using six-membered cyclic phosphites with a fixed conformation.[3]

In the present paper we have studied electroreduction of stereochemically pure *cis*-2-hydro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**1**), in which the methyl and the oxo group are equatorial.[4] We found that the cathodic electrolysis of phosphorinane **1** at a platinum electrode in a 0.25 *N* solution of $Et_4N^+Br^-$ in MeCN in the presence of benzyl chloride affords stereochemically pure 2-benzyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**2**) in 60—70 % yield (Scheme 1).

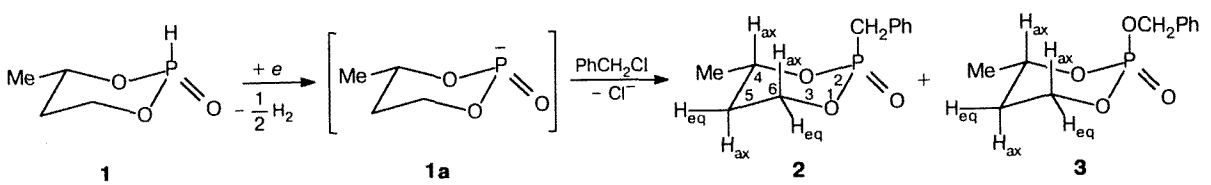
Along with phosphonate **2**, cyclic phosphate (**3**) was isolated. The mechanism of its formation has not been studied.

It has been found previously[1] that electrolysis of diorganyl phosphites in the presence of methyl iodide is accompanied by the formation of methyl phosphonates and gives no substantial amounts of *O*-alkylated products.

The yield of phosphate **3** is considerably affected by the nature of the supporting electrolyte. For example, when $Bu_4N^+Br^-$ is used, the yield of compound **3** is 30 %, whereas the electrolysis of **1** in a solution of $NaClO_4$ gives only phosphorinane **2**. In this case, **1** is entirely converted into its Na salt; however, the rate of alkylation of the salt is much lower, and the yield of **2** under comparable conditions was only 10 %.

The structures of phosphorinanes **2** and **3** were determined by ^1H and ^{31}P NMR spectroscopy. For example, the ^{31}P chemical shift observed for compound **2** is typical of a phosphorinane with an axial benzyl group and an equatorial methyl group.[5] The ^1H NMR spectrum corresponds to a chair-like shape of the 1,3,2-dioxaphosphorinane.[3] For the methine proton at C(4), the vicinal spin-spin coupling constant $^3J_{H_{ax}H_{ax}} = 11$ Hz is manifested, which indicates that this proton is axial and the methyl group is, correspondingly, equatorial. The

Scheme 1



1 **1a** **2** **3**

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Table 1. The main bond (ω) and torsion (τ) angles and bond lengths (*d*) in molecule **2**

Angle	ω/deg	Angle	τ/deg	Bond	*d*/Å
O(1)—P—O(2)	105.4	O(3)=P—O(1)—C(1)	162.9	P=O(3)	1.457
O(1)—P—C(5)	106.0	C(5)—P—O(1)—C(1)	73.8	P—C(5)	1.791
O(2)—P—C(5)	108.5			P—O(1)	1.571
O(3)=P—O(1)	111.6			P—O(2)	1.571
O(3)=P—O(2)	112.0			C(1)—O(1)	1.450
O(3)=P—C(5)	112.9			C(3)—O(2)	1.450

spin-spin coupling constant of the $C\underline{H}_2P$-group protons with the phosphorus atom, equal to 20.5 Hz, attests to the axial orientation of the benzyl group.[5] This stereochemistry of cyclophosphonate **2** was confirmed by X-ray diffraction analysis (Fig. 1). Ring *A* has a chair conformation in which the P—C(5) bond is axial and the P—O(3) bond is equatorial. The phosphorus atom has a distorted tetrahedral environment. The O(1)—P—O(2), O(1)—P—C(5), and O(2)—P—C(5) angles are smaller than 109.5°, while the angles at the phosphoryl bond are larger than 109.5° (Table 1). The deviation of the P atom from the plane of the O(1), O(2), and C(5) atoms is 0.617 Å. The P and C(4) atoms deviate from the central tetraatomic plane (±0.0003 Å) in the opposite directions, by 0.541 and −0.651 Å, respectively. The inflection angles with the O—P—O and C—C—C triatomic planes are 34.7° and 51.7° (normally these angles are 40° and 60°). The O(3) atom is deflected from this plane by 0.103 Å, and the C(5) atom deviates from it by 2.314 Å. The lengths of the P=O(3) phosphoryl bond, the P—C(5) bond, and the P—O and C—O bonds almost do not differ from the standard values.[6] Endocyclic angles (see Table 1) also correspond to those described for 1,3,2-dioxaphosphorinane 2-oxide systems.[7] It has been noted previously[8] that the P—O—C angle in esters containing tetracoordinated phosphorus atoms is a more sensitive parameter of ring strain, than the O—P—O angle; therefore, taking into account the geometric characteristics of ring *A*, one may state that it is not strained.

Ring *B* is planar (±0.006 Å), the average C—C bond length being 1.366 Å, which is somewhat smaller than the standard value for the benzene ring.[6] The C(8)—C(9)—C(10) and C(7)—C(6)—C(11) endocyclic angles are smaller than the standard values, and the Ph—C(5) bond is somewhat shorter than the average value for the $C(sp^3)—C_{Ar}$ bond, equal to 1.513 Å. No contracted intra- or intermolecular contacts have been found in the structure studied.

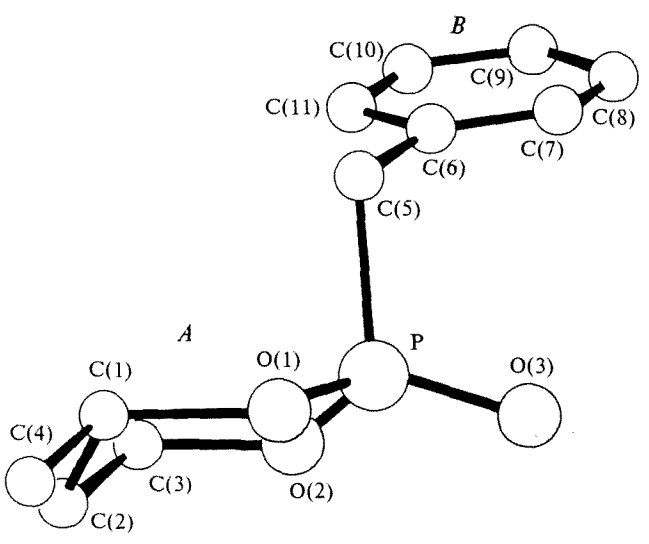

Fig. 1. Molecular structure of 2-benzyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**2**).

Experimental

The ^{31}P NMR spectra were recorded on a Bruker WP-80 SY instrument (32.4 MHz) in benzene with respect to 85 % H_3PO_4 as the external standard with broad-band proton decoupling. The ^1H NMR spectra were obtained in C_6D_6 on a Bruker AM-400 instrument (400 MHz).

Electrolysis was carried out in a diaphragm cell in a 0.25—0.3 *N* solution of the supporting electrolyte in MeCN containing equimolar amounts (0.01 mol) of compound **1** and benzyl chloride (the volume of the catholyte was 50 mL, that of the anolyte was 30 mL). The process was carried out at ~20 °C in an argon atmosphere under galvanostatic conditions at a current density of 2—4 mA cm^{-2}. From 1.1÷1.2 F of electricity per mole of the starting phosphite was consumed. A platinum plate (S = 20 cm^2) was used as the cathode and a magnesium rod (0.5 cm in diameter) served as the anode. The catholyte was concentrated, the residue was dissolved in 100 mL of CH_2Cl_2, and the solution was washed with water (5×30 mL) and dried with $MgSO_4$. Removal of the solvent followed by the column chromatography of the residue on silica gel (using 10 : 1 and 1 : 1 pentane—ethyl acetate mixtures, ethyl acetate, and 10 : 1 and 10 : 3 ethyl acetate—methanol mixtures as eluents) gave compounds **2** and **3**.

Phosphite **1** was prepared by the reaction of 1,3-butanediol with diethyl phosphite as stable *cis*-isomer, m.p. 53—54 °C, δ_P = −1, J_{PH} = 666 Hz, which corresponds to the data reported previously.[4]

2-Benzyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (2). Yield 65 %. M.p. 120—122 °C, which corresponds to the reported data.[5] $^{31}P\{^1H\}$ NMR (C_6H_6), δ: 16.7. ^1H NMR (C_6D_6), δ: 0.75 (m, 1 H, $H_{eq}C(5)$, $^2J_{H_{eq}H_{ax}}$ = −14.5 Hz,

$^3J_{H_{eq}H_{eq}}$ = 2.6 Hz, $^3J_{H_{eq}H_{ax}}$ = 2.6 Hz); 0.95 (dd, 3 H, Me, $^3J_{HH}$ = 6.5 Hz, $^4J_{HP}$ = 1.1 Hz); 1.37 (m, 1 H, $H_{ax}C(5)$, $^2J_{H_{ax}H_{eq}}$ = −14.5 Hz, $^3J_{H_{ax}H_{ax}}$ = 11 Hz); 3.03 (d, 2 H, CH_2P, $^2J_{HP}$ = 20.5 Hz); 3.51 (m, 1 H, $H_{eq}C(6)$, $^2J_{H_{ax}H_{eq}}$ = −10.8 Hz, $^3J_{H_{eq}H_{ax}}$ = 2.6 Hz, $^3J_{H_{eq}H_{eq}}$ = −2.6 Hz, $^3J_{HP}$ = −11.7 Hz); 3.73 (m, 1 H, $H_{ax}C(6)$, $^2J_{H_{ax}H_{eq}}$ = −10.8 Hz, $^3J_{H_{ax}H_{eq}}$ = 2.6 Hz); 3.76 (m, 1 H, $H_{ax}C(4)$, $^3J_{H_{ax}H_{ax}}$ = 11 Hz, $^4J_{HP}$ = 1.1 Hz); 7.14—7.25 (m, 5 H, Ph).

2-Benzyloxy-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (3). Yield 10 %. $^{31}P\{^1H\}$ NMR (C_6H_6), δ: −7.9, which corresponds to the reported data.[9] ^1H NMR (C_6D), δ: 0.70 (m, 1 H, $H_{eq}C(5)$, $^2J_{H_{ax}H_{eq}}$ = −14.7 Hz); 0.94 (dd, 3 H, Me, $^3J_{HH}$ = 6.6 Hz, $^4J_{HP}$ = 2.9 Hz); 1.38 (m, 1 H, $H_{ax}C(5)$, $^3J_{H_{ax}H_{ax}}$ = 11.0 Hz); 3.75 (m, 2 H, H(2)C(6)); 3.97 (m, 1 H, $H_{ax}C(4)$, $^3J_{H_{ax}H_{ax}}$ = 11.0 Hz, $^4J_{H_{ax}P}$ = 1.5 Hz); 5.05 (m, 2 H, OCH_2P, $^2J_{HH}$ = −11.8 Hz, $^3J_{HP}$ = 8.8 Hz); 7.14—7.25 (m, 5 H, Ph).

X-ray structural study of compound 2. X-ray diffraction analysis was carried out on a colorless crystal of dioxaphosphorinane **2** on a NICOLET P-3 diffractometer (λ(Mo-Kα) radiation, Nb filter). 982 reflections with $I > 2\sigma(I)$ were measured to $2\theta_{max}$ = 45. The crystals are monoclininc, a = 22.110(6) Å, b = 18.873(5) Å, c = 5.643(1) Å, γ = 89.48(2)°, V = 2367(1) Å^3. M = 226. $C_{11}H_{15}O_3P$, space group $I\,2/a$, Z = 8. The structure was solved by the direct method and refined by the least-squares method in the anisotropic (P, C, O) and isotropic (H) approximations to R = 0.033 (R_w = 0.038).

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