SPATIAL STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES

COMMUNICATION 7. SYNTHESIS AND SPATIAL ISOMERISM IN SERIES OF 2-METHOXY-4-METHYL-1,3-DIOXA-2-PHOSPHORINANE DERIVATIVES

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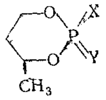
The conformation of 1,3-dioxa-2-phosphorinane derivatives depends both on the nature of the substituents attached to the phosphorus atom [1] and on the steric effect of the substituents found in the carbon portion of the ring. The 4-methyl-1,3-dioxa-2-phosphorinane derivatives are interesting in this respect, which exist as a pair of geometric isomers that differ in the mutual orientation of the exocyclic bonds. The cis- and trans-isomers of the 2-alkoxy-4-methyl-1,3-dioxa-2-phosphorinane [2-7] or of 1,3-butylene phosphite [5-9] are usually used as the starting products in the preparation of the stereoisomeric pairs. In [10] we described the spectrally pure geometric isomers of the 2-methoxy-4-methyl-(I), 2,4-dimethyl-2-oxo-(II), and 2-methoxy-2-thiono-4-methyl-1,3-dioxa-2-phosphorinanes (III).

More complete data are presented in the present communication on the synthesis and study of the spatial structure of (I)-(III) and the isomers of 2-methoxy-2-oxo-4-methyl-1,3-dioxa-2-phosphorinane (IV) employing a complex of physical methods (IR, Raman, ^{1}H, and ^{31}P NMR spectroscopy, dipole moments (DM), Kerr effect).



(I)-(IV)

$X = OCH_3, Y = UEP^*$ (I); $X = CH_3, Y = O$ (II);
$X = OCH_3, Y = S$ (III); $X = OCH_3, Y = O$ (IV)

Compound (I) was first described in [11]. Judging by the constants, apparently the trans-isomer is formed when 2-chloro-4-methyl-1,3-dioxa-2-phosphorinane is reacted with methanol in the presence of pyridine.

Statements exist in the literature on the stereospecific course of the oxidation [5, 12] and addition of sulfur to trialkyl phosphites [3, 4, 13]. The low stereospecificity of the Arbuzov rearrangement is emphasized in [14]. Actually, this reaction when run with cis-(I) under the conditions given in [11] leads to a mixture of the geometric isomers of (II). However, the pure stereoisomers of (II) are formed when the cis- and trans-(I) are treated with catalytic amounts of CH_3I under mild conditions [10]. When cooled, trans-(II) crystallizes easily. Compounds (III) and (IV) were obtained as pairs of the geometric isomers by the respective addition of sulfur and the oxidation of (I) with N_2O_4 under conditions that excluded the presence of traces of moisture. The constants of the investigated compounds (I)-(IV) are given in Table 1.

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*UEP = unshared electron pair.

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TABLE 1

Compound	Configuration	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	$\delta_{^{31}P}$, ppm
(I)	cis	30—32 (10^{-2}) [a]	1,4515	1,1205	—133
		52—54 (8) [a, b]	1,4420	1,1085	—128
	trans	48—50 (7) [a, c]	1,4420	1,1060	—128
(II)	cis	98—99 (10^{-4}) [a]	1,4575	1,2200	—23
	trans	58—59 (10^{-4}) [a]	1,4520	1,1998	—28
(III)	cis	83—84 (10^{-4}) [a]	1,4958	1,2460	—63
	trans	74 (10^{-4}) [a]	1,4920	1,2403	—66
(IV)	cis	97—98 (10^{-4})	1,4375	1,2530	+7
	trans	84—84,5 (10^{-4})	1,4390	1,2561	+5

[a] See/10/.

[b] Obtained from cis-(I).

[c] Obtained by transesterification.

[d] Relative to 85% H_3PO_4.

The isomers of (III), which were obtained in [6] by the reaction of 2-methoxy-2-anilino-4-methyl-1,3-dioxa-2-phosphorinanes with CS_2, differ in their constants from the data given in [3, 10, 13]. The reaction of methanol with cis-2-chloro-2-oxa-4-methyl-1,3-dioxa-2-phosphorinane led to the isolation of the trans*-(IV) with a wide boiling range.

In discussing the spatial structure of the stereoisomers it is necessary to solve the problems: 1) conformation of the ring and arrangement of the 4-CH_3 group; 2) the presence of conformational equilibrium, which can appear both due to inversion of the ring and due to rotation of the CH_3O group around the exocyclic P–O bond in (I), (III), and (IV); and 3) orientation of the substituent at the phosphorus atom.

Conformation of Ring. The spatial structure of the ring in (I) and (III) was studied by NMR spectroscopy [3]. From an analysis of the vicinal spin–spin coupling constants $^3J_{HH}$ and $^3J_{HP}$ and the chemical shifts of the protons it was concluded that the ring has the shape of an armchair. In all cases, except cis-(I), the 4-CH_3 group occupies an equatorial position. cis-(I) was depicted as the conformational equilibrium, in which two forms of the armchair take part. The NMR spectra obtained by us for the pure (II)† (for trans-(II) $^3J_{H_aCCH_A}$ 12 Hz; $^3J_{H_eCCH_A}$ 2.8; $^3J_{POCH_A}$ 2.8; $^3J_{POCH_B}$ 20.0 Hz) also indicate an armchair conformation with the equatorial 4-CH_3 group. Consequently, we adopted this conformation when discussing the IR spectra, DM, and Kerr constants. Evidence in support of the fact that the orientation of the 4-CH_3 group is retained when going from one isomer to another is the large difference in the DM of each stereoisomeric pair of (II)-(IV) (Table 2). In such stereoisomers the conformation of the second substituent should change when the orientation of one of the substituents is retained. A change in the orientation of the 4-CH_3 group does not affect the DM value. An equalizing of the spin–spin coupling constants of phosphorus with the protons ($^3J_{POCH_A} = {^3J_{POCH_B}} = 6$ Hz) is observed in the NMR spectrum of trans-(IV), which can be explained by the equilibrium between the two conformations of the armchair.

Conformational Equilibrium. It is easy to establish the presence or absence of conformational equilibrium by spectral methods. Equilibrium caused by inversion of the ring, as was shown by the NMR method in the preceding section, is absent in most of the discussed cases. When the rotation of the CH_3O group around the ordinary P–O bond is hindered it is possible to have three conformations appear, with a dihedral angle of 0.60 and 180° relative to the unshared electron pair of the phosphorus atom in (I) and to the P=Y– bond in (III) and (IV), as is shown in Fig. 1,‡ which should be manifested in the additional splitting of the bands in the vibrational spectra.

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*The cis-isomer when based on the nomenclature adopted in [7].

†The recording and analysis of the NMR spectra of (I), (II), and (IV) were done by Yu. Yu. Samitov. More complete data on the NMR spectra will be given in a special communication.

‡The oxygen of the CH_3O group is not shown in Fig. 1.

TABLE 2

Compound	Confirmation of P-OCH_3		cis		trans	
			μ, D	$_mK\cdot10^{12}$	μ, D	$_mK\cdot10^{12}$
(I)	Calculated	syn	1,57	6,7	2,55	22
		anti	3,08	21,0	4,25	180
		gauche	2,04	5,25	3,07	6,5
	Experimental		2,87	12,5	3,40	39,3
(II)	Calculated		6,06 *	—	3,97 *	—
	Experimental		6,36	†	3,81	†
(III)	Calculated	syn	5,09	1016	2,85	177
		anti	6,89	2173	4,94	531
		gauche	5,58	848	3,50	170
	Experimental		5,51	929	3,93	298
			5,50 [3]	—	4,20 [3]	—
(IV)	Experimental	syn	5,41	390	3,14	60
		anti	7,6	978	5,22	182
		gauche	5,91	354	3,75	1
	Calculated		6,07 ‡	344	4,46 ‡	165

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* In calculating the DM we took into account the coupling moment, determined for the P-O bond from the corresponding thiophosphonates [15], in which connection a value of 0. 58 D was adopted for the moment of the P-C bond, which was determined from the DM of trimethylphosphine [16].

† We were unable to determine the value of $_mK\cdot10^{12}$.

‡ The DM of the stereoisomers of 2-methoxy-2-oxo-4,6-dimethyl-1,3,2-dioxaphosphorinane, equal to 6. 11 and 4. 69 D [17], are good agreement with our data.

TABLE 3

Compound	Configuration	$\nu_{P=O}$, cm^{-1}*	ν_p, cm^{-1}†
(II)	cis	1270 [10]	701
	trans	1245 [10]	731
(III)	cis	—	671
	trans	—	643, 653
(IV)	cis	1288 ‡	725
	trans	1279 ‡	705, 737

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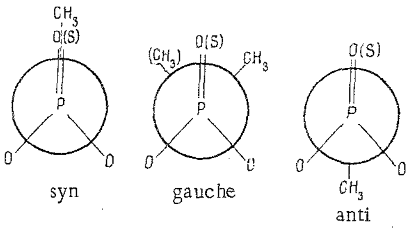
* Frequencies from the IR spectra.

† Frequencies from the Raman spectra.

‡ Differs somewhat from the frequency given in [7].



syn gauche anti

Fig. 1

The spectra of the geometric isomers of (I)-(IV), the same as the stereoisomers of the disubstituted cyclohexanes [18] and 1,3-dioxanes [19], are especially different in the low-frequency region, which is sensitive to conformational changes. The presence of an intense sharply polarized line in the 640-740 cm^{-1} region is characteristic for the Raman spectra of (II)-(IV), which belongs to the "pulsation" vibrations of the ring (ν_p) [21, 21]. As can be seen from Table 3, $\Delta\nu_p$ of the cis- and trans-isomers of (II) and (III), which differ in the orientation of the exocyclic bonds, is 20-30 cm^{-1}. A doublet of the ν_p at 643 and 653 cm^{-1} is observed in the IR and Raman spectra of trans-(III). The splitting of 10 cm^{-1} can be associated with the rotational isomerism of the $POCH_3$ fragment. The data of studying the temperature dependence in the range from −170 to 50° corroborate the presence of rotational isomers. In the Raman spectrum of trans-(III) a redistribution of the intensities occurs in some of the regions with decrease in the temperature, while a number of the lien lines disappears during crystallization (~−50°), including the line at 643 cm^{-1}.

At room temperature the ratio of the conformers is 1 : 1. The difference in the energies of the conformers, calculated as described in [22] from the lines at 643 and 653 cm^{-1}, is $\Delta E = 0.2$ kcal/mole.

Two lines, namely 705 and 737 cm^{-1}, were assigned to the pulsation vibrations in the Raman spectrum of trans-(IV). The large difference of $\Delta\nu_p = 32$ cm^{-1} can apparently indicate the conformational equilibrium that is associated with inversion of the ring, which is manifested in the NMR spectrum. Together with this, a hindered rotation of the CH_3O group also occurs. The contours of the bands at 705 and 737 cm^{-1}

have an asymmetric shape, with weakly expressed shoulders. The shape of the contours changes with variation in the temperature. Besides this, the relative intensity of the doublet at 592 and 607 cm^{-1} in the IR spectrum of trans-(IV) changes on heating.

As a result, the spectral studies indicate the presence of isomerism due to rotation of the CH_3O group in the trans-isomers of (III) and (IV).

Orientation of Substituents Attached to Phosphorus Atom. To establish the arrangement of the substituents attached to the phosphorus atom in space we employed the DM method and the Kerr effect. In the calculations we adopted the previously employed values of the axes of the polarizability ellipsoids and the bond moments [15] for the carbon bonds, and also for the ordinary P–O bond. The anisotropy of the polarizabilities of the P=O and P=S groups was calculated as the difference of the axes of the ellipsoids of the group polarizabilities of the tetra- and tri-coordinated phosphorus atom, which were determined in [23], taking into account the contribution of the polarizability of the unshared electron pair of the trivalent phosphorus atom. The following values were obtained for the polarizability ellipsoids and the dipole moments: for P=O b_l 2.19 Å^3, b_t 1.38 Å^3, 2.95 D; for P=S b_l 6.72 Å^3, b_t 3.46 Å^3, 2.62 D.

The experimental and calculated values of the DM and Kerr constants of (I)-(IV) are given in Table 2. In all cases, where the absence of conformational equilibrium was shown spectroscopically, it is easy to make a conclusion regarding the realized conformation, and here trans-(II) has an axial, while cis-(II) has an equatorial phosphoryl group. In the IR spectrum of trans-(II) the absorption frequency of the P =O group has a lower value than the corresponding frequency of the cis-isomer (see Table 3), which is also proof of the respective axial and equatorial orientation of the phosphoryl group.

From a comparison of the experimental and calculated DM and Kerr constants of the cis-isomers of (III) and (IV), which, the same as in the case of the phosphonates, exists as one fastened conformation, it is possible to conclude that they have a gauche-oriented axial CH_3O group. Apparently, such a structure is also characteristic for the starting trans-(I), which is in agreement with the conformation of the unsubstituted 2-ethoxy-1,3-dioxa-2-phosphorinane, the spatial structure of which was determined by the graphical processing of the data on the DM [24]. As was shown above, trans-(III) exists as an equilibrium mixture of two conformers, which are formed by the rotation of the CH_3O group around the exocyclic P–O bond. A comparison of the experimental and calculated DM and Kerr constants indicates the presence of the anti-conformer.

As a result, in the absence of additional steric interactions (in the cis-isomer this is 1,3-interaction with the syn-axial H atoms of the ring) the anti-conformation becomes the preferred. Based on the DM and the Kerr constants it is also possible to make similar conclusions for the corresponding trans-(IV).

When the IR spectra of the geometric pairs of isomers of (I), (III), and (IV), with a CH_3O group attached to the phosphorus atom, are compared a distinct difference is detected not only in the longwave region, but also in the region of the complex P–O–C vibrations. If the CH_3O group at the phosphorus atom is equatorial [cis-(I), trans-(II), and (IV)], then a characteristic intense band appears in the spectra at 1120 cm^{-1}. Knowing the spatial structure of the studied compounds, it is possible to make accurate conclusions regarding the stereospecificity of the investigated chemical transformations. As can be seen, all of the reactions are stereospecific and proceed with a retention of the configuration at the phosphorus atom. The nomenclature changes for (IV) and (III): the geometric isomerism of the 4-CH_3 group is discussed with respect to the P=Y bond, and not with respect to the CH_3O group, as in the trivalent phosphorus derivatives (I).

The direction of the studied reactions is depicted by the following scheme:

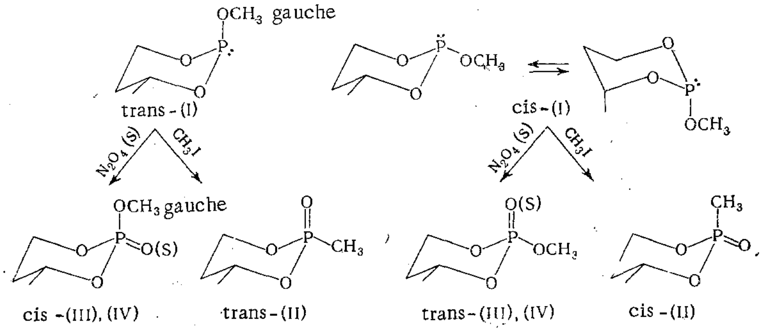


TABLE 4

Compound	Configuration	α	−β	γ	δ	μ, D	$m^{K \cdot 10^{12}}$
(I)	trans	6,3521	−0,3349	−0,1881	14,06	3,40	39,3
	cis	4,6043	−0,3467	−0,0313	8,29	2,87	12,5
(II)	trans	18,8677	—	0,0902	—	3,81	—
	cis	52,4864	—	0,2473	—	6,36	—
(III)	trans	16,55	0,3434	0,1252	224,02	3,93	298
	cis	32,4256	0,3378	0,1476	693,92	5,51	929
(IV)	trans	23,1333	0,3284	−0,0510	141,00	4,46	165
	cis	42,8667	0,3315	−0,0308	20,56	6,07	344

EXPERIMENTAL METHOD

Special attention was given to the purity of the starting reactants and solvents in the preparation of (I)-(I)-(IV). The distillation was run in a dry nitrogen atmosphere at the lowest possible temperatures. The purity of the geometric isomers was checked by IR and NMR spectroscopy. The constants of (I)-(IV) are given in Table 1. The DM and Kerr constants were determined as described in [15] at 25°, in cyclohexane solutions for (I) and in CCl_4 solutions for (II)-(IV). The coefficients of the calculation equations are given in Table 4. The Raman spectra were obtained on a Coderg Model PHO laser spectrometer.

cis-(I). With stirring and cooling (~0°), to a mixture of 8.28 g (0.26 mole) of methanol, 33 g (0.33 mole) of Et_3N and 400 ml of benzene was added a solution of 40 g (0.26 mole) of 2-chloro-1,3-dioxa-2-phospharinane in 40 ml of benzene. On conclusion of addition the stirring was continued for another 30 min at 10°. The precipitate was filtered. The benzene and excess Et_3N were removed in vacuo at a temperature not exceeding 30°. Distillation of the residue gave 32.8 g (84.5%) of cis-(I). Found: P 20.52%; MR 36.07. $C_5H_{11}O_3P$. Calculated: P 20.66%; MR 36.15.

trans-(I). a) To 20 g of cis-(I) was added 10 drops of a saturated solution of CH_3ONa in methanol. The mixture was heated for 1 h at 100°. The reaction mass became turbid. The mass was cooled and distilled to give 25 g (62.5%) of trans-(I).

b) With stirring, 9 g of 1,3-butylene glycol was added to 12.5 g of trimethyl phosphite. Then the mixture was heated to 120° and 6.35 g (99%) of methanol was distilled off. Distillation of the residue gave 6.8 g (54.8%) of trans-(I). Found: MR 35.85. $C_5H_{11}O_3P$. Calculated: MR 36.15.

cis-(II). To 13 g (0.086 mole) of cis-(I) was added 1.5 g (0.01 mole) of CH_3I. The mixture was heated carefully up to 60°. Subsequent heat evolution was removed by cooling. The reaction mixture was allowed to stand for a day at 20-25°. Then the CH_3I was removed and the residue was distilled to give 10.9 g (83.8%) of cis-(II). Found: MR 33.51. $C_5H_{11}O_3P$. Calculated: MR 33.54.

Raman spectrum of cis-(II) (ν, cm^{-1}): 122 (0.83; 0.7*), 257 sh (dp; 0.6), 275 (0.85; 1.5), 295 (0.82; 2), 376 (0.8; 0.3), 401 (0.66; 3), 429 (0.74; 1.5), 456 (0.9; 1.8), 483 (dp; 0.3), 495 (0.45; 1.7), 585 (0.05; 2.5), 701 (0.05; 10), 725 (p; 0.8), 754 (0.2; 0.4), 781 (dp; 0.4), 801 (0.71; 1.3), 851 (0.63; 0.8), 880 (0.39; 0.3), 898 sh (dp; 0.2), 909 (dp; 0.2), 950 (0.64; 0.2), 974 (dp; 0.1), 990 (0.79; 0.3), 1040 (0.8; 0.3), 1072 (0.67; 0.8), 1135 (0.62; 0.7), 1159 (0.45; 0.5), 1226 (0.74; 0.4), 1257 (0.52; 2), 1315 (0.78; 0.5), 1355 (dp; 0.3), 1378 (0.76; 0.3), 1390 (dp; 0.1), 1440 (0.83; 1.2), 1449 (0.85; 0.9), 1483 (0.8; 0.5), 2883 sh (p; 0.4); 2923 (0.1; 2.2), 2988 (0.68; 1.2).

trans-(II). Under conditions similar to those described above, from 12.4 g (0.082 mole) of trans-(I) and 1.4 g (~0.01 mole) of CH_3I we obtained 11 g (88%) of trans-(II). Found: MR 33.24. $C_5H_{11}O_3P$. Calculated: MR 33.54.

Raman spectrum of trans-(II) (ν, cm^{-1}): 117 (0.85; 0.7), 234 (0.85; 1), 260 (dp; 0.4), 281 (0.78; 2.8), 315 (dp; 0.2), 390 (0.63; 3.1), 434 (0.77; 0.8), 483 (0.69; 4), 496 (0.22; 3.2), 585 (0.05; 4.5), 678 (p; 0.8), 731 (0.1; 10), 764 (dp; 0.4), 805 (0.79; 1), 849 (0.46; 1), 892 (0.33; 0.2), 900 (0.26; 0.2), 939 (0.53; 0.2), 970 (dp; 0.1), 988 (0.8; 0.4), 1035 (0.8; 0.4), 1077 (0.66; 0.9), 1137 (0.5; 1), 1158 (0.4; 0.7), 1240 (0.33; 2.2), 1251 (0.67; 1.9), 1317 (0.84; 0.5), 1344 (0.69; 0.5), 1377 (0.77; 0.4), 1390 (dp; 0.2), 1421 (0.85; 1.1), 1449 (0.85; 1.1), 1475 (0.82; 0.9), 2873 (p; 0.6), 2905 (0.19; 1.9), 2925 (0.1; 4), 2977 (0.7; 1.7).

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*In parentheses are, respectively, given the degree of depolarization and the relative intensity; dp = depolarized; p = polarized.

cis-(III). Using the method given in [3], the reaction of trans-(I) with sulfur in CS_2 solution gave cis-(III). Found: P 17.10%. $C_5H_{11}O_3SP$. Calculated: P 17.03%.

Raman spectrum of cis-(III) (ν, cm^{-1}): 100 (dp; 0.4), 205 (0.85; 2.1), 258 (0.8; 0.2), 300 (0.4; 1.8), 320 sh (0.46; 0.2), 374 (0.56; 0.7), 393 (0.67; 1.7), 431 (0.42; 3.2), 446 (0.39; 1.2), 468 (dp; 0.3), 500 (0.25; 1.2), 565 (0.05; 6.8), 671 (0.06; 10), 766 (0.54; 1.6), 809 (0.62; 0.4), 828 (0.64; 0.3), 854 (0.74; 0.9), 895 (0.27; 0.3), 942 (0.78; 0.1), 970 (0.38; 0.2), 988 (0.55; 0.4), 1030 (0.68; 0.7), 1045 sh (0.61; 0.4), 1070 (0.46; 1.2), 1135 (0.59; 0.6), 1158 (0.58; 0.4), 1178 (dp; 0.1), 1225 (0.86; 0.3), 1250 (0.85; 0.8), 1315 (0.85; 0.4), 1341 (0.82; 0.3), 1379 (0.73; 0.3), 1390 (0.77; 0.1), 1424 (0.82; 0.4), 1446 (0.83; 0.8), 1459 (dp; 0.6), 1470 (0.81; 0.7), 2740 (0.18; 0.2), 2845 (0.07; 0.4), 2873 (p; 0.3), 2907 sh (0.17; 0.9), 2924 sh (0.19; 1.3), 2935 (0.15; 1.5), 2949 (0.23; 1.2), 2984 (0.63; 0.8).

trans-(III). The compound was obtained as described in [3] from cis-(I).

Raman spectrum of trans-(III) (ν, cm^{-1}): 100 (dp; 2.4), 184 (0.72; 2), 208 sh (0.86; 1), 247 (0.79; 0.9), 265 sh (dp; 0.3), 300 (0.54; 1.5), 326 (0.46; 1), 348 (–; 0.1), 372 (0.73; 0.9), 397 (0.41; 3.5), 409 (0.5; 5), 457 (0.6; 2.9), 497 (0.35; 1.8), 566 (0.04; 9.2), 619 (0.08; 2.3), 643 (0.05; 10), 653 (0.05; 10), 670 sh (p; 1.1), 752 (dp; 0.3), 791 (0.73; 0.9), 833 (0.79; 1.5), 854 (0.6; 1.7), 891 (0.33; 0.5), 939 (dp; 0.3), 964 (0.6; 0.4), 986 (0.79; 0.7), 1035 (0.6; 0.8), 1076 (br) (0.49; 1.2), 116 (0.62; 0.2), 1135 (0.68; 1), 1157 (0.5; 0.7), 1180 (dp; 0.1), 1227 (0.84; 0.7), 1249 (dp; 1.5), 1315 (dp; 0.7), 1339 (dp; 0.8), 1376 (dp; 0.7), 1387 sh (dp; 0.2), 1429 sh (dp; 0.9), 1446 (dp; 1.7), 1466 (dp; 1.5), 2740 (0.27; 0.4), 2849 (p; 0.8), 2875 (p; 0.6), 2905 sh (0.18; 1.7), 2934 (0.13; 2.9), 2955 (0.25; 2.6), 2985 (0.67; 1.7). trans-(III) undergoes thione–thiol isomerization at 120°.

cis-(IV). As described in [12], to a solution of 10 g of N_2O_4 in 100 ml of CH_2Cl_2 at –50° was slowly added 15.6 g of trans-(I). Vigorous reaction was observed, accompanied by the evolution of white fumes. The N_2O_4 solution assumed a green color. After removal of the CH_2Cl_2 and nitrogen oxides the residue was distilled in a high vacuum to give 12.75 g (75.8%) of cis-(IV). Found: P 18.52; MR 34.74. $C_5H_{11}O_4P$. Calculated: P 18.67%; MR 35.08.

Raman spectrum of cis-(IV) (ν, cm^{-1}): 220 (0.76; 0.4), 272 (0.8; 1.0), 332 (0.52; 2.1), 401 (0.67; 2.0), 424 (0.7; 0.5), 446 (0.86; 0.1), 460 (0.86; 0.3), 481 (0.53; 0.3), 501 (0.56; 0.6), 519 (0.29; 1.0), 602 (0.06; 1.62), 725 (0.07; 10.0), 810 (0.79; 0.4), 830 (0.81; 0.4), 860 (0.66; 1.0), 900 (0.82; 0.15), 955 (0.67; 0.2), 975 (0.86; 0.12), 993 (0.85; 0.4), 1035 (0.84; 0.5), 1045 sh (0.84; 0.5), 1075 (0.67; 0.7), 1138 (0.66; 0.7), 1163 (0.47; 0.6), 1186 (0.67; 0.1), 1227 (0.86; 0.3), 1251 (0.86; 0.9), 1228 (0.19; 1.3), 1315 (0.78; 0.4), 1344 (0.73; 0.4), 1378 sh (0.8; 0.3), 1428 (0.86; 0.45), 1453 (0.85; 1.1), 1476 (0.86; 0.8), 2853 (0.06; 0.6), 2880 (0.1; 0.4), 2915 (0.2; 1.4), 2935 (0.15; 2.0), 2955 (0.22; 1.4), 2984 (0.6; 1.0).

trans-(IV). Using a similar procedure [see cis-(IV)], from cis-(I) we obtained trans-(IV) in 86.1% yield. Found: P 18.60%; MR 34.76. $C_5H_{11}O_4P$. Calculated: P 18.67%; MR 3508. The compound turns to a glass when cooled (–150°).

Raman spectrum of trans-(IV) (ν, cm^{-1}): 218 (0.52; 1.3), 265 (0.71; 1.0), 295 (0.74; 0.4), 331 (0.64; 1.7), 351 (0.75; 1.8), 370 (0.68; 0.5), 393 (0.58; 2.5), 434 (0.56; 1.6), 470 (0.59; 2.0), 503 sh (0.57; 1.5), 513 (0.41; 3.0), 530 sh (0.71; 0.6), 590 (0.04; 3.1), 604 (0.06; 1.0), 705 (0.07; 10.0), 738 (0.07; 8.6), 808 (0.46; 1.2), 839 (0.7; 1.4), 858 (0.53; 2.0), 900 (0.7; 0.5), 961 (br) (0.59; 0.66), 994 (0.8; 1.0), 1008 (0.33; 0.54), 1037 (0.79; 0.9), 1051 (0.78; 0.92), 1085 (0.63; 1.35), 1121 (0.67; 0.9), 1135 (0.52; 1.4), 1160 (0.43; 1.1), 1185 (0.6; 0.2), 1235 (0.7; 1.0), 1252 (0.72; 2.4); 1279 (0.26; 2.6), 1316 (0.76; 0.72), 1343 (0.71; 0.9), 1378 (0.67; 0.84), 1391 sh (0.71; 0.4), 1433 (0.82; 1.4), 1452 (0.78; 2.7), 1476 (0.78; 1.92), 2855 (0.07; 1.4), 2880 sh (0.1; 1.0), 2910 sh (0.19; 2.8), 2934 (0.15; 4.4), 2959 (0.3; 3.7), 2981 (0.53; 2.8).

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CONCLUSIONS

1. The geometric isomers of the corresponding tetra-coordinated phosphorus derivatives were obtained from the stereoisomeric cis- and trans-2-methoxy-4-methyl-1,3-dioxa-2-phosphorinanes by reaction with methyl iodide, the addition of sulfur, and oxidation. It was shown that the indicated reactions are stereospecific.

2. Conclusions regarding the spatial structure of the obtained compounds were made on the basis of determining the dipole moments, Kerr constants, and the IR and Raman spectra.

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