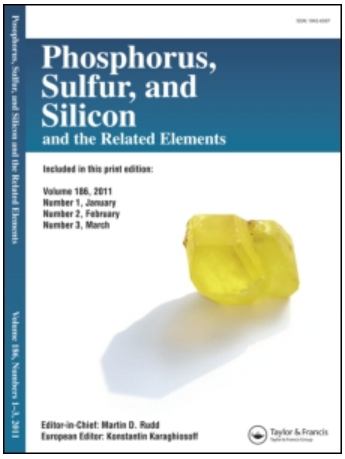

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SYNTHESIS AND STRUCTURE OF SOME STABLE PHOSPHOLANE-PHOSPHOLANES

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SYNTHESIS AND STRUCTURE OF SOME STABLE PHOSPHOLANE-PHOSPHOLANES

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Bicyclophosphites based on linear 1,2,3-triols with terminal substituents were found to be stable. Thus a series of hitherto unknown phospholane-phospholane esters, including optically active ones, was synthesized and their promise for synthetic use was demonstrated. The structure of the new compounds was proved by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and, for one of them, by X-ray analysis.

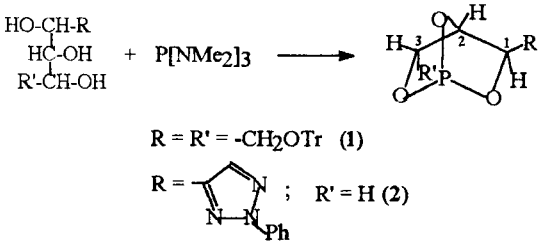
Key words: Phosphorylation, triols, phospholane-phospholane skeletons, bicyclic phosphites.

INTRODUCTION

Glycerol and 2-methylglycerol bicyclophosphites are known to be unstable compounds, polymerizing on standing.[2–4] This fact restricts the use of these phosphites for organic synthesis and coordination chemistry. Meanwhile a related 2,3,4-bicyclophosphite-β-methyl-D-ribopyranoside system is quite stable.[5,6] Taking into account the foregoing, we suggested that the phospholane-phospholane ester stability can be dependent on terminal substituents. The present paper is devoted to elucidation of this possibility.

RESULTS AND DISCUSSION

We synthesized a series of new phospholane-phospholane bicyclophosphites containing bulky terminal substituents. At first, 1,5O-dityrityl-L-arabite and D-xylose phenylozotriazol were used as initial compounds. These triols were found to enter easily into phosphorylation with phosphorous hexamethyltriamide giving mainly 3,5-bistrityloxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.1]heptan (**1**) and 3-(2′-phenyl-1′,2′,3′-triazolyl-4′)-2,6,7-trioxa-1-phosphabicyclo [2.2.1]heptan (**2**).



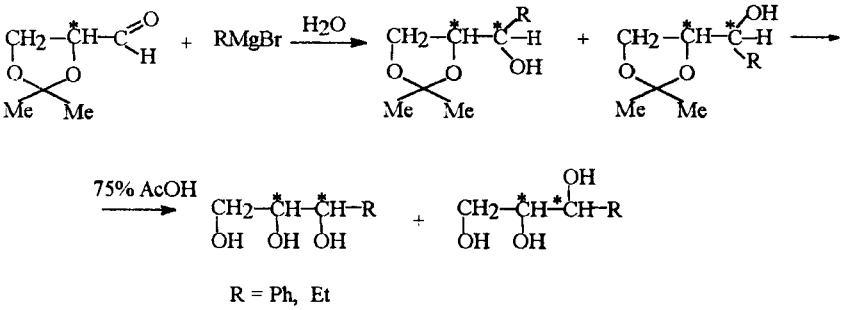
Scheme 1

Compounds **1** and **2** are stable in the solid state and in solution in the absence of moisture and oxygen for two months of storage, i.e. they are much more stable than glycerol and 2-methylglycerol bicyclophosphites.

Bicyclophosphite structures were established by means of ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The signal-proton assignments were derived from ^{1}H $\{^{31}P\}$ resonances and two-dimensional spectroscopy (COSY and HETCOR ^{1}H-^{13}C) and refined by the ^{31}P NMR spectroscopy (at 162.0 MHz) without suppression of specific $J_{H,P}$ coupling.

Single signals with chemical shift δ_P 113.5 (**1**) and 106.8 ppm (**2**) were observed in the ^{31}P NMR spectra. Note that the bicyclophosphite based on glycerol shows resonances in the same region (δ_P 106 ppm). The ^{1}H and ^{13}C NMR spectral analyses of bicyclo-phosphites **1** and **2** prove the splitting of carbon and proton signals on the phosphorus nucleus (Tables I and II). This fact points to the addition of phosphorus to oxygens of all 1,2,3-triol carbons. The absence of $^{3}J_{H,P}$ splitting for the proton 3H in the ^{1}H NMR spectrum of **1** should be noted. The structural analysis of 1 using Dreiding models shows that the dihedral angle H—C—O—P of the phosphorus electron lone pair with that proton approaches 90 deg. The absence of the corresponding vicinal coupling constant appears thus explicable. Note that $^{3}J_{H,P}$ and $^{3}J_{H,H}$ values for **1** and **2** are often close to each other, e.g. $^{3}J_{1H,P}$ (3.6 and 3.3 Hz), $^{3}J_{2H,P}$ (15.7 and 15.9 Hz), $^{3}J_{1H,2H}$ (0.6 and 0.6 Hz); it is the case for the $^{2}J_{C,P}$ values too. Such agreement indicates a close geometrical similarity for the bicyclic systems **1** and **2**.

In the present work we studied also the bicyclophosphorylation of the 1,2,3-triol diastereomeric mixture, which contain terminal substituents of smaller size. These triols were obtained by treatment of stereoisomeric 2,3,O-isopropylidene-D-glyceraldehydes with Grignard reagent:



Scheme 2

The composition of resulting mixtures was determined by the signal integral in-

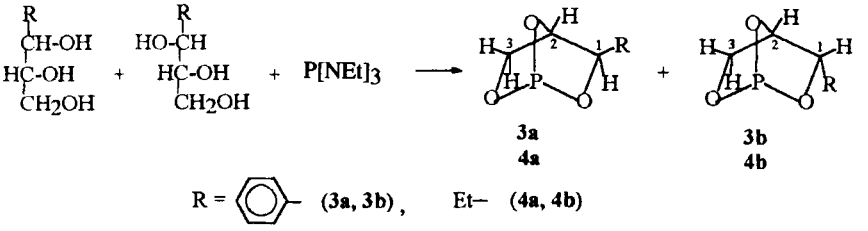
TABLE I

^{1}H NMR spectral parameters of the compounds **1–4, 7**

Assign-ment	Compounds						
	1	**2**	**3a**	**3b**	**4a**	**4b**	**7**
	Chemical shifts (δ, ppm)						
1H	4.02(m)	5.48(d)	5.16(t)	5.11(d)	3.70(m)	3.45(m)	5.31(d)
2H	5.41(dd)	5.65(dd)	5.62(m)	5.31(dd)	4.53(m)	4.38(dd)	5.12(m)
3H	4.18(m)	4.19(dd)	3.34(m)	3.58(dd)	3.32(dd)	3.39(m)	4.56(m)
3'H	-	3.70(dd)	3.48(dd)	4.05(dd)	3.83(m)	3.83(m)	4.30(m)
	Coupling constants (J, Hz)						
1H,2H	<0.6	<0.6	3.4	<0.6	3.2	<0.6	8.6
1H,3H	<0.6	<0.6	2.2	<0.6	1.9	<0.6	<0.6
2H,3H	3.3	<0.6	3.4	<0.6	3.3	1.6	6.4
2H,3'H	—	3.4	<0.6	3.4	<0.6	1.6	<0.6
3H,3'H	—	8.3	8.7	8.2	8.7	8.1	9.3
1H,P	3.6	3.3	<0.6	3.0	<0.6	3.1	<0.6
2H,P	15.7	15.9	16.0	15.8	16.0	16.0	7.9
3H,P	<0.6	3.6	<0.6	3.7	<0.6	4.2	16.4
3'H,P	—	<0.6	3.9	<0.6	4.2	<0.6	5.6

Note: - The other protons chemical shifts (δ_H, ppm):
compound **1** 7.2-7.7 (aromatic protons); 2.9, 3.12, 3.55 (CH_2-O-CPh_3)
compound **2** 7.42-8.01 (aromatic protons)
compounds **3a** and **3b** 7.0-8.0 (aromatic protons)
compound **4a** 0.91 (methyl protons); 1.35, 1.63 (methylene protons)
compound **4b** 0.93 (CH_3), 1.42, 1.52 (CH_2)
compound **7** 7.40-7.50 (aromatic protons); 1.37-2.99 (piperidine protons)

tensity ratios in the ^{1}H and ^{13}C NMR spectra of the glycerols isolated. It was shown that the ratio of tryols isometric on the C^1 atom in the composition was 1:1 for the phenylglycerol derivative and 1:4 for the ethylglycerol derivative. These isomeric triol compositions are found to be phosphorylated with phosphorous hexaethyltriamide very easily.



Scheme 3

TABLE II

^{13}C NMR spectral parameters of the compounds **1–4**

Assign-ment	Compounds					
	1	**2**	**3a**	**3b**	**4a**	**4b**
	Chemical shifts (δ, ppm)					
C^1	76.30	72.06	78.72	78.60	80.02	81.44
C^2	79.50	78.15	78.34	79.24	78.60	77.48
C^3	72.85	66.80	62.38	67.43	62.87	68.42
	Coupling constants ($^2J_{C,P}$, Hz)					
C^1-P	1.5	1.8	2.0	1.5	2.0	2.0
C^2-P	5.9	5.8	5.0	5.5	5.1	5.6
C^3-P	2.0	2.0	<1	1.0	<1	<1

Note: - The other carbons chemical shifts (δ_P, ppm):

compound **1** 62.0 and 64.3 ($\underline{C}H_2$-OPh); 118-129 (aromatic carbons)

compound **2** 118.4-134.6 (aromatic carbons)

compounds **3a** and **3b** 117.9-136.9 (aromatic carbons)

compounds **4a** and **4b** 11.73 (CH_3), 27.7 (CH_3-$\underline{C}H_2$-CH)

Bicyclophosphites (**3, 4**) have been isolated as diastereomeric mixtures by vacuum distillation. All triol isomers underwent an efficient bicylophosphorylation; therefore the isomeric phosphite fractions in the resulting mixtures were fully consistent with those in the initial compositions.

The resulting diasteromeric bycyclophosphite pairs have similar boiling points and R_f values, but their ^1H, ^{13}C and ^{31}P NMR features are significantly distinct; e.g. in the ^{31}P NMR spectra, the isomer composition of **3** is manifested in two signals with chemical shifts δ_P 106.8 and 116.0 ppm in the integral ratio 1:1, that of **4** shows closely related values 107.5 and 114.5 ppm in the ratio 1:4. ^1H and ^{13}C NMR spectra (2D-spectroscopy COSY and HETCOR ^1H-^{13}C) reveal signals from all the carbons and protons of bicyclic moiety as well as from those of terminal substituents and allow an unambiguous signal assignment (see Tables I and II). The peak set assigned to the bicyclic skeleton for **3** and **4** is double of that for **1** and **2**. The ^1H and ^{13}C NMR spectra for the two isomer pairs (**3a,b** and **4a,b**) are similar. In the proton spectra of those compounds examined, the value of $^3J_{2H,P}$ (15.8–16.0 Hz) is large. It is unaffected by the character or orientation of the substituent at the first position. Such a value of $^3J_{2H,P}$ is consistent with the near-zero dihedral angle formed by the phosphorus lone pair plane with the proton 2H. For the proton in the first position the steric arrangement is of importance. So, $^3J_{1H,P}$ is not found for **3a**, **4a** isomers while $^3J_{1H,P}$ is 3.0–3.1 Hz for **3b**, **4b** isomers; such a difference in the value of ^1H coupling constant stems from its steric orientation.

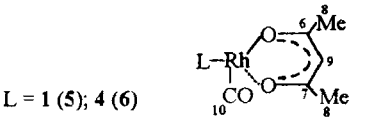
It should be noted that a phenyl substituent has a profound effect on the chemical

shifts of bicyclophosphite methylene protons so that one of the protons falls within the domain of additional shielding (δ_{3H} 3.58 ppm) and the other one falls within the domain of deshielding (δ_{3H} 4.05 ppm). This fact allows a conclusion to be drawn on the phenyl group orientation in the bicyclophosphite **3b** molecule. For isomer **3a**, the difference in chemical shift of methylene protons is negligible (Δ_δ 0.14 ppm). The opposite situation occurs in the case of bicyclophosphites **4a,b**: $\Delta_\delta = 0.14$ ppm for methylene protons of the upfield isomer (δ_p 105.93 ppm) and $\Delta_\delta = 0$ for those of the downfield isomer (δ_P 112.84 ppm). This fact is attributable to the difference in magnetic anisotropy of C—C bonds and benzene ring.

The bicyclophosphites **3** and **4** are rather stable, in solution at +15°C the racemate **3a,b** is stable for more than 1 month and **4a,b** for two weeks.

It is notable that, for glycerols, the character and the size of terminal substituents affect the stability of correspondent 1,2,3-bicyclophosphites. Generally the smaller the terminal substituent, the lower is the chemical stability of the phosphorus esters to polymerization.

We have also investigated some chemical features of bicyclophosphites **1** and **4**. They are shown to give easily rhodium(I) coordination compounds. The complexes with one bicyclophosphite ligand are formed during addition of the phospholane-phospholane diluted solutions to an equal quantity of dissolved acetylacetonato-dicarbonylrhodium(I).

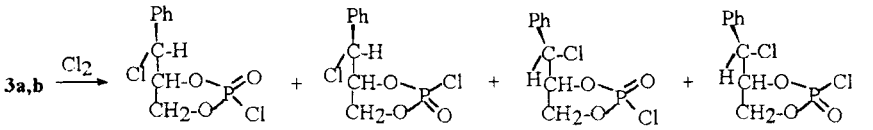


5, 6

Scheme 4

The ^{31}P NMR spectra of adducts (**5**, **6**) present doublets with chemical shifts δ_P 143.0 and 141.3 ppm, coupling constants $J_{P,Rh}$ 279.45 and 281.97 Hz, respectively. These values are close to those for β-methylribopyranoside 2,3,4-bicyclophosphite.[6] The ^{13}C NMR spectra of **5** and **6** show signals from all the carbons of bicyclophosphite and acetylacetonate fragments as well as from those of the carbonyl groups. The signals assigned to the bicyclic fragment are generally split into doublets due to coupling to phosphorus.

Phospholane-phospholane ester **3a,b** reacts easily with chlorine. We have found the chlorination to be regioselective. According to the PMR spectroscopic data, the phospholane ring at the phenyl substituent is opened. Therewith four diasteromeric chlorophosphates are formed, as would be expected:



Scheme 5

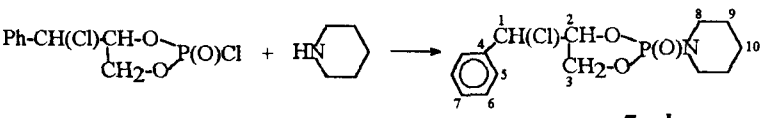
The ^{31}P NMR spectrum of the reaction mixture shows four signals with chemical shifts δ_P 15.9, 9.5, 6.9, and 4.1 ppm of approximately equal integral intensities.

The resulting chlorocyclophosphates are readily transformed to piperidides.

TABLE III

^{13}C NMR spectral parameters of the compounds **5–12**

Compounds	δ_C, ppm (J, Hz)									
	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
5	79.40 (6.25)	77.13 (1.20)	75.97 (7.84)	62.15 (5.06)	64.38 (4.82)	187.60	486.10	27.20 (8.01)	101.21 (1.48)	188.00 (73.00 36.20)
6	82.31 (5.80)	76.23 (<1)	65.17 (7.27)	23.24 (4.26)	10.38	187.70	185.70	27.34 (9.46)	101.01 (2.50)	188.22 (73.20 36.10)
7	68.43 (<1)	79.09 (1.78)	62.29 (2.76)	128.63 (2.30)	136.87	128.63	127.12	45.41 (2.30)	25.78 (3.81)	24.14
10	86.86 (7.27)	71.34 (4.36)	73.31 (5.81)	30.03 (7.27)	13.29	56.27	31.58			
11a	80.72 (5.10)	68.46 (5.05)	70.54 (3.80)	140.51 (8.90)	127.60	126.79	126.43	50.59	27.20	
11b	79.31 (5.00)	6.70 (3.80)	68.39 (4.27)	140.12 (8.98)	127.37	126.68	126.43	50.59	27.20	
12a	83.19 (4.53)	69.60 (1.83)	72.45 (5.29)	140.74 (8.75)	129.16	128.49	127.29	45.57	23.68	23.09
12b	81.70 (4.13)	68.92 (2.36)	70.21 (4.75)	140.07 (9.66)	129.06	128.41	127.29	45.57	23.68	23.09



7a-d

Scheme 6

The ^{31}P NMR spectrum of the reaction mixture gives four signals with closely spaced chemical shifts δ_P 23.92, 23.74, 23.47, and 23.39 ppm. One of the isomeric piperidides (**7a–d**) was isolated by means of column chromatography. The PMR spectrum of the purified compound has signals of all the protons of 2-oxo-2-piperidido-4-chlorobenzylene-1,3,2-dioxaphospholane **7**. The proton bonded to the phenyl ring and the chlorine atom appears as a weak-field doublet typical for PhCHCl group (δ_{1H} 5.31 ppm, $J_{1H,2H}$ 8.6 Hz). At the same time, it loses $J_{1H,P}$ which points to the rupture of O—C^1 bond in the bicyclic phosphite **3** under chlorination. The ^{13}C NMR spectrum presents analogous information (see Table III). The protons 2H, 3H, and 3′H of the five-membered ring have vicinal coupling constants with the phosphorus atom as determined by the homonuclear double resonance experiment as well as by ^1H NMR spectra with phosphorus decoupling $^1H\{P\}$. An increase in $^3J_{1H,P}$ values of **7**, as compared with the phosphite **3**, is caused by the increased coordination of the phosphorus atom. Such a direction of chlorination reaction of phospholane-phospholane ester **3a,b** does not agree with the results of chlorination of structurally close 1,2,3-bicyclophosphite-D-lixopyranose reported previously.[7] Nevertheless, this result would be expected as the most probable. The influence of the phenyl substituent in the ester under study presumably results in a marked increase of electron density at the C^1 atom that becomes the most electrophilic center in the molecule of **3**.

Another interesting example of destructive reactions of bicyclophosphites is their oxidation with hydrogen peroxide. Treatment of symmetric phosphorinane-phosphorinanes with 25–35% H_2O_2 is known to result in oxidation of the phosphorus

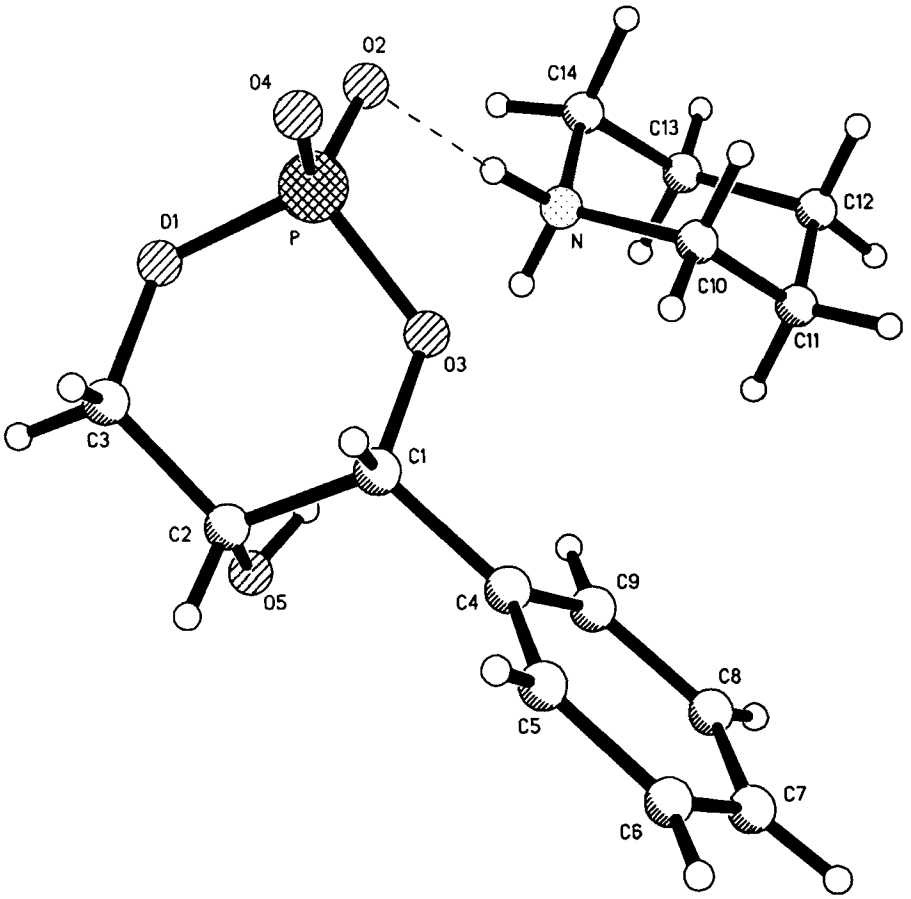
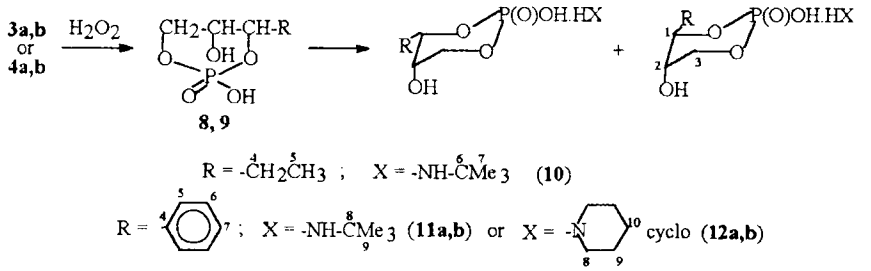


FIGURE 1

atom and in formation of corresponding bicyclophosphates.[8-10]. In the case of constrained bicyclophosphites such an oxidation is followed by a phosphorus skeleton hydrolysis as is reported.[6,11,12] Phospholane-phospholanes **3** and **4** react analogously:



Scheme 7

The reaction being studied is heat-liberating; it is accomplished in 7–10 minutes. The resulting monocyclic phosphoric ester (**8**) is manifested in the ^{31}P NMR spectrum as two signals with δ_P −5.30 and −6.40 ppm in the ratio 1:4 conforming to the

phosphite fractions in **3a,b**. At the same time, the ^{31}P NMR spectrum of the acid (**9**) presents two signals of equal intensities with δ_P −5.02 and −6.45 ppm. Hence the presence of isomers is explicable on the basis of axial or equatorial orientation of the phenyl (ethyl) substituent relative to 1,3,2-dioxaphosphorinane ring. To yield crystalline products, after completing the reaction, some amines (such as *t*-$BuNH_2$ and piperidine) were added to the reaction mixture. Salt adducts (**10–12**) crystallize spontaneously from a dioxane solution, with the salt on the base of dominating isomer precipitating first. It is along this pathway that the sterically pure salt **10** with δ_P −1.68 ppm was derived from the acid **9**, whereas the phenylglycerol derivatives **11, 12** were precipitated as isomer mixtures with chemical shifts δ_P −2.15 and −2.95 ppm (**11a,b**) δ_P −2.05 and −3.04 ppm (**12a,b**). The structure of phosphorinanes **10–12** was confirmed by ^{13}C NMR spectroscopy, that of compound **12a,b** by X-ray analysis.

Figure 1 illustrates the perspective view of the anion showing chair conformation of dioxaphosphorinane with phenyl group in equatorial position and hydroxy-group in axial. Atoms O(1), O(2), C(1), and C(3) are coplanar to 0.023(3) Å, atoms P and C(2) are displaced from this plane in opposite directions by 0.713(2) and 0.716(3) Å, respectively. The cation molecule of piperidine is in normal chair conformation with three types of intermolecular hydrogen bonds: two NH···O and one OH···O.

Thus, we can state that the oxidative hydrolysis of bicyclic phosphites **3** and **4** operates regioselectively with the rupture of just central bridge bond P—OCH to result in a phosphorinane system only. The obtained result agrees with that described previously and presumably is of a general character.

CONCLUSION

For the first time, the synthesis and directional transformations of stable skeleton phospholane-phospholane bicyclophosphites, based on linear triols, were performed. It was shown that they often differ in their chemical features from related carbohydrate bicyclophosphites and symmetric skeleton esters.

EXPERIMENTAL

General. All syntheses were performed using dry benzene, dioxane, or CH_2Cl_2 under dry nitrogen atomosphere. The thin-layer chromatography was used with plates Silufol UV 254; the column chromatography, with silica gel L 100/160 mcm. Benzene (for **1** and **2**); benzene:dioxane, 3:1 (A); and heptan:dioxane, 3:1 (B) (for **7**) were used as eluents. Recrystallization of salts (**10–12**) was performed from the system dioxane: ethanol, 1:1. The NMR spectra were recorded in DMSO-d_6 (0.4–0.5 mol/l) on a Bruker AMX-400 instrument relative to 85% H_3PO_4 (^{31}P NMR) and TMS (^1H and ^{13}C NMR). The main parameters of the experiment of X-ray analysis for compound **12a** are given in Table IV.

1,5-O-dirityl-L-treo-2,3,4-trioxypropane (**13**) was prepared by treatment of L-arabite with triphenylchloromethane in pyridine; 2-phenyl-4-(D-treo-trioxypropyl)-2H-1,2,3-triazol (**14**) was prepared from D-xylose after a known procedure[13]; 1-phenyl- (**15a,b**) and 1-ethyl-1,2,3-trioxypropane (**16a,b**) were prepared after the original scheme given above; (+)-2,3-O-isopropylidene-sn-glyceraldehyde was prepared from D-mannitol after a known technique[14]; acacRh$(CO)_2$ was prepared after the procedure.[15]

3,5-Bistrityloxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.1]heptan (**1**). Hexamethyltriamide phosphite (0.25 g) was added to a solution of **13** (0.8 g) in benzene (40 ml). The reaction mixture was boiled

TABLE IV

Crystal data and structure refinement for **12**

Identification code	ps52
Empirical formula	C14 H23 N O5 P
Formula weight	316.30
Temperature	293(2) K
Wavelength	1.54180 A
Crystal system	monoclinic
Space group	P 2(1)
Unit cell dimensions	a = 7.4340(10) A alpha = 90 deg. b = 5.6150(10) A beta = 91.07(3) de c = 18.197(4) A gamma = 90 deg.
Volume	759.4(2) A^3
Z	2
Diffractometer	Syntex P-1
Collection method	theta/2theta
Radiation type	CuK\a (Ni-filter)
Density (calculated)	1.383 Mg/m^3
Absorption coefficient	1.803 mm^-1
F(000)	338
Crystal size	0.30 x 0.25 x 0.15 mm
Theta range for data collection	2.43 to 63.28 deg.
Index ranges	-8<=h<=8, -6<=k<=0, 0<=l<=20
Reflections collected	1368
Independent reflections	1368 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1368 / 0 / 278
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0677
R indices (all data)	R1 = 0.0236, wR2 = 0.0677
Absolute structure parameter	-0.04(2)
Extinction coefficient	0.0057(11)
Largest diff. peak and hole	0.253 and -0.226 e.A^-3

(81°C) for 1.5 hrs. The reaction was monitored by TLC. The solvent was removed under vacuum. The residue was eluted from silica gel with benzene, and fractions with R_f 0.75 (A) were collected. The product was dried under vacuum without heating. Yield is 0.27 g (32%), m.p. 85–86°C, R_f 0.75 (benzene), 0.89 (B), δ_P 113.5 ppm. Found, %: C, 77.91; H, 5.69; P, 4.58. $C_{43}H_{37}O_5P$. Calcd., %: C, 77.71; H, 5.57; P, 4.67.

3-(2'-Phenyl-1',2',3'-triazolyl-4')-2,6,7-trioxa-1-phosphabicyclo[2.2.1]heptan (**2**). $P[NMe_2]_3$ (0.35 g) was added to a solution of **14** (0.5 g) in 85 ml of the system A. After heating, the reaction mixture was

TABLE V

Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (A^2 × 10^3) for **12**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
P	6417(1)	5000	6989(1)	35(1)
O(1)	8397(2)	5933(4)	7187(1)	44(1)
O(2)	5918(2)	5896(4)	6247(1)	48(1)
O(3)	5218(2)	6450(3)	7566(1)	38(1)
O(4)	6245(2)	2395(3)	7128(1)	45(1)
O(5)	7729(2)	9755(4)	8298(1)	46(1)
C(1)	5761(3)	6227(4)	8333(1)	36(1)
C(2)	7655(3)	7266(4)	8426(1)	39(1)
C(3)	8949(3)	5875(6)	7953(1)	44(1)
C(4)	4344(3)	7368(4)	8800(1)	38(1)
C(5)	3872(3)	6246(5)	9448(1)	45(1)
C(6)	2574(3)	7212(6)	9894(1)	54(1)
C(7)	1712(3)	9266(6)	9687(1)	57(1)
C(8)	2174(4)	10416(5)	9045(2)	56(1)
C(9)	3507(3)	9496(5)	8604(1)	47(1)
N	3814(2)	9785(4)	6242(1)	38(1)
C(10)	2077(3)	9237(5)	6600(2)	50(1)
C(11)	894(4)	11416(6)	6609(2)	59(1)
C(12)	564(3)	12376(6)	5838(2)	56(1)
C(13)	2354(4)	12853(6)	5463(2)	55(1)
C(14)	3557(4)	10691(6)	5481(1)	53(1)

chromatographed analogously to the synthesis of **1**. Yield is 0.25 g (49%), m.p.112–114°C, R_f 0.45 (benzene), 0.88 (A), δ_P 106.8 ppm. Found, %: 65.92; H, 3.91; N, 15.78; P, 11.70. $C_{11}H_{10}N_3O_3P$. Calcd., %: C, 65.78; H, 3.80; N, 15.97; P, 11.79.

3-Phenyl-2,6,7-trioxa-1-phosphabicyclo[2.2.1]heptan (**3a,b**). Phosphorous hexaethyltriamide (4.95 g) was added to a solution of **15a,b** (3.3 g) in dioxane (50 ml). The reaction mixture was boiled (102°C) for 80 min, the reaction was monitored by TLC. The solvent was removed under a slight vacuum, and the residue was distilled. Yield is 2.2 g (57.1%), b.p. 104–106°C/1–2 mm Hg, m.p. 38–39°C, R_f 0.83 (A), 0.68 (B), δ_P 106.8 and 116.0 ppm. Found, %: C, 55.74; H, 4.83; P, 15.24; $C_9H_9O_3P$. Calcd., %: C, 55.10; H, 4.59; P, 15.82.

3-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.1]heptan (**4a,b**). Analogously to the synthesis of **3a,b**, the bicyclophosphite **4** was prepared from 3.25 g of **16a,b** and 6.85 g of $P[NEt_2]_3$ with yield of 2.5 g (62.3%), b.p. 68–71°C/6–7 mm Hg, R_f 0.78 (A), 0.65 (B), δ_P 107.3 and 114.5 ppm. Found, %: C, 40.68; H, 6.24; P, 20.59. $C_5H_9O_3P$. Calcd., %: C, 40.54, H, 6.08; P, 20.04.

[3,5-Bistrityloxymethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,1]heptan]rhodium(I) acetylacetonatocarbonyl (**5**). The phosphite **1** (0.3 g) in 15 ml of benzene was added dropwise under stirring to a solution of $acacRh(CO)_2$ (0.12 g) in 30 ml of benzene. The solvent was removed under vacuum without heating, the residue was washed with pentane (2 × 10 ml) and dried under vacuum. Yield is 0.078 g (64.8%), syrup, R_f 0.64 (benzene), 0.77 (B), δ_P 141.3 ppm. Found, %: C, 65.85; H, 5.01; P, 3.39; $C_{49}H_{44}O_8PRh$. Calcd., %: C, 65.77; H, 4.92; P, 3.47.

[3-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.1]heptan]rhodium(I) acetylacetonato-carbonyl (**6**). Analogously to the complex adduct **5**, from 0.09 g of $acacRh(CO)_2$ and 0.05 g of **4a,b** was prepared the complex **6**. Yield is 0.093 g (73.2%), syrup, R_f 0.62 (A), 0.42 (benzene), δ_P 143.0 ppm. Found, %: C, 34.66; H, 4.64; P, 8.39. $C_{11}H_{16}O_6PRh$. Calcd., %: C, 34.92; H, 4.23; P, 8.20.

2-Oxo-2-piperidido-4-chlorobenzylene-1,3,2-dioxaphospholane (**7**). Dry chlorine was passed through a solution of **3a,b** (1.44 g) in CH_2Cl_2 (10 ml) until the reaction mixture turns green (for 12 min). The reaction was monitored by TLC and ^{31}P NMR. Four compounds with δ_P 15.9, 9.5, 6.9, and 4.2 ppm were revealed in the reaction mixture. The solvent was evaporated under vacuum; 1.6 g of piperidine in 20 ml of CH_2Cl_2 was added at 0°C to 2.0 g of the syrupous residue dissolved in 10 ml of CH_2Cl_2. The reaction was monitored in an analogous way. After 15 hrs the precipitated piperidine chlorhydrate was filtered

TABLE VI

Bond lengths [A] and angles [deg] for **12**

P-O(2)	1.482(2)
P-O(4)	1.490(2)
P-O(1)	1.597(2)
P-O(3)	1.610(2)
O(1)-C(3)	1.445(3)
O(2)-C(1)	1.451(2)
O(5)-C(2)	1.418(3)
C(3)-C(2)	1.520(3)
C(2)-C(1)	1.531(3)
C(1)-C(4)	1.508(3)
C(4)-C(9)	1.390(3)
C(4)-C(5)	1.388(3)
C(5)-C(6)	1.383(4)
C(6)-C(7)	1.369(5)
C(7)-C(8)	1.383(4)
C(8)-C(9)	1.387(4)
N-C(14)	1.485(3)
N-C(10)	1.490(3)
C(10)-C(11)	1.507(4)
C(11)-C(12)	1.519(4)
C(12)-C(13)	1.530(4)
C(13)-C(14)	1.508(4)
O(2)-P-O(4)	117.81(11)
O(2)-P-O(1)	107.97(10)
O(4)-P-O(1)	111.44(10)
O(2)-P-O(3)	106.85(9)
O(4)-P-O(3)	109.62(10)
O(1)-P-O(3)	101.89(8)
C(1)-O(1)-P	117.00(14)
C(1)-O(3)-P	115.83(12)
O(1)-C(3)-C(2)	111.3(2)
O(5)-C(2)-C(3)	112.7(2)
O(5)-C(2)-C(1)	113.3(2)
C(3)-C(2)-C(1)	109.4(2)
O(2)-C(1)-C(4)	108.7(2)
O(2)-C(1)-C(2)	108.2(2)
C(4)-C(1)-C(2)	115.2(2)
C(9)-C(4)-C(5)	119.2(2)
C(9)-C(4)-C(1)	122.3(2)
C(5)-C(4)-C(1)	118.4(2)
C(6)-C(5)-C(4)	120.7(3)
C(7)-C(6)-C(5)	119.8(3)
C(6)-C(7)-C(8)	120.2(2)
C(9)-C(8)-C(7)	120.4(3)
C(8)-C(9)-C(4)	119.5(2)
C(14)-N-C(10)	112.4(2)
N-C(10)-C(11)	110.4(2)
C(10)-C(11)-C(12)	111.3(2)
C(11)-C(12)-C(13)	110.3(2)
C(14)-C(13)-C(12)	111.7(3)
N-C(14)-C(13)	111.3(2)

Symmetry transformations used to generate equivalent atoms

off, the solvent was evaporated under vacuum. The residue was put on a silica gel column, eluated with system A, and a raw product with R_f 0.6 (A) was collected. 1.12 g of residue was rechromatographed with system B. Fractions with R_f 0.15 (B) were combined, the solvent was removed, and the product was dried under vacuum. Yield is 0.68 g (29.5%), syrup, R_f 0.6 (A), 0.15 (B), δ_P 23.5 ppm. Found, %: C, 53.31; H, 6.14; N, 4.36; P, 9.74. $C_{14}H_{19}ClNO_5P$. Calcd., %: C, 53.25; H, 6.02; N, 4.44; P, 9.82.

2-Oxo-2,5-dihydroxy-4-phenyl-1,3,2-dioxaphosphorinane (**8**). A solution of 33% H_2O_2 (0.5 g) in 5 ml of dioxane was added to a solution of **3a,b** (1.0 g) in 15 ml of dioxane. Monitoring by ^{31}P NMR indicated that the reaction was completed in 7–10 min. The solvent was evaporated under vacuum. The acid **8a,b**

TABLE VII

Anistropic displacement parameters (A^2 × 10^3) for **12**. The anisotropic displacement factor exponent takes the form: −2 pi^2 [h^2 a*^2 U11 + ··· + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
P	39(1)	29(1)	35(1)	-1(1)	-1(1)	5(1)
O(1)	42(1)	44(1)	44(1)	-3(1)	7(1)	0(1)
O(2)	64(1)	43(1)	36(1)	-1(1)	0(1)	15(1)
O(3)	40(1)	38(1)	36(1)	-4(1)	-3(1)	7(1)
O(4)	56(1)	28(1)	50(1)	0(1)	-5(1)	3(1)
O(5)	57(1)	34(1)	45(1)	0(1)	-9(1)	-6(1)
C(1)	42(1)	32(1)	35(1)	2(1)	-2(1)	2(1)
C(2)	44(1)	37(1)	36(1)	2(1)	-5(1)	-1(1)
C(3)	37(1)	45(1)	49(1)	2(1)	-4(1)	1(1)
C(4)	39(1)	36(1)	38(1)	-5(1)	-1(1)	-2(1)
C(5)	41(1)	46(2)	47(1)	2(1)	2(1)	-4(1)
C(6)	40(1)	74(2)	47(1)	-4(1)	6(1)	-10(1)
C(7)	38(1)	75(2)	57(1)	-26(1)	2(1)	1(1)
C(8)	53(1)	49(2)	67(2)	-18(1)	-12(1)	14(1)
C(9)	51(1)	43(2)	47(1)	-4(1)	-4(1)	7(1)
N	40(1)	34(1)	40(1)	-1(1)	-2(1)	6(1)
C(10)	47(1)	48(2)	54(1)	7(1)	6(1)	3(1)
C(11)	49(1)	64(2)	64(2)	1(2)	13(1)	14(2)
C(12)	45(1)	51(2)	70(2)	-3(1)	-9(1)	13(1)
C(13)	60(2)	50(2)	55(1)	12(1)	-2(1)	15(1)
C(14)	60(1)	55(2)	43(1)	6(1)	8(1)	18(1)

was dried over P_2O_5 under vacuum. Yield is 1.1 g (94%), syrup, R_f 0 (A, B), δ_P −5.3 and −6.4 ppm. Found, %: C, 46.88; H, 4.85; P, 13.38. $C_9H_{11}O_5P$. Calcd., %: 46.96; H, 4.78; P, 13.48.

2-Oxo-2,5-dihydroxy-4-ethyl-1,3,2-dioxaphosphorinane (**9**). Analogously to the synthesis of **8**, cyclic acid **9a,b** was prepared from 0.5 g of **4a,b** and 0.45 g of 28% H_2O_2. Yield is 0.59 g (96.7%), syrup, R_f 0 (A, B), δ_P −6.45 and −5.02 ppm. Found, %: C, 32.89; H, 6.12; P, 16.96; $C_5H_{11}O_5P$. Calcd., %: C, 32.97; H, 6.04; P, 17.03.

Tret.butylammonium salt of 2-oxo-2,5-dihydroxy-4-ethyl-1,3,2-dioxaphosphorinane (**10**). A solution of *t*-$BuNH_2$ (0.1 g) in 1 ml of EtOH was added to 0.25 g of acid **9** dissolved in the mixture of dioxane (5 ml) and EtOH (2 ml). The salt **10** was being crystallized from the solution over a period of 2 days over P_2O_5 under partial solvent evaporation. The crystals were filtered, washed with hexane, dried in the vacuum. Yield is 0.28 g (80.1%), m.p. 154–155°C, R_f 0 (A, B), δ_P −1.68 ppm. Found, %: C, 51.52; H, 7.31; N, 4.67; P, 10.15. $C_{18}H_{22}NO_5P$. Calcd., %: C, 51.48; H, 7.26; N, 4.62; P, 10.23.

Tret.butylammonium salt of 2-oxo-2,5-dihydroxy-4-phenyl-1,3,2-dioxaphosphorinane (**11a,b**). A solution of *t*-$BuNH_2$ (0.17 g) in 3 ml of dioxane was added under stirring to 0.5 g of **8** dissolved in 5 ml of dioxane. The precipitate was filtered, washed with dioxane, ether, and dried at vacuum. Yield is 0.25 g (83.5%), m.p. 214°C, R_f 0 (A, B), δ_P −2.15 and −2.95 ppm. Found, %: C, 51.52; H, 7.31; N, 4.67; P, 10.15. $C_{13}H_{22}NO_5P$. Calcd., %: C, 51.48; H, 7.26; N, 4.62; P, 10.23.

Piperidinium salt of 2-oxo-2,5-dihydroxy-4-phenyl-1,3,2-dioxaphosphorinane (**12a,b**). Analogously to **11**, from 0.5 g of **8** and 0.18 g of piperidine was prepared 0.6 g of syrupous product **12**, which crystallized on keeping for 3 days. The crystals were washed with dioxane, ether, and dried under vacuum. Yield is 0.56 g (85.3%), m.p. 146–148°C, R_f 0 (A, B), δ_P −2.0 and −3.0 ppm. Found, %: C, 53.39; H, 6.17; N, 4.54; P, 9.75. $C_{14}H_{22}NO_5P$. Calcd., %: C, 53.33; H, 5.98; N, 4.44; P, 9.84.

SUPPLEMENTARY MATERIAL AVAILABLE

The atomic coordinates, bond distances and angles for compound **12** are given in Tables V, VI and VII. (4 pages) Ordering information for thermal parameters (4 pages), listing of observed and calculated structure factors is given on any current masthead page.

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