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ANALOGUES OF BRANCHED-CHAIN TETRAFURANOSIDES HAVING PHOSPHORUS IN THE ANOMERIC POSITION*

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Abstract - Treatment of [(2R)-2,4-dibenzyloxy-3-oxo-butyl] dimethyl phosphite (2) with water afforded a 2:1 mixture of (2R, 3R, 4R)-(3a) and (2S, 3R, 4R)-4-O-benzyl-3-(benzyloxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (3b) and 1,3-di-O-benzyl-2-C-(dimethoxyphosphoryl)-D-erythritol (4) together with a trace of 1,3-di-O-benzyl-2-C-(dimethoxyphosphoryl)-D-threitol (6). Addition of dimethyl (trimethylsilyl) phosphite to 1,3-di-O-benzyl-4-O-(tert-butyldimethylsilyl)-D-glycero-tetrulose (7) gave a 1:1 mixture of the phosphonates 5 and 6. Triethylamine-catalysed cyclisations of 5 as well as of 6 produced 2:1 mixtures of 3a and 3b and their C-3 epimers 4a and 4b, respectively. Isopropylidenation studies on the debenzylated 3 and 4 allowed us to assign the configurations at C-3 to be R in 3a and 3b, and S in 4a and 4b. Stereochemistry of the 1,2-oxaphospholane ring closure is discussed.

Several biologically important C-alkyl sugars were found in plants and microorganisms.[1] Current efforts in the chemistry of these compounds[2] involve the synthesis of components of various antibiotics. On the other hand, sugars containing the C-P bond have been extensively studied in the last decade.[3] Some of them were designed as isosteres of natural phosphates[4,5] and they display interesting biological activity.[4] Analogues of furanoses[6], pyranoses[7] and septanoses[8] with phosphorus as the ring heteroatom have been also synthesized and their chemistry has been reviewed.[9]

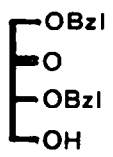
Recently, we have shown that γ-ketoalkyl phosphites can be easily transformed into diastereomeric 1,2-oxaphospholan-3-ols and the corresponding α,β-dihydroxyalkylphosphonates.[10,11] Furthermore, triethylamine-catalysed cyclisation of these phosphonates afforded 1,2-oxaphospholan-3-ols.[10] These results have prompted us to synthesize analogues of C-2 branched-chain furanosides with P in the anomeric position. For the synthesis of the appropriate phosphite, four-carbon sugar γ-hydroxyketones were selected as starting materials.[12] In this paper we wish to present the full account[13] for the synthesis and stereochemistry of the analogues derived from the suitably protected D-glycero-tetrulose.

*Stereochemistry of 1,2-oxaphospholanes, part VII.

RESULTS

Syntheses

The intramolecular Abramov reaction of γ-ketoalkyl phosphites with water[10,11] and/or an intramolecular transesterification of δ-hydroxyalkylphosphonates[10] are the two synthetic ways to the protected 3-(hydroxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diols 3 and 4 employed in these studies. In our first approach 1,3-di-O-benzyl-D-glycero-tetrulose[14] (1) was treated with dimethyl phosphorochloridite under standard conditions[15] to give the phosphite 2. It was found by ^{1}H- and ^{31}P-NMR that the crude 2 was sufficiently pure for the subsequent transformation. The addition of the equivalent amount of water to 2 either at



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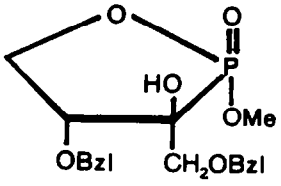
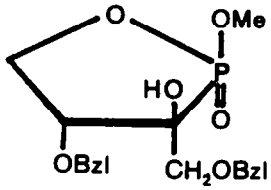


3a



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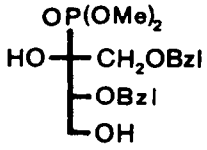

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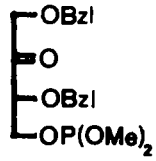

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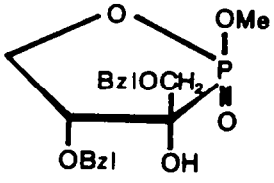
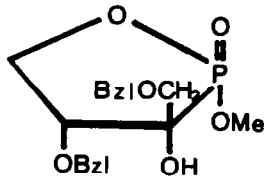
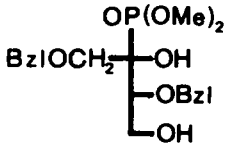


4a



4b



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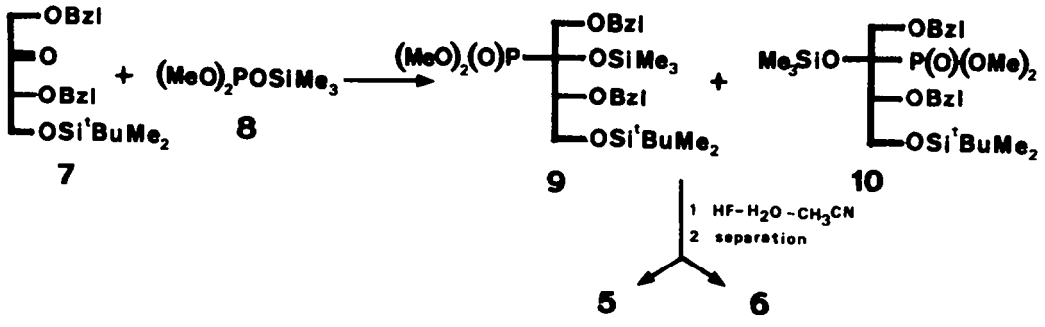
room temperature or at 5°, afforded a mixture of (2R, 3R, 4R)-(3a) and (2S, 3R, 4R)-4-O-benzyl-3-(benzyloxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (3b), and 1,3-di-O-benzyl-2-C-(dimethoxyphosphoryl)-D-erythritol (5) and 1,3-di-O-benzyl-2-C-(dimethoxyphosphoryl)-D-threitol (6) which were contaminated by two unidentified α-hydroxyphosphonates. The ^{31}P-NMR spectrum of the crude product revealed further features of this reaction: (i) 3a and 3b were formed in a 2:1 ratio, (ii) the C-3 epimeric 1,2-oxaphospholanes 4a and 4b were absent, (iii) the ratio of the cyclic to acyclic products was 1:4, and (iv) large excess (>95:5) of 5 over 6 was obtained. A careful column chromatography on silica gel allowed us to separate the 2:1 mixture of 3a and 3b as an oil in 23% yield and pure 5 as a colorless syrup in 22% yield.

In the alternative approach to 1,2-oxaphospholan-3-ols, 5 was treated with 10 mol% triethylamine in benzene at 20° and the progress of the reaction was monitored by ^{31}P-NMR. After 24 h the cyclisation of 5 was completed affording, after column chromatography, the 2:1 mixture of 3a and 3b in 73% yield. The 2:1 ratio of 3a and 3b remained unchanged throughout the observation time.

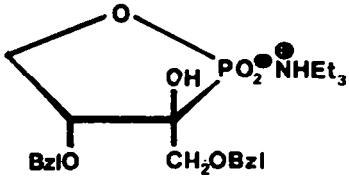
Because 4a and 4b were not obtained in the cyclisation of 2, and 6 was a trace contaminant in this reaction, we have designed a new approach to the δ-hydroxyphosphonates 5 and 6. The addition of dimethyl (trimethylsilyl) phosphite[16] (8) to 1,3-di-O-benzyl-4-O-(tert-butyldimethylsilyl)-D-glycero-tetrulose[14] (7) (Scheme 1) gave a 1:1 mixture of 1,3-di-O-benzyl-4-O-(tert-butyldimethylsilyl)-2-O-(trimethylsilyl)-2-C-(dimethoxyphosphoryl)-D-erythritol (9) and its C-2 epimer 10. The hydrolysis of both silyl protecting groups was readily accomplished using aqueous hydrogen fluoride in acetonitrile[17] to give



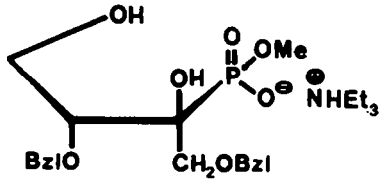
Scheme 1

5 and 6 contaminated with substantial amounts of 3a, 3b, 4a, and 4b. The deprotected α-hydroxyphosphonates were separated by column chromatography on silica gel to give pure 5 and 6 as oils in 24% and 19% yield, respectively. Triethylamine-catalysed intramolecular transesterification of 6 proceeded slower than that of 5. After 48 h still ca. 7% of 6 was present in the reaction mixture, from which a 2:1 mixture of 4a and 4b was isolated by column chromatography in 78% yield. Similarly as for the cyclisation of 5, the 2:1 ratio of 4a and 4b remained unchanged throughout the cyclisation of 6.

The intramolecular transesterification of the phosphonate 5 was significantly accelarated by the presence of the equimolar amount of triethylamine. In less than 1 h the 2:1 mixture of 3a and 3b was produced, but simultaneously ca. 10% of two other P-containing compounds were formed. Although these compounds were not isolated, the structure 11 and 12 were assigned to them on the basis of



11



12

^{31}P-NMR shifts (32.4 and 17.5 ppm, respectively)[18] and a t.l.c. analysis. After immediate purification on silica gel, 3a and 3b were isolated in 82% yield.

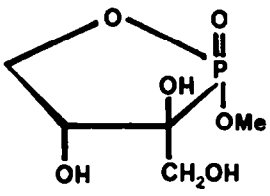
Under basic conditions α-hydroxyphosphonates are capable of the retro--Abramov reaction to give the starting phosphites and carbonyl compounds. This reaction leads to epimerization at C-1 in the chiral α-hydroxyphosphonates. It was expected that selective cyclisation of 5 into a mixture of 3a and 3b as well as of 6 into 4a and 4b in the triethylamine-catalysed processes could only be attained when no competition from the retro-Abramov reaction would have occured. This was true in the case of the triethylamine-catalysed cyclisation of 5 or 6, because when carried out at room temperature, less than 2% of the C-3 epimeric 1,2-oxaphospholanes were detected in the crude products by ^{31}P-NMR. However, when the 1:1 mixture of 5 and 6 was treated at 40° with 10 mol% triethylamine, after 1 h the 2:1 ratio of 5 to 6 was established and remained constant till the end of the reaction. Simultaneously, in slower processes as from 5 so from 6 diastereomeric pairs 3a and 3b, as well as 4a and 4b were produced in the 2:1 ratios. As it could be expected the ratios of 3a to 3b, and 4a to 4b were again

found to be of 2:1. At 40° the equilibration of 5 as well as of 6 in the retro-Abramov reaction appeared to be dominant process.

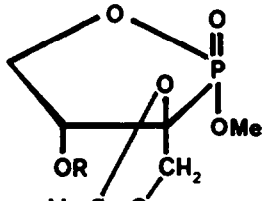
Numerous attempts at separation of 3a, 3b, 4a, and 4b, from the respective mixtures by column chromatography on silica gel failed.

Stereochemistry at C-3

The assignment of the absolute configuration at C-3 in 3a, 3b, 4a, and 4b was particularly important for the discussion of stereochemistry of the intramolecular Abramov reaction of the phosphite 2. We anticipated that isopropylidenation of the debenzylated epimeric triols 13a/13b and 14a/14b could be useful in configurational studies.[19] Reaction of polyols with an excess of 2,2-dimethoxypropane in the presence of catalytic toluene-p-sulfonic acid recently reported by Lipták, et al.[20] is one of the cleanest and fastest methods for isopropylidenation. Thus, the 2:1 mixture of 3a and 3b was hydrogenolyzed and the crude 2:1 mixture of the triols 13a and 13b was immediately treated with 2,2-dimethoxypropane-toluene-p-sulfonic acid. From the crude product (2R, 3R, 4R)-3^1,4-O-isopropylidene-(17a), and (2R, 3R, 4R)-(15a) and (2S, 3R, 4R)-3,3^1-O-isopropylidene-3-(hydroxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (15b) were isolated by column chromatography in 8.1, 22.6, and 10.2% yield, respectively.

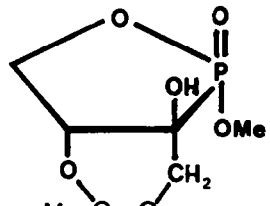


13a

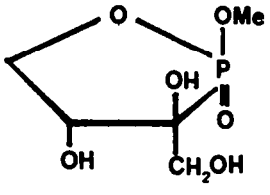


15a R=H

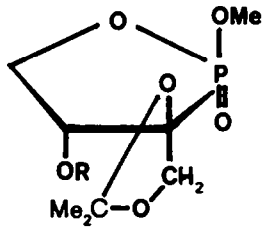
16a R=COC$_6$H$_4$NO$_2$-p



17a

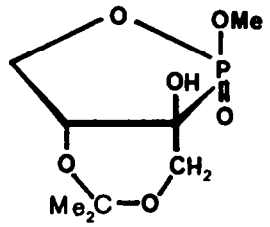


13b



15b R=H

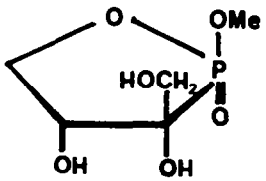
16b R=COC$_6$H$_4$NO$_2$-p



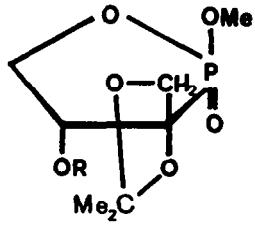
17b

The presence of the 1,3-dioxane ring in 17a was evident from the ^{13}C-NMR chemical shifts at 99.15 ($\underline{C}Me_2$), and 19.97 and 28.17 ppm ($C\underline{Me}_2$).[21] Detailed configurational and conformational analysis of 17a based on the ^{1}H-NMR spectrum allowed us to assign unequivocally the R configuration at C-3.[13] Undoubtedly, the C-3 atoms in 15a as well as in 15b have the same configuration. The ^{13}C-NMR resonances of the isopropylidene carbons in 15a (25.48, 26.29, and 112.43 ppm) and in 15b (25.38, 26.10, and 111.91 ppm) showed the presence of two non-fused 5-membered rings in these acetals.[21] Furthermore, the three-bond coupling of $\underline{C}Me_2$ to P of 4.4 Hz in both acetals suggested that the tertiary hydroxyl group underwent the reaction. After p-nitrobenzoylation of 15a and 15b substantial deshielding of H-C-4 down to 5.4 ppm was observed in the ^{1}H-NMR spectra of 16a and 16b. These data proved the formation of 3,3^1-O-isopropylidene derivatives in acetalation of the triols 13a and 13b.

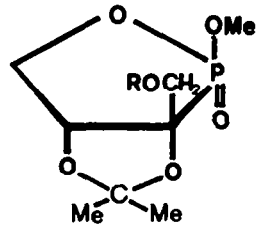
Further evidence for the R configuration at C-3 in 3a and 3b came from the isopropylidenation studies of C-3 epimeric 1,2-oxaphospholanes 4a and 4b. Treatment of a crude mixture of 14a and 14b with 2,2-dimethoxypropane afforded a mixture of four O-isopropylidene derivatives which were identified as (2S, 3S, 4R)--(20a) and (2R, 3S, 4R)-3,4-O-isopropylidene-3-(hydroxymethyl)-2-methoxy-2-oxo--1,2-oxaphospholane-3,4-diol (20b), and (2S, 3S, 4R)-(18a) and (2R, 3S, 4R)--3,3^1-O-isopropylidene-3-(hydroxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4--diol (18b). Column chromatography of these acetals gave crystalline 20a in 14% yield and an inseparable mixture of 20b, 18a and 18b in the 32% total yield.



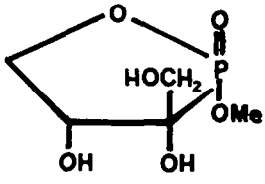
14a



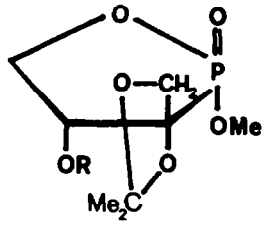
18a R = H
19a R = $COC_6H_4NO_2$-p



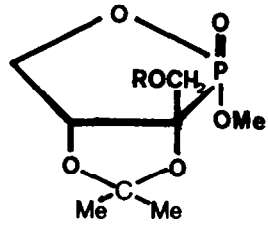
20a R = H
21a R = $COC_6H_4NO_2$-p



14b



18b R = H
19b R = $COC_6H_4NO_2$-p



20b R = H
22b R = Si^tBuMe_2

Deshielding of the $\underline{C}Me_2$ signal down to 114.52 ppm with respect to those for 15a and 15b together with the appearence of the broad ^{13}C-NMR signal at 26.94 ppm for $\underline{Me}_2C$ in 20a confirmed the presence of the two fused 5-membered rings.[21] The p-nitrobenzoate of 20a displayed in the ^{1}H-NMR spectrum a complex pattern at 4.0 - 4.8 ppm and showed no resonances at the region 5.4 - 5.6 ppm as it was found for H-C-4 in 16a and 16b, as well as in 19a and 19b. These data clearly showed that C-3 in 20a as well as in 20b, 18a and 18b have the S absolute configuration.

When the reaction of the mixture of 18a, 18b and 20b with tert-butyldimethylsilyl chloride[22] had been monitored by ^{31}P-NMR the loss of the signal at 39.98 ppm characteristic of 20b and the appeareance of a new signal at 38.69 ppm of the silyl ether 22b was observed. A mixture of 18a and 18b was separated from 22b by column chromatography and it was esterified to give 19a and 19b. From the ^{1}H-NMR shifts of H-C-4 in 19a (5.59 ppm) and in 19b (5.58 ppm) it was concluded that the secondary hydroxy groups in 18a and 18b reacted. Thus, compounds 18a and 18b had the 3,3^1-O-isopropylidene moiety.

Stereochemistry at P

Configurations at P in the substituted 1,2-oxaphospholan-3-ols described in this paper could not be unambiguously established from the ^{1}H-and ^{13}C-NMR spectra. In earlier studies on model 2-methoxy-2-oxo-1,2-oxaphospholan-3-ols we have found that the ^{31}P-NMR signals of the isomers with the P=O and HO-C-3 groups of cis configuration were shifted downfield in comparisons to these of trans isomers.[23]

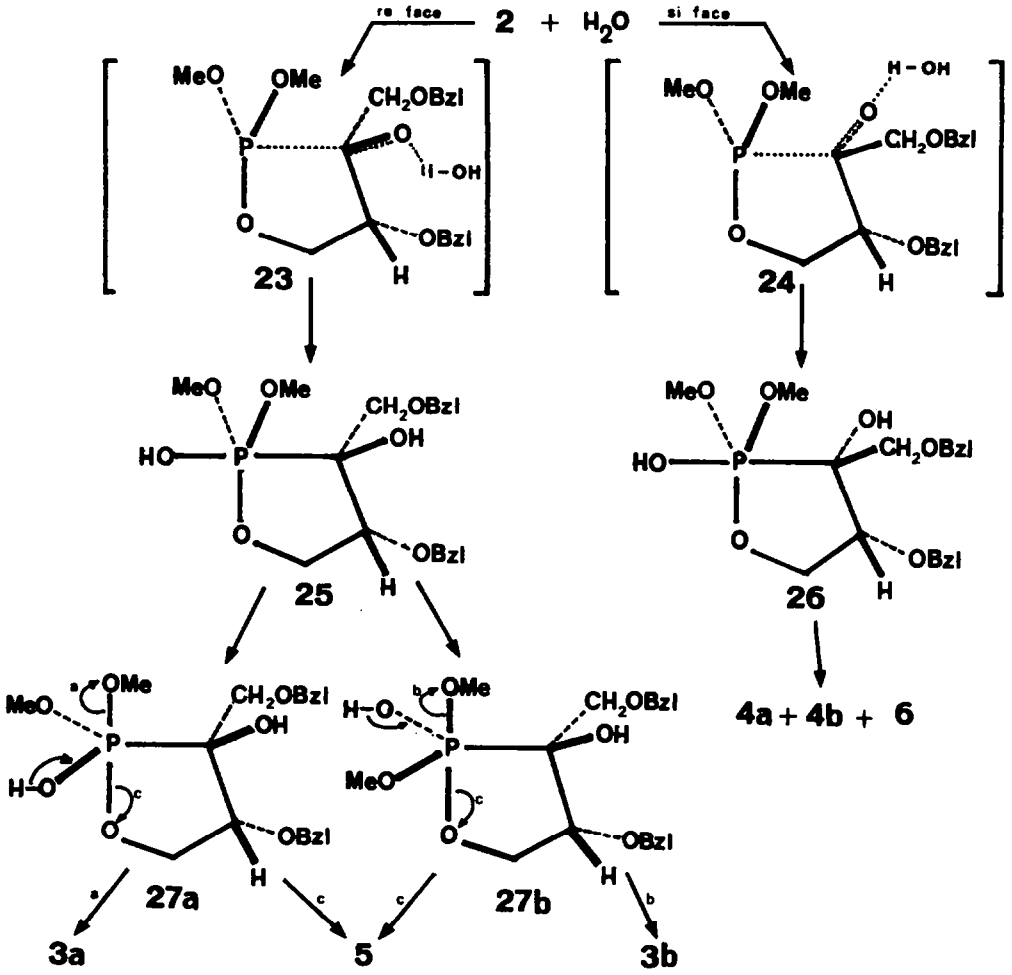
According to this relation the R_P and S_P absolute configurations were assigned to 3a (δ^{31}P 41.73 ppm) and 3b (δ^{31}P 39.30 ppm), respectively. From a 2:1 mixture of 3a and 3b a mixture of the triols 13a and 13b of the same ratio was obtained after hydrogenolysis, and for this reason 13a has the R_P and 13b has the S_P absolute configurations. In the ^{31}P-NMR spectra of the crude products after isopropylidenation of the mixture of triols, the 2:1 ratios of 15a and 15b as well as of 17a and 17b were retained and this allows us to assign the R_P configurations for 15a and 17a and the S_P configurations for 15b and 17b. Furthermore, as for the triols 13a (δ^{31}P 44.41 ppm) and 13b (δ^{31}P 42.95 ppm) so for their isopropylidene derivatives: 15a (δ^{31}P 38.56 ppm) and 15b (δ^{31}P 36.62 ppm), and 17a (δ^{31}P 43.38 ppm) and 17b (δ^{31}P 40.28 ppm) the ^{31}P-NMR signals of the a isomers were shifted downfield in agreement with the relationship of the ^{31}P-NMR chemical shifts and the P configuration in 2-methoxy-2-oxo-1,2-oxaphospholan-3--ols.[23]

In a similar manner the S_P and R_P configurations were assigned to 4a (δ^{31}P 39.17 ppm), 14a (δ^{31}P 41.70 ppm) and 18a (δ^{31}P 35.35 ppm), and 4b (δ^{31}P 37.65 ppm), 14b (δ^{31}P 41.09 ppm) and 18b (δ^{31}P 34.75 ppm), respectively. However, for the pair of epimers 20a (δ^{31}P 39.08 ppm) and 20b (δ^{31}P 39.98 ppm) the opposite relationship in the ^{31}P-NMR shifts was noticed. We suggest that the cis fusion of the 1,2-oxaphospholane and 1,3-dioxolane rings brought some extra strain to the ring system and thus influenced chemical environments around the phosphorus nuclei in 20a and 20b. We now propose to extend the correlation of the ^{31}P-NMR chemical shifts and the phosphorus configuration in 2-methoxy-2--oxo-1,2-oxaphospholan-2-ols[23] also on their strain-free bicyclic acetals.

DISCUSSION

Similarly as for γ-(N,N-dimethylhydrazono)alkyl phosphites[18], the intramolecular Abramov reaction of γ-ketoalkylphosphites involves the water-promoted nucleophilic addition of phosphorus to the C=O group. Inspection of the Dreiding model of the phosphite 2 revealed that the nucleophile can easily approach the plane of the carbonyl group on the trajectory of *ca.* 109°.[24] The attack on the *re*-face of the carbonyl group leads to the transition state 23 (Scheme 2), while 24 would result from the *si*-face attack. The 1,2-oxaphospholanes 3a and 3b of the R configuration at C-3 as well as the phosphonate 5 of the R configuration at C-2 could be formed as the major products in the reaction of the phosphite 2 with water when phosphorus approaches the *re*-face of the carbonyl group preferentially. We suggest that repulsions of the lone pairs of O⋯C-3 and O—C-4 disfavour the transition state 24 to such an extent that the *re*-face attack preponderates, although in 23 steric interactions of the two largest synperiplanar substituents around the C-3—C-4 bond (OBzl and CH_2OBzl) occur. At this stage differentiation of the configurations at C-3 in the 1,2-oxaphospholane ring as well as at C-2 in the acyclic phosphonates takes place. On the other hand, no diastereoselectivity was observed in the intermolecular addition of dimethyl (trimethylsilyl) phosphite to 7, although chemical environments of the carbonyl groups in 1 and 7 are almost identical. It is likely that a high temperature of this reaction accounts for the lack of asymmetric induction.[25]

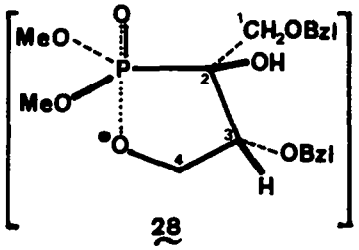
The 1,2-oxaphospholane ring closure *via* the transition state 23 affords the intermediate 25[26] with the P-C bond in the energetically unfavourable position.[27] Ligand reorganization by pseudorotation, taking as pivots either one or the other methoxy groups in 25, gives the trigonal bipyramides 27a and 27b (Scheme 2). After the departure of the apical methoxy group from 27a (pathway *a*) 3a is formed, while from 27b (pathway *b*) 3b is produced. In these processes the



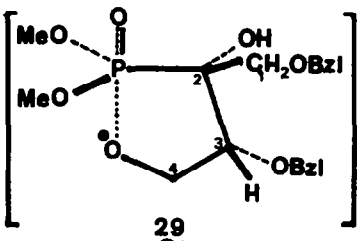
Scheme 2

configuration at P is differentiated. Furthermore, in both intermediates 27a and 27b the ring-opening occurs by pathway c to form the acyclic phosphonate 5. It seems that the stereoelectronic effects[28] of basal oxygens facilitate the departures of both apical ligands from 27a as well as from 27b to the same extent. For this reason a substantial excess of the acyclic product 5 over the isomeric 1,2-oxaphospholanes 3a/3b observed under neutral conditions of the reaction of 2 with water appears to be a result of the steric interactions within the 1,2-oxaphospholane ring, mainly around the C-3—C-4 bond. The formation of a 2:1 mixture of 3a and 3b from the intermediates 27a and 27b, respectively, indicates that the decomposition of 27a is faster than that of 27b, probably because the hydrogen bond in 3a is being formed.

In the presence of catalytic amounts of base or even acid the intramolecular cyclisation of the γ-hydroxyphosphonates 5 and 6 to 1,2-oxaphospholanes readily occurs. A displacement of the methoxy groups from phosphorus in 5 proceedes via the transition state 28 to give the intermediates 27a and 27b or their protonated forms. The slower cyclisation of 6 as compared with that of 5 can be rationalized in terms of the repulsive interactions of the oxygen HO—C-2 and Bzl-O—C-3 lone pairs which takes place in the transition state 29 and we suggest that these interactions are stronger than the steric ones of the BzlO—C-3 and $BzlOCH_2$—C-2 groups in 28. A driving force for the triethylamine-catalysed cyclisation of 5 as well as of 6 is an irreversible formation of



28



29

1,2-oxaphospholane.[9] A differentiation of configuration at phosphorus is again governed by the faster decomposition of the trigonal bipyramide intermediates leading to the isomers with the P=O·····H-O—C-3 bond.

EXPERIMENTAL

General. Carbon NMR spectra were recorded at room temperature on Bruker HX-72 spectrometer at 22.63 MHz operating in the pulsed Fourier transform mode for the computer resolution of 0.7 Hz/point. ^{31}P-NMR spectra were taken on Bruker HX-72 (36.43 MHz) or on Jeol JNM FX 60 (24.3 MHz) spectrometers. The purity of products was monitored by t.l.c. on Silica Gel 60 F254 (Merck) with chloroform/methanol mixtures: A (20:1), and B (50:1). Other instrumentation and general procedures were the same as described earlier.[14]

[(2R)-2,4-Dibenzyloxy-3-oxo-butyl] dimethyl phosphite (2). To the cooled (5°C) solution of 1,3-di-O-benzyl-D-glycero-tetrulose (1) (3.53 g, 11.75 mmol) and triethylamine (1,8 mL, 12.9 mmol) in benzene (15 mL) a solution of dimethyl phosphorochloridite (1.70 g, 12.9 mmol) in benzene (5 mL) was added dropwise. The mixture was stirred for 2 h, the solid was filtered off, and washed with benzene (3x5 mL). The filtrate and washings were combined and after evaporation of benzene, all volatile impurities were removed in vacuo to leave 2 (4.47 g, 97%) as a slightly yellowish oil. ^{1}H-NMR (CCl_4, 60 MHz): δ 3.39 (d, 6 H, J 11.5, CH_3OP), 3.8 - 4.2 (m, 3 H, H-1a, 1b, 2), 4.29 (s, 2 H, H-4a, 4b), 4.47 and 4.53 (2 s, 4 H, O-CH_2-C_6H_5), 7.3 (m, 10 H, 2 Ph); ^{31}P-NMR (CCl_4): δ 139.5.

Reaction of 2 with water. To the well stirred 2 (4.47 g, 11.4 mmol) water (0.225 mL, 12.5 mmol) was added drop by drop. The mixture became homogeneous immediately. Purification was performed on the silica gel columns with chloroform-methanol and ethyl acetate-hexanes solvent systems to give:

a 2:1 mixture of 3a and 3b (0,97 g, 23%) as a colorless oil, R_F 0.60 (ethyl acetate, R_F 0.42 (solvent A); ν_{max}^{neat} 3300 (OH), 1250 (P=O), and 1010 cm^{-1} (C-O-P). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 3.77 (d, J 10.6, CH_3OP in 3a), 3.79 (d, J 10.6, CH_3OP in 3b), and 3.5 - 4.3 (m, H-3'a, 3'b, 4, 5a, 5b, OH) - total of 9 H, 4.4 - 4.7 (m, 4 H, O-CH_2-Ph), 7.1 - 7.6 (m, 10 H, 2 Ph). ^{13}C-NMR (C_6D_6, 22.63 MHz): 3a δ 54.49 (d, J 7.4, H_3COP), 69.41 (d, J 7.4, C-3' or C-5), 71.05 (d, J 8.1, C-5 or C-3'), 72.86 and 74.61 (2 s, OCH_2Ph), 74.68 (d, J 135.3, C-3), 83.32 (d, J 14.7, C-4); 3b δ 54.56 (d, J 7.4, H_3COP), 68.89 (d, J 5.9, C-3' or C-5), 72.86 and 74.61 (2 s, OCH_2Ph), 74.84 (d, J 136.8, C-3), 82.35 (d, J 19,1, C-4).[29] ^{31}P-NMR ($CDCl_3$, 36.43 MHz): 3a δ 41,73; 3b δ 39.30. Anal. Calc. for $C_{19}H_{23}O_6P$: C, 60.31; H, 6.13; P, 8.19. Found: C, 59.40; H, 6.06; P. 8.15%.

1,3-di-O-benzyl-2-C-(dimethoxyphosphoryl)-D-erythritol (5) (1.05 g, 22%) as a colorless oil, $[\alpha]_D^{20}$ - 13.4° (c 2.4, chloroform), R_F 0.35 (ethyl acetate), R_F 0.22 (solvent A); ν_{max}^{film} 3380 (OH), 1210 (P=O), and 1030 cm^{-1} (C-O-P). ^{1}H-NMR ($CDCl_3$, 60 MHz): δ 3.60 and 3.67 (2 d, J 10.5, CH_3OPOCH_3) and 3.6 - 4.75 (m, H-1a, 1b, 3, 4a, 4b, OH, OCH_2Ph) - total of 17 H, 7.3 (m, 10 H, 2 Ph). ^{13}C-NMR (C_6D_6, 22.63 MHz): δ 53.32 and 53.64 (2 d, J 7.3, $H_3COPOCH_3$), 61.48 (d, J 3.7, C-4), 71.55 (d, J 7.3, C-1), 73.66 and 73.92 (2 s, OCH_2Ph), 78.78 (d, J 158.7, C-2), 80,12 (d, J 3.7, C-3). ^{31}P-NMR ($CDCl_3$, 36.43 MHz): δ 26.1. Anal. Calc. for $C_{20}H_{27}O_7P$: C, 58.53; H, 6.63; P, 7.55. Found: C. 58.25; H, 6.87; P, 7.39%.

Addition of dimethyl (trimethylsilyl) phosphite to 7. A homogeneous mixture of 7 (3.29 g, 7.9 mmol) and 8 (2.3 ml, 11.9 mmol) was maintained at 95° for 12 h under a positive pressure of argon. To the cooled very thick yellowish oil 5% solution of hydrogen fluoride (40% solution in water) in acetonitrile (16 mL) was slowly added. After 1 h barium carbonate (4 g) and magnesium sulfate (2 g, anhydrous) were added and the suspension was stirred for 1 h at room temperature. Filtration of solids and evaporation of solvent left a colorless syrup (3.4 g) which was repeatedly chromatographed on silica gel to give the following fractions:

Fraction A: a mixture of 3a, 3b, 4a and 4b (0.39 g, 13%). ^{31}P-NMR ($CDCl_3$, 36.43 MHz): δ 3a 42.65; 3b 39.91; 4a 39.54; 4b 38.02.

Fraction B: compound 5 (0,795 g, 24.4%), $[\alpha]_D^{20}$ - 15.3° (c 1.04, chloroform).

Fraction C: a 1:1 mixture of 5 and 6 (0.41 g, 12.6%). ^{31}P-NMR ($CDCl_3$, 36.43 MHz): δ 5 26.1; 6 26.6.

Fraction D: 1,3-di-O-benzyl-2-C-(dimethoxyphosphoryl)-D-threitol (6) (0.63 g, 19.3%), $[\alpha]_D^{19}$ -10.7° (c 1.37, chloroform); ν_{max}^{film} 3330 (OH), and 1210 cm^{-1} (P=O). ^{1}H-NMR ($CDCl_3$, 60 MHz): δ 3.63 and 3.67 (2d, J 10.5, $H_3COPOCH_3$) and 3.4 - 4.3 (m, H-1a, 1b, 3, 4a, 4b, OH) - total of 13 H, 4.49 (s, 2 H, OCH_2Ph), 4.57 and 4.72 (AB, 2 H, J 11.5, OCH_2Ph), 7.1 - 7.5 (m, 10 H, 2 Ph). ^{13}C-NMR (C_6D_6, 22.63 MHz): δ 53.36 and 53.77 (2 d, J 7.3, $H_3COPOCH_3$), 62.05 (d, J 4.9, C-4), 70.94 (d, J 3.7, C-1), 73.42 and 73.83 (2 s, OCH_2Ph), 78.74 (d, J 159.9, C-2), 80.12 (d, J 6.1, C-3). ^{31}P-NMR ($CDCl_3$, 36.43 MHz): δ 26.6. Anal. Calc. for $C_{20}H_{27}O_7P$: C, 58.53; H, 6.63; P, 7.55. Found: C, 58.31; H, 6.70; P, 7.63%.

General procedure for cyclisation of 5 and 6. To 1 M solution of 5 or 6 in benzene, triethylamine (10 mol%) was injected and the progress of the reaction was monitored by ^{31}P-NMR. When cyclisation was completed the solvent was evaporated, the yellowish residue was dissolved in chloroform and chromatographed on silica gel columns.

From 5 (0.95 g, 2.32 mmol) the 2:1 mixture of 3a and 3b was obtained as a colorless syrup (0.64 g, 73%). ^{31}P-NMR ($CDCl_3$, 24.3 MHz): δ 3a 41.73; 3b 39.30.

From 6 (0.63 g, 1.53 mmol) the 2:1 mixture of 4a and 4b was obtained as a colorless syrup (0.455 g, 78.5%), R_f 0.56 (ethyl acetate); ν_{max}^{film} 3330 (OH), 1250 (P=O), and 1010 cm^{-1} (C-O-P). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 2.6 - 3.4 (bs. 2 H, 2 OH), 3.75 (d, J 11.0, CH_3OP in 4a), 3.84 (d, J 11.0, CH_3OP in 4b) and 3.6 - 4.3 (m, H-3a, 3b, 4, 5a, 5b) total of 11 H, 4.0 (m, 4 H, OCH_2Ph), 7.3 (m, 10 H, 2 Ph). ^{13}C-NMR (C_6D_6, 22.63 MHz): 4a δ 54.35 (d, J 6.6, CH_3OP), 67.88 (d, J 4.4, C-3^1 or C-5), 72.60 (d, J 4.4, C-5 or C-3^1), 73.05 (d, J 138.2, C-3), 73.31 and 74.38 (2 s, OCH_2Ph), 77.94 (d, J 22.8, C-4); 4b δ 55.01 (d, J 4.4, CH_3OP), 68.34 (d, J 4.4, C-3^1 or C-5), 72.79 (d, J 4.4, C-5 or C-3^1), 73.55 (d, J 140.5, C-3), 73.60 and 74.58 (2 s, OCH_2Ph), 78.40 (d, J 21.3, C-4). ^{31}P-NMR ($CDCl_3$, 24.3 MHz): δ 4a 39.17; 4b 37.65.

Isopropylidenation of the deprotected 13a and 13b. To the suspension of 10% Pd-C (0.22 g) in methanol (10 mL) the 2:1 mixture of 3a and 3b (0.605 g, 1.6 mmol) was added and the suspension was stirred until the required volume of hydrogen (72 mL) was absorbed. The catalyst was filtered off and washed thoroughly with methanol (5 x 5 mL). The filtrate and washings were evaporated to give a crude 2:1 mixture of 13a and 13b (0.317 g, 100%) as a slightly yellowish syrup. ^{31}P-NMR (CH_3OH, 24.3 MHz): δ 13a 44.41; 13b 42.95. The mixture of the triols was shaken at room temperature together with 2,2-dimethoxypropane (1.0 mL, 8.13 mmol) and toluene-p-sulfonic acid monohydrate (5 mg) for 30 min and after that time the ^{31}P-NMR spectrum was taken. ^{31}P-NMR (24.3 MHz): δ 15a 37.97; 15b 35.86; 17a 42.77; 17b 40.28. Solid sodium hydrogen carbonate (100 mg) was added to the reaction mixture and after 1 h, it was filtered off. After evaporation of solvents the crude product was separated by column chromatography on silica gel to give:

(i) (2R, 3R, 4R)-3^1,4-O-isopropylidene-3-(hydroxymethyl)-2-methoxy-2-oxo--1,2-oxaphospholane-3,4-diol (17a) (31 mg, 8.1%), m.p. 99-100° (from chloroform-hexane), $[\alpha]_D^{18}$ +4.2° (c 1.1, chloroform), R_f 0.32 (solvent A); ν_{max}^{KBr} 3300 (OH), and 1220 cm^{-1} (P=O). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.41 and 1.50 (2 s, 6 H, CH_3CCH_3), 3.91 (d, 3 H, J 11.1, CH_3OP), 4.00 (dd, 1 H, $J_{3^1a,3^1b}$ 13.5, $J_{3^1a,P}$ 23.7, H-3^{1}a), 4.08 (dd, 1 H, $J_{5a,5e}$ 10.3, $J_{5e,P}$ 18.2, H-5e), 4.14 (dd, 1 H, $J_{3^1e,P}$ 12.9, H-3^{1}e), 4.25 (dd, 1 H, $J_{4,5a}$ 3.2, $J_{4,P}$ 24.5, H-4), 4.55 (ddd, 1 H, $J_{5a,P}$ 3.2, H-5a). ^{13}C-NMR (C_6D_6, 22.63 MHz): δ 19.97 and 28.17 (2 s, $\underline{C}H_3\underline{C}CH_3$), 54.28 (d, J 6.6, CH_3OP), 63.58 (d, J 11.0, C-3^1 or C-5), 65.74 (d, J 133.8, C-3), 71.02 (d, J 9.6, C-5 or C-3^1), 76.19 (d, J 15.4, C-4), 99.15 (s, $CH_3\underline{C}CH_3$); ($CDCl_3$): δ 19.40 and 27.72 (2 s, $\underline{C}H_3\underline{C}\underline{C}H_3$), 54.72 (d, J 6.6, CH_3OP), 62.50 (d, J 10.3, C-3^1 or C-5), 64.48 (d, J 133.8, C-3), 70.74 (d, J 9.6, C-5 or C-3^1), 75.08 (d, J 14.7, C-4), 98.84 (s, $CH_3\underline{C}CH_3$). ^{31}P-NMR ($CHCl_3$, 24.3 MHz): δ 43.38. Anal. Calc. for $C_8H_{15}O_6P$: C, 40.34; H, 6.35; P, 13.00. Found: C, 40.05; H, 6.59; P, 12.84%.

(ii) a mixture of (2R, 3R, 4R) - (15a) and (2S, 3R, 4R)-3,3^1-O-isopropylidene-3-(hydroxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3.4-diol (15b) (141 mg, 42%) as an oil which partially solidified on standing. Two recrystallizations from benzene gave 15a (86 mg, 22.6%) as fluffy needles, m.p. 140 - 140.5°, $[\alpha]_D^{20}$ - 6.4° (c 1.43, chloroform), R_f 0.22 (solvent A); ν_{max}^{KBr} 3250 (OH), and 1220 cm^{-1} (P=O). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.45 and 1.49 (2 s, 6 H, CH_3CCH_3), 3.86 (d, 3 H, J 10.8, CH_3OP), 3.9 - 4.6 (m, 5 H, H-3^1 a, 3^{1}b, 4, 5a, 5b). ^{13}C-NMR ($CDCl_3$, 22.62 MHz): δ 25.48 and 26.29 (2 s, $\underline{C}H_3\underline{C}CH_3$), 53.95 (d, J 7.4, H_3COP), 64.84 (d, J 5.9, C-3^1 or C-5), 71.99 (d, J 5.9, C-5 or C-3^1), 73.81 (d, J 27.9, C-4), 79.06 (d, J 152.2, C-3), 112.43 (d, J 4.4, $CH_3\underline{C}CH_3$). ^{31}P-NMR ($CHCl_3$, 24.3 MHz): δ 38.56. Anal. Calc. for $C_8H_{15}O_6P$: C, 40.34; H, 6.35; P, 13.00. Found: C, 40.52; H, 6.27; P, 12.91%.

The residue after recrystallizations deposited impure 15a (17 mg) and the remaining oil was subjected to column chromatography on silica gel to give 15b

(39 mg, 10.2%) as a colorless oil, $[\alpha]_D^{20}$ -22.3° (c 1.14, chloroform), R_f 0.22 (solvent A); ν_{max}^{film} 3350 (OH), and 1250 cm^{-1} (P=O). ^{1}H-NMR ($CDCl_3$, 90 MHz); δ 1.46 (s, 6 H, CH_3CCH_3), 3.88 (d, 3 H, J 10.9, CH_3OP), 3.9 - 4.6 (m, 5 H, H - 3'a, 3'b, 4, 5a, 5b). ^{13}C-NMR ($CDCl_3$, 22.63 MHz); δ 25.38 and 26.10 (2 s, CH_3CCH_3), 54.93 (d, J 7.4, H_3COP), 64.96 (d, J 8.1, C-3' or C-5), 71.37 (d, J 4.4, C-5 or C-3'), 73.41 (d, J 28.8, C-4), 79.55 (d, J 146.3, C-3), 111.91 (d, J 4.4, CH_3CCH_3). ^{31}P-NMR ($CHCl_3$, 24.3 MHz): δ 36.62.

Isopropylidenation of the deprotected 14a and 14b. A 2:1 mixture of 4a and 4b (0.57 g, 1.51 mmol) was hydrogenolysed as described above to give a crude 2:1 mixture of 14a and 14b (0.299 g, 100%) as a yellowish syrup. ^{31}P-NMR (CH_3OH, 24.3 MHz): δ 14a 41.70, 14b 41.09. Isopropylidenation was also carried out as for 13a and 13b. The mixture of crude O-isopropylidene derivatives was subjected to column chromatography on silica gel to give fractions A and B.

Fraction A (115 mg, 32%), colorless oil, R_f 0.30 (solvent A) was composed of (2S, 3S, 4R)-(18a) and (2R, 3S, 4R)-3,3'-O-isopropylidene-3-(hydroxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (18b), and (2R, 3S, 4R)-3,4-O-isopropylidene-3-(hydroxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (20b) in the ratio of 58:24:18, respectively. ^{31}P-NMR ($CHCl_3$, 24.3 MHz): δ 18a 35.35, 18b 34.75, 20b 39.98.

Fraction B was twice recrystallized from benzene to give (2S, 3S, 4R)-3,4-O-isopropylidene-3-(hydroxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (20a) (50 mg, 14.0%) as white plates, m.p. 126 - 127°, $[\alpha]_D^{20}$ -46.7° (c 1.03, chloroform), R_f 0.18 (solvent A); ν_{max}^{KBr} 3400 (OH), and 1260 cm^{-1} (P=O). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.45 and 1.64 (2 s, 6H, CH_3CCH_3), 3.86 (d, 3 H, J 10.7, CH_3OP), 3.9 - 4.8 (m, 5 H, H-3'a, 3'b, 4, 5a, 5b). ^{13}C-NMR ($CDCl_3$, 22.63 MHz): δ 26.94 (s, CH_3CCH_3), 53.68 (d, J 6.6, CH_3OP), 62.52 (d, J 11.0, C-3' or C-5), 66.97 (d, J 6.6, C-5 or C-3'), 81.03 (d, J 13.2, C-4), 114.52 (d, J 6.6, CH_3CCH_3). ^{31}P-NMR ($CHCl_3$, 24.3 MHz): δ 39.08.

(2R, 3R, 4R)-3,3'-O-Isopropylidene-3-(hydroxymethyl)-4-O-(p-nitrobenzoyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (16a). Conventional p-nitrobenzoylation of 15a gave 16a (82%) as a yellowish oil, R_f 0.58 (solvent A); ν_{max}^{film} 1730 (CO), and 1270 cm^{-1} (P=O). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.52 and 1.57 (2 s, 6 H, CH_3CCH_3), 3.98 (d, 3 H, J 11.0, CH_3OP), 4.2 - 4.7 (m, 4 H, H-3'a, 3'b, 5a, 5b), 5.41 (ddd, 1 H, $J_{4,5a}$ 3.8, $J_{4,5b}$ 1.8, $J_{4,P}$ 20.7, H-4), 8.1-8.9 (AA'BB', 4 H, O_2N-C_6H_4-CO). ^{31}P-NMR ($CHCl_3$, 24.3 MHz): δ 36.13.

(2S, 3R, 4R)-3,3'-O-Isopropylidene-3-(hydroxymethyl)-4-O-(p-nitrobenzoyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (16b). Conventional p-nitrobenzoylation of 15b gave 16b (95%), m.p. 124.5 - 125° (from chloroform-hexane), $[\alpha]_D^{20}$ -95.9° (c, 1.2, chloroform), R_f 0.66 (solvent A); ν_{max}^{KBr} 1725 (CO), and 1270 cm^{-1} (P=O). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.48 and 1.50 (2 s, 6 H, CH_3CCH_3), 3.96 (d, 3 H, J 11.0, CH_3OP), 4.2 - 4.6 (m, 4 H, H-3'a, 3'b, 5a, 5b), 5.50 (ddd, 1 H, $J_{4,5a}$ 4.0, $J_{4,5b}$ 4.7, $J_{4,P}$ 14.5, H-4), 8.3 (m, 4 H, O_2N-C_6H_4-CO). ^{13}C-NMR ($CDCl_3$, 22.63 MHz): δ 25.27 and 26.17 (2 s, CH_3CCH_3), 55.09 (d, J 7.4, CH_3OP), 65.69 (d, J 7.4, C-3'), 68.55 (d, J 4.4, C-5), 75.92 (d, J 32.7, C-4), 77.91 (d, J 145.6, C-3), 112.84 (d, J 5.9, H_3CCCH_3), 123.90, 131.31, 134.10, and 151.40 (4 s, aromatic carbons), 163.62 (s, COO), ^{31}P-NMR ($CHCl_3$, 24.3 MHz): δ 32.66.

(2S, 3S, 4R)-(19a) and (2R, 3S, 4R)-3,3'-O-Isopropylidene-3-(hydroxymethyl)-4-O-(p-nitrobenzoyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (19b). After the removal of 20b from a mixture of 18a, 18b, and 20b as 3'-O-(tert-butyldimethylsilyl) ether 22b, a 2:1 mixture of 18a and 18b (47 mg, 0.2 mmol) was esterified with p-nitrobenzoyl chloride (55 mg, 0.3 mmol) in the presence of pyridine. Separation on silica gel column gave 19a (10 mg, 13%) and 19b (6 mg, 7.7%) as yellowish oils.

Compound 19a, R_f 0.19 (solvent B). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.40 and 1.52 (2 s, 6 H, CH_3CCH_3), 3.93 (d, 3 H, J 11.0, CH_3OP), 4.2 - 4.4 (m, 4 H, H-3'a, 3'b, 5a, 5b), 5.59 (ddd, 1H, $J_{4,5a}$ 5.7, $J_{4,5b}$ 6.2, $J_{4,P}$ 9.7, H-4), 8.3 (m, 4 H, O_2N-C_6H_4-CO).

Compound 19b, R_f 0.19 (solvent B). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.39 and 1.45 (2 s, 6 H, CH_3CCH_3), 3.98 (d, 3 H, J 11.2, CH_3OP), 4.2 - 4.6 (m, 4 H, H-3'a, 3'b, 5a, 5b), 5.58 (ddd, 1 H, $J_{4,5a}$ 4.0, $J_{4,5b}$ 3.0, $J_{4,P}$ 19.8, H-4), 8.3 (m, 4 H, O_2N-C_6H_4-CO).

(2S, 3S, 4R)-3,4-O-Isopropylidene-3-(hydroxymethyl)-3'-O-(p-nitrobenzoyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (21a). Conventional p-nitrobenzoylation of 20a (9 mg, 0.04 mmol) afforded 21a (9 mg, 61%), m.p. 172 - 174° (chloroform-hexane), $[\alpha]_D^{25}$ -52.5° (c 0.2, chloroform), R_f 0.46 (solvent B); ν_{max}^{KBr} 1720 (CO), 1270 (P=O), and 1095 and 1030 cm^{-1} (C-O-P). ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.45 and 1.64 (2 s, 6 H, CH_3CCH_3), 3.82 (d, 3 H, J 10.8, CH_3OP), 4.0 - 4.8 (m, 5 H, H-3'a, 3'b, 4, 5a, 5b), 8.3 (m, 4 H, O_2N-C_6H_4-CO).

(2R, 3R, 4R)-3-(Hydroxymethyl)-2-methoxy-2-oxo-1,2-oxaphospholane-3,4-diol (13a). A mixture of 15a (0.1 g, 0.42 mmol) and toluene-p-sulfonic acid monohydrate (5 mg) in chloroform (1 ml) was maintained at 44° for 1 h. Then methanol (0.1 mL) was added and solvents were evaporated. The solid residue was recrystallized from chloroform — methanol to give 13a (60 mg, 72%) as colorless crystals, m.p. 145 - 146° (decomp.), $[\alpha]_D^{22}$ - 14.4° (c 0.97, methanol), R_f 0.25 (chloroform-methanol 4:1); ν_{max}^{KBr} 3200 - 3450 (OH), and 1200 cm^{-1} (P=O). ^1H NMR (CD_3OD), 90 MHz); δ 3.84 (d, 3 H, J 11.0, CH_3OP), 3.9 - 4.6 (m, 5 H, H-3', 3'a, 3'b, 4, 5a, 5b). ^{13}C NMR (CD_3OD, 22.63 MHz): δ 54.78 (d J 6.6, CH_3OP), 63.20 (d,J 8.1, C-3'), 73.99 (d, J 8.1, C-5), 76.17 (d, J 136.8, C-3), 76.41 (d, J 14.7, C-4). ^{31}P NMR (CD_3OD, 24.3 MHz); δ 43.3. Anal. Calc. for $C_5H_{11}O_6P$: C, 30.31; H, 5.60; P; 15.63. Found: C, 29.97; H 5.83; P 15.55%.

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30. The erroneous value of 26.29 ppm was cited in ref. 13.

31. Doublet of quaternary C-3 could not be found in the spectrum.