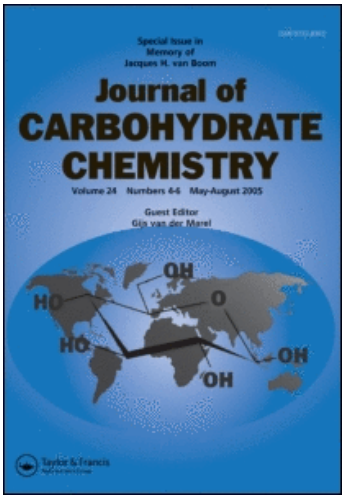

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Monosaccharides with Phosphorus in the Sugar Ring

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MONOSACCHARIDES WITH PHOSPHORUS IN THE SUGAR RING

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INTRODUCTION

In recent years attention has been directed toward the synthesis of modified sugars wherein the oxygen atom in the sugar ring is replaced by sulfur, selenium or phosphorus. Synthesis of sugar analogs with phosphorus as the ring heteroatom is interesting from the point of view of their possible biological activity.

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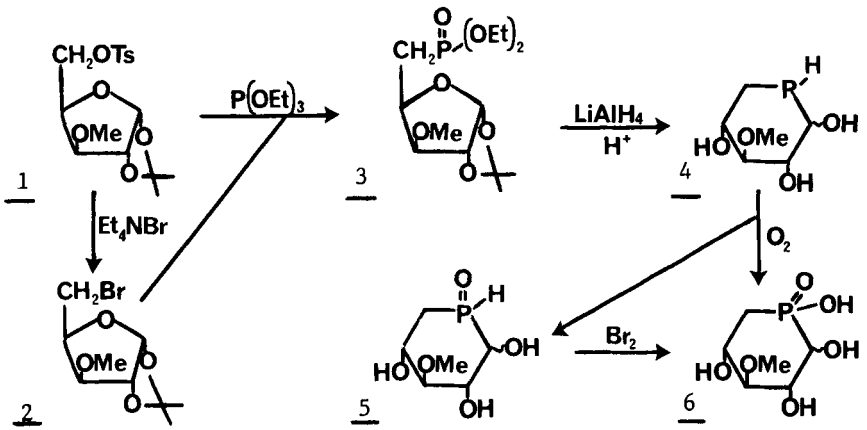
Phosphorus-containing carbohydrates (except phosphate esters) are less well known than the corresponding sulfur- or selenium-containing species. The results of synthetic work in this area has been briefly reviewed by Inokawa (1969 in Japanese)[1] and by Whistler and Anisuzzaman (1976).[2] Reviews on thiosugars[4] and selenosugars[4] have appeared, also.

EARLY WORK

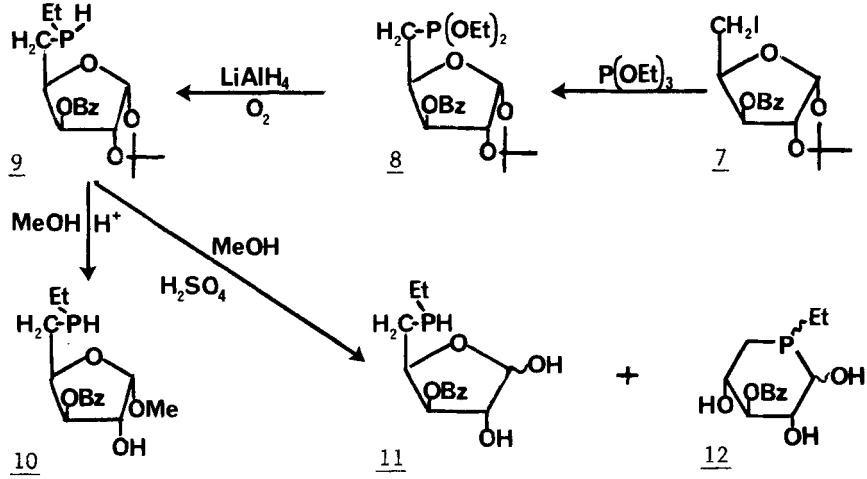
The first introduction of phosphorus into the sugar ring, reported by Whistler and Wang,[5] used the Michaelis-Arbuzov reaction for placing phosphorus at position C-5. Earlier, phosphine had been added photochemically[6] to a 5,6-unsaturated hexofuranose. The reaction sequence began with 1,2-O-isopropylidene-3-O-methyl-5-O-p-tolylsulfonyl-α-D-xylofuranose (1) or 5-bromo-5-deoxy-1,2-O-isopropylidene-3-O-methyl-α-D-xylofuranose (2) which was reacted with triethylphosphite to give the 5-deoxy-5-(diethylphosphinyl) derivative (3). Reduction with lithium aluminum hydride, followed by hydrolysis of the isopropylidene group, afforded the hemiacetal with phosphorus in the ring. The 5-deoxy-3-O-methyl-5-phosphino-D-xylopyranose (4) so obtained reacts readily with oxygen to form stable crystalline 5-deoxy-3-O-methyl-5-(phosphineoxido)-D-xylopyranose (5) and 5-deoxy-3-O-methyl-5-(phosphinic acid)-D-xylopyranose (6).
The phosphinic acid (6) was obtained also from the phosphine oxide (5) by bromine oxidation at 25° C.

By using reactions similar to those described, Inokawa and associates[7] synthesized 3-O-benzyl-5-deoxy-5-(ethylphosphinyl)-α-D-xylopyranose (9). The starting material was 3-O-benzyl-5-deoxy-5-iodo-1,2-O-isopropylidene-α-D-xylofuranose (7) which in the Michaelis-Arbuzov reaction with diethylphosphonite gave an 87% yield of 3-O-benzyl-5-deoxy-5-(ethyoxyethylphosphinyl)-1,2-O-isopropylidene-α-D-xylofuranose (8). Reduction of (8) with lithium



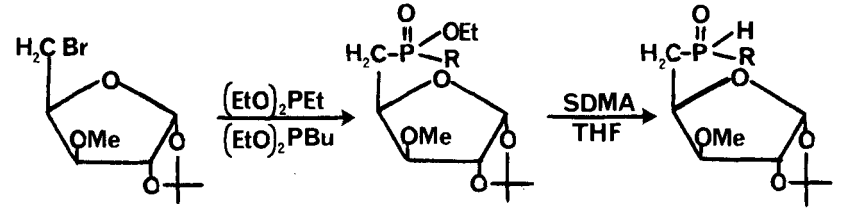
aluminum hydride, followed by oxidation with air, produced an 85% yield of 3-O-benzyl-5-deoxy-5-(ethylphosphinyl)-1,2-O-isopropylidene-α-D-xylofuranose (9). Methanolysis of (9) does not produce a methyl glycoside with phosphorus in the sugar ring, but instead gives methyl 3-O-benzyl-5-deoxy-5-(ethylphosphinyl)-D-xylofuranoside (10) in 82% yield.

Moreover, the hydrolysis of (9) in 50% aqueous methanol by 2N-sulfuric acid afforded two major products in the ratio 1:1 (11) and (12).

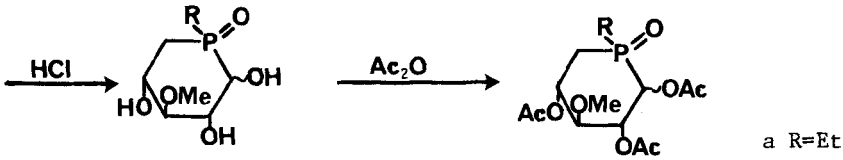


METHOD OF INTRODUCTION OF PHOSPHORUS INTO THE SUGAR RING

The modification of an earlier synthesis, using the same kind of starting material, has been reported by Seo and Inokawa[8] in the synthesis of 5-deoxy-5-(ethylphosphonyl)-3-O-methyl-α-D-xylopyranose (16a) and 5-(butylphosphonyl)-5-deoxy-3-O-methyl-α-D-xylopyranose (16b).



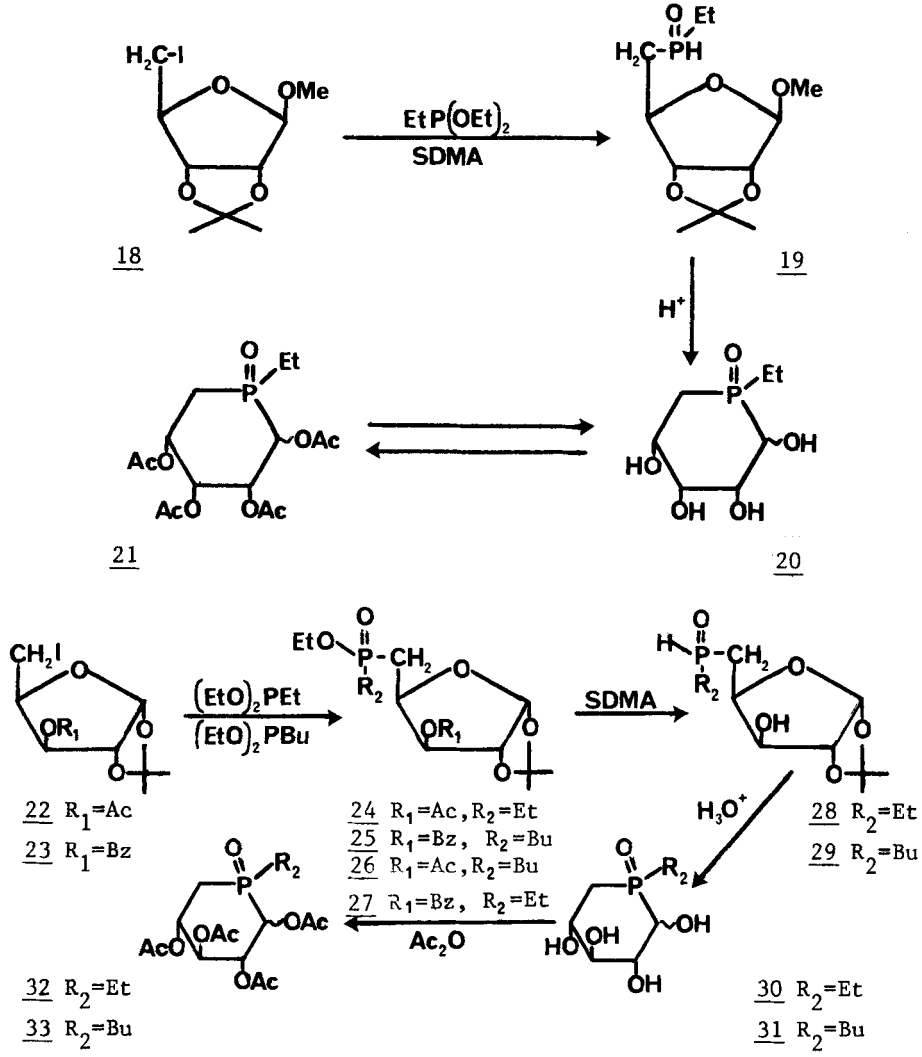
13 14a 14b 15a 15b



16a 16b 17a 17b

a R=Et
b R=Bu

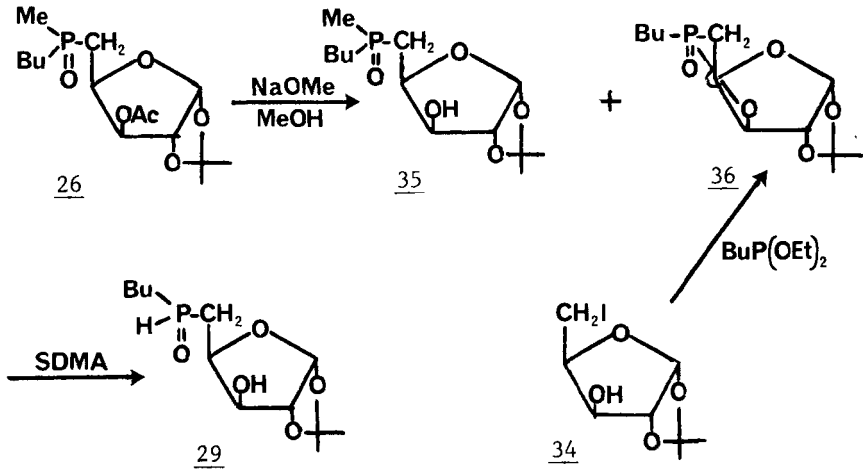
The Inokawa group[9] also synthesized a D-ribose derivative with phosphorus in the sugar ring. The starting product was 5-deoxy-5-iodo-2,3-O-isopropylidene-β-D-ribofuranoside (18) which in the Michaelis-Arbuzov reaction with diethylphosphonite gave methyl-5-deoxy-5-(ethoxyethylphosphinyl)-2,3-O-isopropylidene-β-D-ribofuranoside. Reduction with sodium dihydrobis(2-methoxyethoxy) aluminate (SDMA) in THF afforded methyl 5-deoxy-5-(ethylphosphinyl)-2,3-O-isopropylidene-β-D-ribofuranoside (19). Acid hydrolysis yielded a mixture of the anomeric 5-deoxy-5-(ethylphosphinyl)-D-ribopyranoses (20). Evidence for the pyranose structure of (20) is derived from the absence of signals due to the PH group in the ^1H NMR spectrum as well as in the IR spectrum.



Attempts to form glycosides have been unsuccessful in that treatment of (20) with acidified methanol left it unchanged. However, treatment of the anomeric mixture (20) with acetic anhydride in pyridine solution gave a syrupy mixture of the two 1,2,3,4-tetra-O-acetyl-5-deoxy-5-(ethyl-phosphinyl)-D-ribopyranoses (21) which reverted to (20) on Zemplén deacetylation.

Seo and Inokawa[10] have also reported the synthesis of the 5-deoxy-D-xylopyranoses using the approach previously employed in the synthesis of D-ribose derivatives.[9]

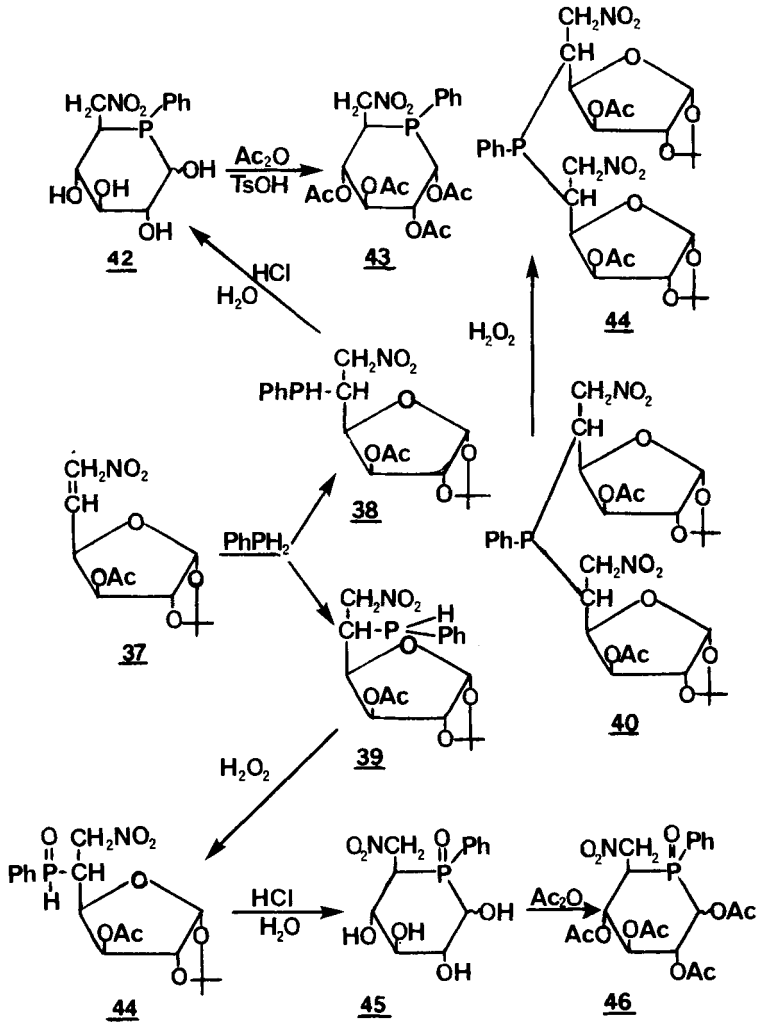
The reaction sequence started with 5-iodo-5-deoxy-1,2-O-isopropylidene-α-D-xylofuranose derivatives (22) and (23). Treatment of (26) with sodium methoxide in methanol gave a mixture of (35) and (36) which when reduced with SDMA produced (29). Compound (36) was independently prepared from (34) by heating the latter with butylphosphonite.



26 35 36 29 34

Inokawa and coworkers also described the synthesis of a phosphorus analog of 6-deoxy-D-glucose[11,12] by the addition of phosphine to 3-O-acetyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-α-D-xylo-hex-5-enofuranose (37). Treatment of (37) with a large excess of phenylphosphine led to a mixture of D-gluco and the L-ido compounds in 3:1 ratio as well as to the 1:2 adduct (40) (Scheme 1).

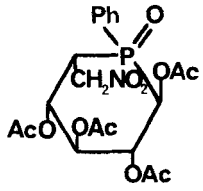
The D-gluco isomer (38) after oxidation by hydrogen peroxide and hydrolysis gave 5,6-deoxy-6-C-nitro-5-(phenylphosphinyl)-D-glucopyranose (45) which was characterized as the crystalline 1,2,3,4-tetraacetate derivative (46).



Scheme 1

Direct hydrolysis of the D-gluco isomer (38) yielded the appropriate 5-(phenylphosphine)-derivative (42), which upon acetylation in the presence of p-toluenesulfonic acid gave the crystalline 1,2,3,4-tetraacetate (43). The ^1H NMR spectrum of (43) in contrast to the complicated spectrum of (46) showed that compound (43) is the α-D-anomer in the $^4C_1$(D) conformation. Conclusions are based on the large diaxial coupling between H_2 and H_3 ($J_{2,3}$ = 9.6 Hz), as well as by that between H_3 and H_4 ($J_{3,4}$ = 9.6 Hz) which was determined in a double-resonance experiment.

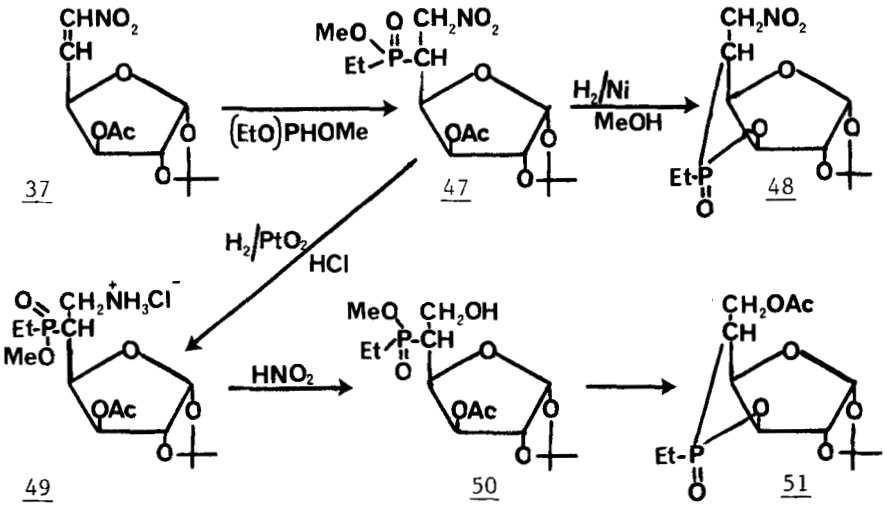
This is a first example of assignment of configuration and conformation of sugars with phosphorus in the ring. In a later publication,[13] the authors, on the basis of an X-ray crystallographic analysis, established the configuration of (48) as L-ido. The pyranoid ring is in the $^4C_1$(L) conformation, and the substituents at C-1 and C-5, as well as the phenyl ring at P-5, are linked axially, while those substituents at C-2, C-3 and C-4 are linked equatorially.



46

Addition of methyl ethylphosphonite to (37) gave a mixture of the D-gluco and L-ido compounds in a 1:1 ratio from which the D-gluco isomer was separated (47). Direct reduction of the D-gluco isomer (47) with Raney nickel gave crystalline 6-acetamido-5-(3-O-cyclo-ethylphosphinate)-5,6-dideoxyl,2-O-isopropylidene-α-D-glucofuranose (48). Under acidic (hydrochloric acid-methanol) conditions, the phosphinate group in (47) is stable and no acetyl migration takes place which allows a smooth reduction of (47) with

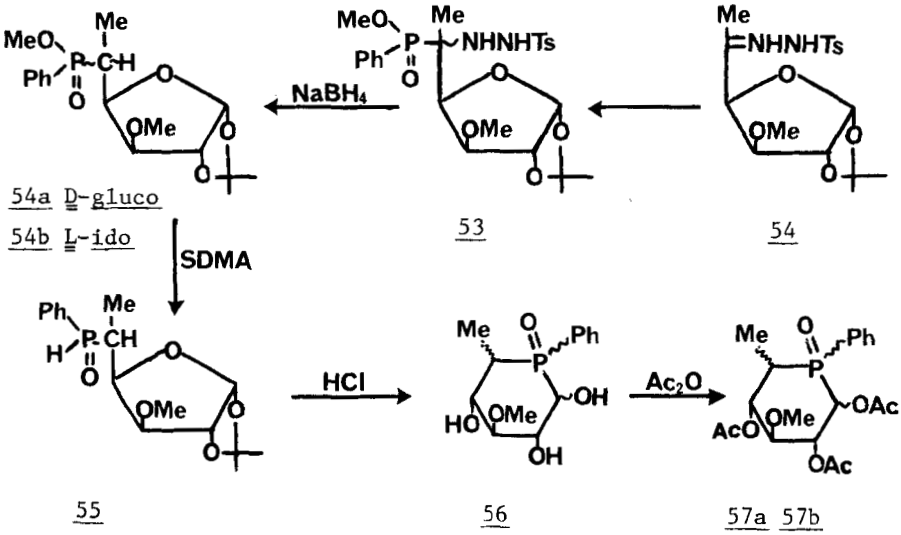
platinum oxide to give (49). Deamination of (49) with nitrous acid gave compound (50), which is unstable and is spontaneously converted to compound (51) with migration of the acetyl group. All attempts to convert the phosphinate group into a phosphine oxide group were unsuccessful. The previous method of addition of phenylphosphine to an active olefinic bond in sugars has been more convenient.



37 47 48 49 50 51

In 1977 Inokawa and coworkers reported the first successful introduction of a phosphorus atom into the furanose ring.[14] In the same communication, they described a new, efficient method for preparing sugar derivatives with a phosphorus atom in the hemiacetal ring. This is done by treatment of 6-deoxy-1,2-O-isopropylidene-3-O-methyl-α-D-xylo-hexofuranose-5-ulose-5-p-tolylsulfonylhydrazone (54) with methyl phosphonite in the presence of p-toluenesulfonic acid to give a mixture of (5R)- and (5S)-5,6-dideoxy-1,2-O-isopropylidene-5-C-[(methoxy)phenylphosphinyl)]-3-O-methyl-5-C-(N-p-tolylsulfonylhydrazino)-α-D-xylohexofuranose (53).

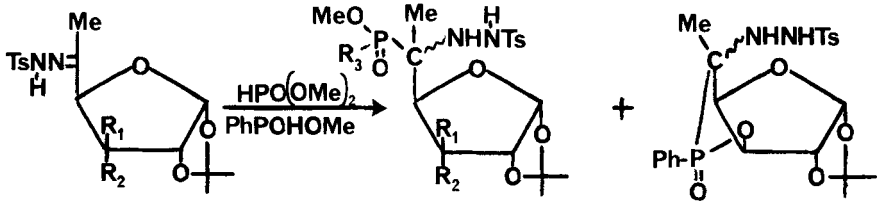
Treatment of (53) with sodium borohydride in tetrahydrofuran gave (54), which on reduction with an excess of sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA) gave (5R)- and (5S)-5,6-dideoxy-1,2-O-isopropylidene-5-C-(phenylphosphinyl)-3-O-methyl-α-D-xylo-hexofuranose (55). Hydrolysis of (55) followed by acetylation afforded a mixture of 1,2,4-tri-O-acetyl-5,6-dideoxy-3-O-methyl-5-C-(phenylphosphinyl)-D-glucopyranose (57a) and the corresponding L-idopyranose isomer (57b).



The crystalline isomers (57a) and (57b) have widely separated melting points; the former melting at 304-306°, and the latter melting much lower at 164-165°.

Conformational analysis of compound (57a) by X-ray crystallography[15] showed that it is the β-D-anomer in the $^4C_1$(D) conformation. Comparison of the chemical shift of the acetyl group at C_1 in compound (57a) appearing at high field (δ = 1.90) with that in compound (57b) appearing at lower field (δ = 2.07) established that compound (57b) is the α-L-ido isomer.

Acid-catalyzed addition reaction of methyl phenylphosphonite or dimethyl phosphite to some hexofuranos-5-ulose-5-(p-tolyl-sulfonylhydrazones) has been reported also.[15] Synthesis followed that previously employed in the production of the 5,6-deoxy-5-C-(phenylphosphinyl)-D-glucopyranose derivatives.[14]

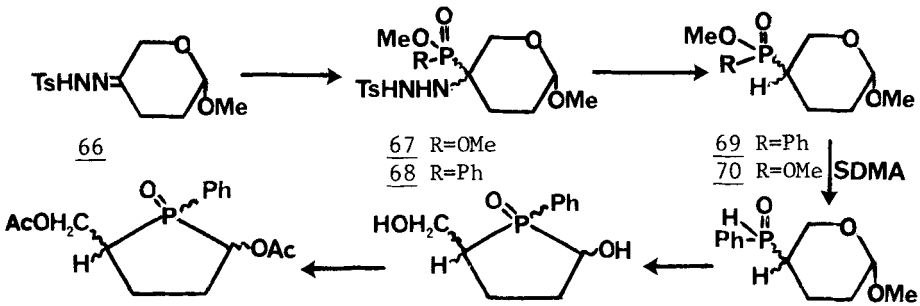


58 R_1=OMe, R_2=H
59 R_1=H, R_2=OBn
60 R_1=H, R_2=OH

61 R_1=OMe, R_2=H, R_3=OMe
62 R_1=H, R_2=OBn, R_3=OMe
63 R_1=H, R_2=OH, R_3=Ph
64 R_1=OMe, R_2=OH, R_3= Ph

65

The introduction of a phosphorus atom into the furanose ring[14,16] has been accomplished by the treatment of (1S)-2,3-deoxy-DL-pentopyranoside-4-ulose-4-(p-toluenesulfonylhydrazone) (66) with methyl phenylphosphonite to give (67), which on treatment with sodium borohydride afforded methyl (1S)2,3,4-trideoxy-4-C[(methoxy)-phenylphosphinyl]-DL-glyceropentopyranoside (70). Reduction of (70) with SDMA, followed by hydrolysis and acetylation, led to the 1,5-diacetyl derivative (73) of 2,3,4-trideoxy-4-C-(phenyl-phosphinyl)-DL-glyceropentofuranose (72).



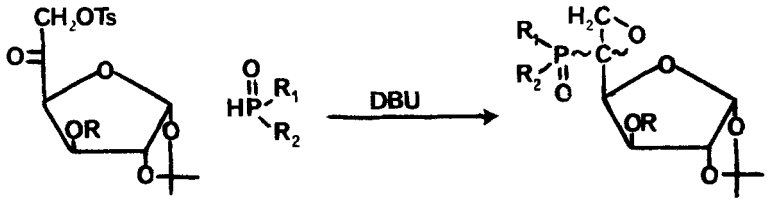
66

67 R=OMe
68 R=Ph

69 R=Ph
70 R=OMe

73 72 71

The synthesis of some 5,6-anhydro-1,2-O-isopropylidene-5-C-phosphinyl-α-D-xylohexofuranose derivatives has been reported[17] by Inokawa and coworkers who used a previously reported method[18,19] for conversion of 2-oxo-1-(p-tolylsulfonyloxy)-propane into 1,2-epoxy-1-methylethanephosphonate conducting the reaction with dimethylphosphonite in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).



74 R=$PhCH_2$
75 R=Me

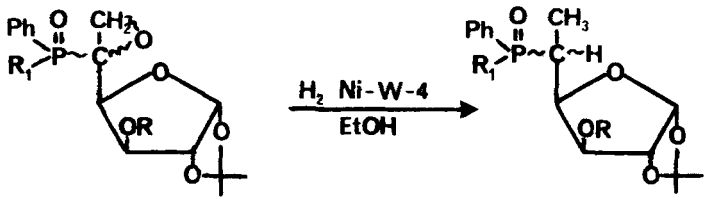
76 R_1=R_2=OMe
77 R_1=OEt, R_2=Ph
78 R_1=OMe, R_2=Ph

79 R=$PhCH_2$, R_1=R_2=OMe
80 R=$PhCH_2$, R_1=OEt, R_2=Ph
81 R=OMe, R_1=R_2=OMe
82 R=Me, R_1=OMe, R_2=Ph

A new and convenient method[18] for the synthesis of 5,6-dideoxy-5-C-phosphinyl-D-xylohexose derivatives uses the general procedure previously employed.[15,17]

Hydrogenation of the previously described 5,6-anhydro-1,2-O-isopropylidene-5-C-[(methoxy)phenylphosphinyl]-3-O-methyl-α-D-glucofuranose (82)[17] in ethanol with hydrogen in the presence of Raney Ni (W-4) gave a mixture of the D-gluco- (84) and L-ido-isomers in the ratio 3:2, which was separated by silica gel column chromatography.

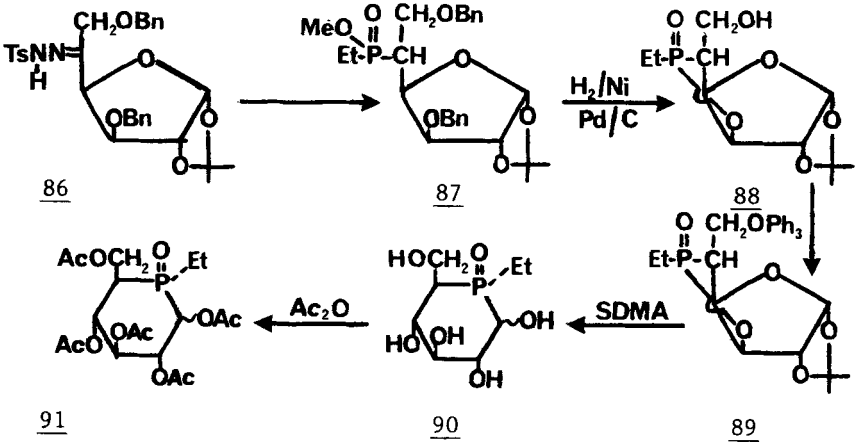
A similar procedure produced (5R,S)-3-O-benzyl-5,6-dideoxy-5-C-[(ethoxy)phenylphosphinyl]-1,2-O- isopropylidene-α-D-xylo-furanose (85) in 90% yield and two isomers [(5R)- and (5S)-] of (85) were separated by preparative TLC and characterized by ^{1}H NMR.



82 R=Me, R_1=OMe
83 R=$PhCH_2$, R_1=OEt

84 R=Me, R_1=OMe
85 R=$PhCH_2$, R_1=OEt

Inokawa and coworkers also reported a new and convenient route for preparation of an unsubstituted 5-deoxy-5-C-phosphinyl-α-D-glucopyranoses.[20]

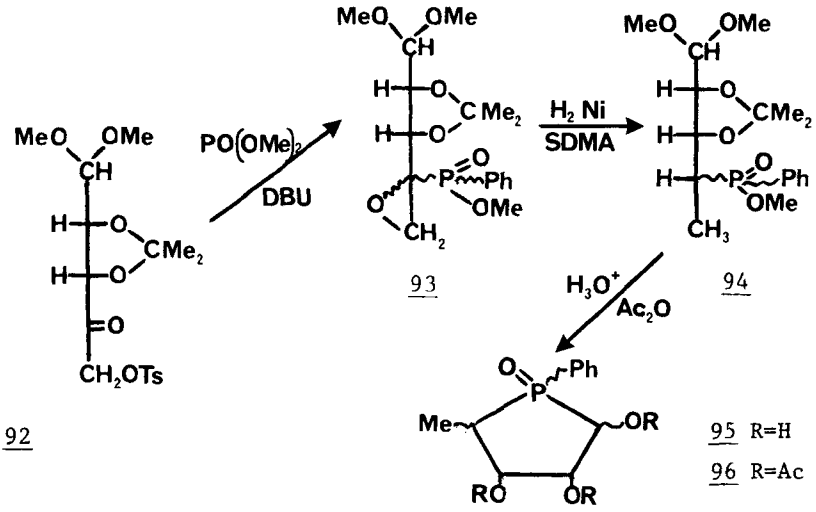


86 87 88 89 90 91

In a recent report,[21] Inokawa and coworkers described a new approach to the preparation of 4-deoxy-4-phosphinyl-ribo- and lyxo-furanose derivatives employing a new method[18,19] for C-P bond formation.

The sequence started from 2,3-O-isopropylidene-5-O-(p-tolylsulfonyl)-D-erythropentos-4-ulose dimethyl acetal (92), which was reacted with dimethyl phosphinate in the presence of 1.2 equivalents of DBU at 25° C gave a mixture of the (4S)- and (4R)-isomers of (93).

This procedure was previously applied for the preparation of (5R)- and (5S)- 5,6-anhydro-1,2-O-isopropylidene-5-C-(phenylphosphinyl)-α-D-xylo-hexafuranoses.[18]

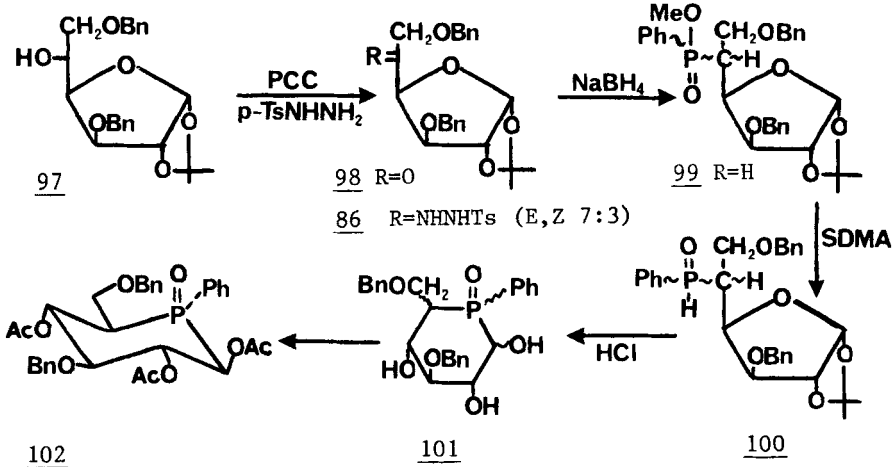


92 93 94 95 R=H 96 R=Ac

Reduction with SDMA, hydrolysis and acetylation yielded 4,5-dideoxy-4-C-[(R,S)-phenylphosphinyl]-D-ribo- and L-lyxofuranose (96) as a mixture of seven diastereomers (eight are theoretically possible) which was separated by preparative TLC. The structural assignment of each diastereomer was made by 400 MHz ^1H NMR analysis. A general dependence of the $^2J_{PH}$ and $^3J_{PH}$ values on the O=P-CH and P-C-C-H dihedral angles permits the assignment of configuration and conformation of the above diastereomers.

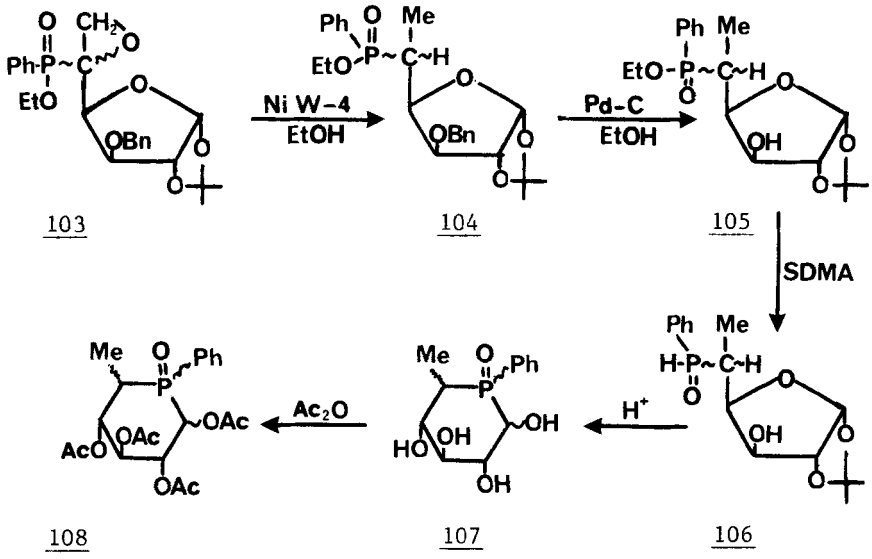
Recently, the synthesis of the first gluco type of hexopyranose derivative with the phosphorous in the hemiacetal ring, that is, 1,2,4-tri-O-acetyl-3,6-di-O-benzyl-5-deoxy-5-C-[(S)-phenylphosphinyl]-β-D-glucopyranose (102) has been reported by Inokawa.[22] The sequence starts from 3,6-di-O-benzyl-1,2-O-iso-

propylidene-α-D-glucofuranose (97) which upon oxidation with pyridinium chlorochromate, followed by conversion to the p-tolylsulfonylhydrazone (E/Z mixture), addition of methyl phenylphosphinate and reduction with sodium borohydride gave the key intermediate (5R,S)-3,6-di-O-benzyl-5-deoxy-1,2-O-isopropylidene-5-C-[(methoxy)-phenylphosphinyl]-α-D-xylohexofuranose (99). Treatment of (99) with SDMA, followed by the action of acid and acetic anhydride, produced the crystalline (102) as the only isolable diastereomer in 2% overall yield from (99). The authors established the structure of (102) on the basis of mass and 400 MHz ^1H NMR spectra. There was a general dependence of $^2J_{PH}$ values on the O=P-C-H dihedral angles provided full evidence for assigning the configuration of C-1 and C-5, as well as the ring phosphorous atom, with the $^4C_1$(D) conformation of the pyranoid ring.



A new approach to the preparation of (5R,S)-5,6-dideoxy-5-C-[(R,S)phenylphosphinyl]-hexopyranoses, starting from (5R,S)-5,6-anhydro-3-O-benzyl-5-C-[(ethoxy)-phenylphosphinyl]-1,2-O-isopropyidene-α-D-xylo-hexofuranose[17,18] has been recently described.[23]

The crude peracetylated products (108) were separated by preparative TLC for five diastereomers. Among these products two

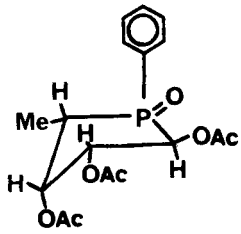


103 104 105 106 107 108

crystalline compounds were determined by X-ray crystallographic analysis to be 1,2,3,4-tetra-O-acetyl-5,6-dideoxy-5-C-[(S)-phenylphosphinyl]-α- and -β-L-idopyranose-$^4C_1$.

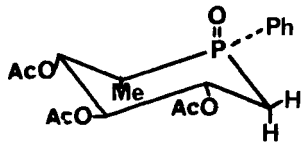
Structures of the other three products were established by 400 MHz ^{1}H NMR.[24] The results of these spectral analyses, showed that all the five products had the L-ido configuration with the pyranoid ring in the $^4C_1$(L) conformation. Three of them were diastereomeric isomers at C_1 and the ring phosphorus atom, and the fifth was the 4-deoxy-compound (109).

The previously described 1,2,3-tri-O-acetyl-4,5-dideoxy-4-C-(phenylphosphinyl)-pentofuranose (96)[21] has been recently examined by X-ray crystallographic analysis.[25] The results showed that the compound has the five-membered ring in the E_3 conformation, with a tendency towards the $^3T_2$ form. The substituents at P-5 and C-5 are linked bisectionally, the acetoxyl group at C-2 and the methyl group at C-4 are linked quasiequatorially, and the acetoxyl group at C-3 is linked axially.



96

Recently, the results of X-ray crystallographic analysis of previously synthesized (5R,S)-2,3,4-tri-O-acetyl-1,5-anhydro-5,6-dideoxy-5-C-[(R,S)-phenylphosphinyl[-D-xylo-hexitol[23,24] has been reported.[26] The results show that the compound's structure is 2,3,4-tri-O-acetyl-1,5-anhydro-5,6-dideoxy-5-C-[(S)-phenylphosphinyl]-L-iditol-$^4C_1$ (109).



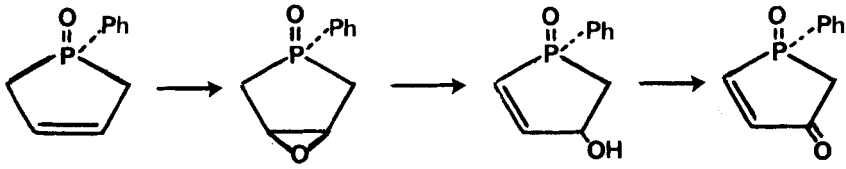
109

Yamashita and coworkers[27] reported a new approach to the important intermediate, 5,6-dideoxy-5-C-(diphenylphosphinyl)-1,2-O-isopropylidene-3-O-methyl-6-C-nitro-β-L-idofuranose[11,12] in the synthesis of previously obtained derivatives having phosphorous in the hemiacetal ring. They added diphenylphosphine oxide to a reactive alkenic sugar such as 5,6-dideoxy-1,2-O-isopropylidene-3-O-methyl-6-C-nitro-α-D-xylo-hex-5-enofuranose, and converted the 6-C-nitro group into a hydroxyl group via the aldehyde (by treatment with ozone-sodium methoxide), followed by reduction with sodium borohydride.

Recently Inokawa and coworkers[28] have reported a novel and convenient approach to the synthesis of unsubstituted 5-deoxy-5-C-phosphinyl-D-glucopyranoses using the general methodology previously described.[20] Separation of the previously described 1,2,3,4,6-penta-O-acetyl-5-deoxy-5-C-[(R,S)-ethylphosphinyl]-α- and -β-D-glucopyranoses (91) by fractional crystallization for four diastereomers and examination of each by 400 MHz ^{1}H NMR has been done. The results showed that the above diastereomers exist in the $^4C_1$ (D) conformation as judged mainly by the large values of $J_{2,3}$ and $J_{3,4}$. Moreover, the large values of $J_{4,5}$ (12-14 Hz) indicate the gluco configuration, whereas the small values $J_{4,5}$ (4-5 Hz) are compatible with the L-ido configuration as has been previously established.[22,24]

It is interesting to know that the first synthesis of 4-oxo-1-phenyl-2-phospholene-1-oxide (112) (which can be considered as an unsaturated ketofuranose with phosphorous in the sugar ring) from noncarbohydrate precursors has been reported.[29]

The sequence started from 1-phenyl-3-phospholene-1-oxide (110) which was converted into the oxirane (111) on treatment with



110 111 112 113

m-chloroperbenzoic acid in refluxing chloroform. Isomerization of (111) to (112) was accomplished in high yield in the presence of triethylamine in ethanol.

A racemic mixture of (112) when treated with 2-camphanyl chloride afforded a 1:1 mixture of diastereomeric ω-camphanates. The ratio of diastereomers was precisely evaluated on the basis of

the ^{31}P NMR spectrum (δ = 55.5 ppm and δ = 55.7 ppm). Moreover, the authors isolated the pure crystalline enantiomer [(+) (112)] after hydrolysis of crystalline (+) ω-camphanate and determined the absolute configuration by a single-crystal X-ray analysis. Oxidation of [(+) (112)] using Collins reagent gave a title compound (113) in moderate yield.

CONCLUSION

While there is interesting chemistry involving sugar phosphates, phosphites, phosphonates, thiophosphates and others, this review was restricted to only those sugars containing phosphorous in the sugar ring. Recent papers on the synthesis and stereochemistry of cyclic sugar phosphates[30-35] have also appeared.

The potential utility of phosphoro-sugars as modified biological substrates as well as synthetic intermediates is a subject and target of many papers and the search for new and interesting phosphoro-sugars continues. The field of phosphoro-sugars will remain a rich area of investigation for many years to come.

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