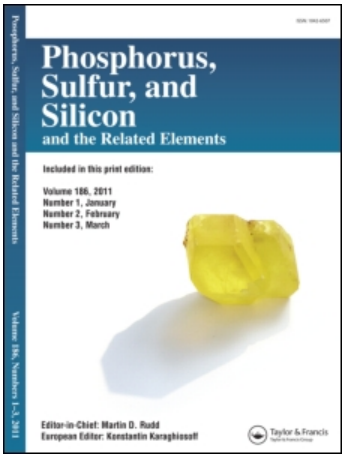

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PENTOSE AMIDOPHOSPHITES. SYNTHESIS, PALLADIUM COMPLEXES

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PENTOSE AMIDOPHOSPHITES. SYNTHESIS, PALLADIUM COMPLEXES

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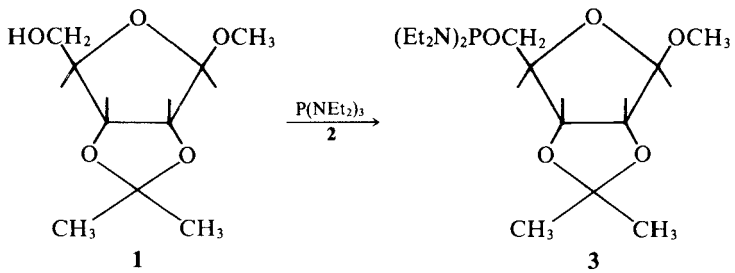
Glycoamidophosphites in the pentose series have been synthesized based on 2,3-O-isopropylidene-β-methyl-D-ribofuranoside, 1,2-O-isopropylidene-α-D-xylofuranose, xylitane and 3,5-O-isopropylidenexylitane. Some of these compounds are used as ligands for the synthesis of the palladium complexes. Consideration is given to the behavior of these complexes as catalysts in the asymmetric hydrogenation of itaconic acid.

Hydrocarbon amidophosphites have been already found to be interesting species for stereochemical studies[1] and valuable intermediates for a fine organic synthesis,[2,3] which makes it advisable to persue their further chemical development.

The purpose of this paper is to extend the synthesis of glycoamidophosphites in the pentose series and to produce and study the complexes of these compounds with palladium. The latter direction is of special importance as it combines the abundant chemical potentialities of sugar amidophosphites with the requirements of metal complex catalysis.

The first stage of the study is concerned with phosphorylation of 2,3-O-isopropylidene-β-methyl-D-ribofuranoside **1** with an excess of hexaethyltriamidophosphite **2**:



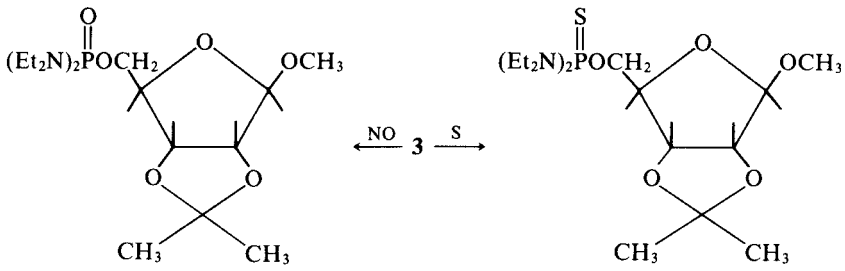
1 **3**

The reaction was carried out at 110°C. Amidophosphite **3** was isolated by high-vacuum distillation in a 77% yield. The individual character of the product was shown by ^{31}P n.m.r. (δ 138 ppm) and t.l.c. methods, and its structure follows from the p.m.r. spectra.

H-1 is matched with a practically unsplit signal (δ 4.75 ppm). The vicinal H-2 and H-3 protons form an AB system (δ 4.58 and 4.38 ppm) with a spin coupling constant 6 Hz. H-4 is matched with a symmetrical triplet (δ 4.15 ppm, J_{4-5} 4.5 Hz).

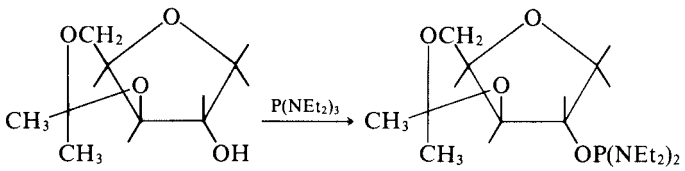
H-5 gives a doublet (δ3.45 ppm, J_{4-5} 4.5 Hz). Other signals are shown by the OCH_3 group (δ 3.14 ppm), two singlets of the isopropylidene group (δ 1.35 and 1.20 ppm) and symmetrical multiplets of the N-ethyl protons (δ 2.90 and 0.96 ppm). The integrated intensity of all the signals agrees with the theoretical values.

The presence of the amidophosphite moiety in the product obtained is additionally supported by its oxidation and sulfurization. Along with the analytical significance these reactions are important as regards synthesis in so far as they ensure high yields of isopropylideneriboside amidophosphate **4** and amidothiophosphate **5**:



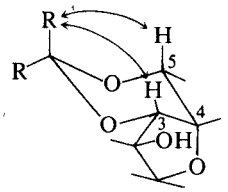
4 **5**

3,5-O-isopropylidenexylitane **6** was used as the hydrocarbon component with a free secondary hydroxyl. Phosphorylation with an excess of triamide **2** in this case also gave a good result, 3,5-O-isopropylidenexylitane 2-tetraethyldiamidophosphite **7** being formed in a 70% yield:



6 **7**

The structure of the bicyclic amidophosphite was confirmed by the p.m.r. method; however, some overlapping of the signals and unusual data were observed. Thus, for example, the methylene H-1 and H-5 protons resonated as a practically unsplit narrow multiplet. Therefore we studied additionally the ^{13}C n.m.r. spectrum of **7** (see Table I). For comparison purposes we measured the spectrum of the initial 3,5-O-isopropylidenexylitane **6** and 3,5-O-methylidenexylitane **6a**. It was shown by correlation of the data obtained that replacement of the methylidene hydrogens in **6a** by methyls leads to a significant up-field signal shift of the C-3 and C-5 atoms within the dioxane ring (by 5.6 and 7.6 ppm, respectively), which corresponds to the known rule of the γ-affect:[4]



6, R = CH_3
6a, R = H

TABLE I

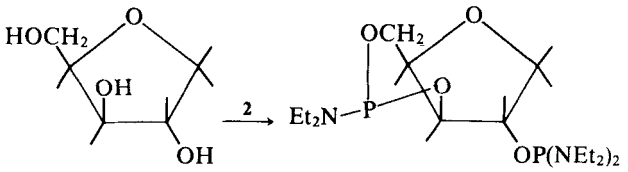
^{13}C n.m.r. chemical shifts and $^{13}C—^{31}P$ spin coupling constants, Hz (the latter are parenthesized)

Compound	C-1	C-2	C-3	C-4	C-5	$C_{quart.\ isopropylid.}$	$CH_{3\,isopropylid.}$	CH_2N	CH_3CH_2N	$C_{aromat.}$	
Xylitane	74.2	78.6	78.4	82.2	61.4						
6a	74.2	76.0	76.6	81.2	67.7	92.4					
6	73.6	75.8	71.5	75.0	60.1	96.5	28.1				
							19.3				
7	79.3	83.7	77.5	76.6	63.9	103.0	28.9	40.3	14.2		
	(5.6)	(19.2)	(4.2)				19.2	(21.3)			
8	75.7	81.3	73.7	74.0	61.4	98.5	28.5	40.9	14.2		
	(6.9)	(2.7)	(4.1)				20.1	(5.5)			
9	74.4	79.3	72.8	72.5	60.4	98.3	28.2	39.9	14.7		
	(4.8)	(3.6)	(>0)				19.9	(2.7)			
14	104.8	85.5	74.8	80.7	60.1	111.9	26.3				
							25.7				
16a	103.8	83.6	78.9	71.8	65.0	111.7	26.3	46.1	14.4	126.2,	127.7
		(11.2)	(5.0)	(7.5)	(6.2)		25.8	(9.2)		128.4,	134.4
16b	104.1	84.0	79.8	72.6	65.6	111.2	26.6	46.7	11.4	122.4,	127.6
		(9.5)	(1.5)	(2.5)	(3.0)		26.3			128.8,	134.9

When passing from **6** to **7**, one can observe significant α- and β-effects resulting from the replacement of the hydroxyl group at C-2 by a diethylaminophosphite group, the down-field shift being 7.9 ppm for C-2, and 5.7 and 5.9 ppm for C-1 and C-3, respectively. This fact together with a C—P spin coupling at C-1, C-2 and C-3, and appearance of the signals belonging to the carbons of the ethyl radicals confirm the structure of **7**.

Compound **7** undergoes ready oxidation and sulfurization to give 3,5-O-isopropylidenexylitane 2-tetraethyldiamidophosphate **8** and 3,5-O-isopropylidenexylitane 2-tetraethyldiamidothiophosphate **9**. The ^{31}P n.m.r. spectra of these compounds contain lone signals (δ 16.8 and 78.8 ppm). This fact together with the p.m.r. spectra showing a higher resolution as compared with that of **7** (see the Experimental Section) substantiate the structure of the products obtained.

We have also carried out phosphorylation studies of xylitane **10** with an excess of 2 (1:5). In this case xylitane diphosphite **11** was formed as two geometric isomers whose ratio changes on storage:

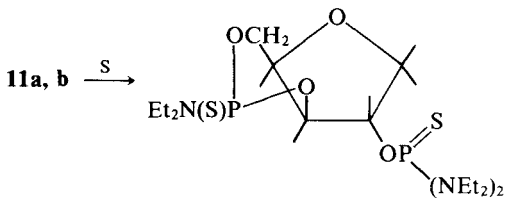


10 **11a, b**

a Et_2N eq
b Et_2N ax

The ^{31}P n.m.r. spectra of the product obtained by distillation contains three signals. The band with δ 134 ppm corresponds to an acyclic diamidophosphite moiety (cf. the spectrum of **7**, δ 137 ppm). Two bands (δ 141 and 130 ppm) whose total intensity is equal to the intensity of the first signal are characteristic of geometrically isomeric 2-amino-1,3,2-dioxaphosphorinans[5] including those from the xylitane series.[1] The p.m.r. spectrum also confirms the structure of the products obtained in that there are symmetrical multiplets of the methyl protons of the diethylamido groups of the acyclic moiety (δ 0.86 ppm for 12 H) and the cyclic moiety (δ 1.25 ppm for 6 H), a multiplet of the methylene N-ethyl protons (δ 2.92 ppm for 12 H), a multiplet of the methylene H-1 and H-5 protons (δ 3.53–3.82 ppm for 4 H) and an unresolved multiplet from H-2, H-3 and H-4 (δ 3.90–4.19 ppm).

Diamidophosphites **11a,b** undergo ready sulfurization to give a mixture of the geometric isomers of xylitane diamidothiophosphates **12a,b**:



12a, b

The ^{31}P n.m.r. spectrum of **12a,b** agrees with this structure in that there exists a signal typical of the acyclic moiety (δ 77.7 ppm) and two signals of stereoisomeric cyclic phosphorus moieties (δ 68.6 and 66.2 ppm).

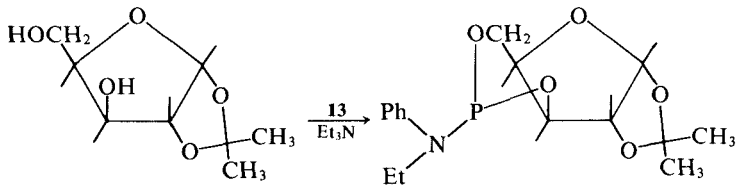
During our studies of amidophosphites (pentafuranose derivatives) we have synthesized cycloamidophosphites with an unsymmetrically substituted N-atom at phosphorus. Recently a description has been made of cycloamidophosphites based on α-D-xylofuranose, viz., 1,2-0-isopropylidene-α-D-xylofuranose 3,5-dimethyl-and 3,5-diethylamidophosphites.[6] Isomers with equatorially arranged dialkylamido groups were shown to have the highest stability and to form in a higher yield. It was interesting to synthesize a similar derivative where one of the alkyl groups is replaced by a phenyl group and to study the stereochemistry of this compound.

N-ethylanilinedichlorophosphite was prepared on the interaction of a two-fold excess of phosphorus trichloride with N-ethylaniline in the presence of triethylamine followed by the distillation. The product obtained (**13**) was used as phosphorylating agent.

$$C_6H_5EtNH + PCl_3 \xrightarrow{Et_3N} C_6H_5EtNPCl_2$$

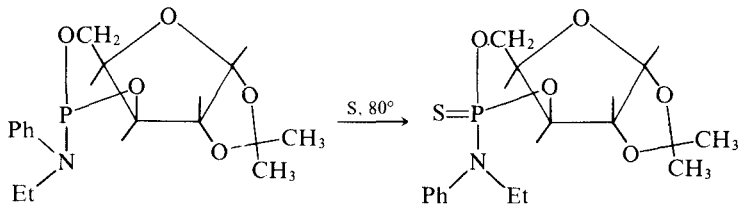
Its ^{31}P n.m.r. spectrum contained a signal (δ 155.7 ppm) corresponding to the assigned structure.

1,2-O-isopropylidene-α-D-xylofuranose **14** was phosphorylated by compound **13** at room temperature in the presence of two equimoles of triethylamine to give a theoretical amount of triethylamine chlorohydrate:



14 **15a, b**

The ^{31}P n.m.r. spectrum of the reaction mixture contained two signals (δ 137.8 and 121.5 ppm), which corresponds to two geometric isomers, with one isomer predominating. In contrast to the xylitane and 1,2-O-isopropylidenexylose diethylamidophosphite derivatives, for which the preponderating species was the isomer with an equatorially arranged amido group (and, consequently, with a larger down-field shift in the ^{31}P n.m.r. spectrum [1,6]), for N-(ethyl)-anilido-phosphite **15** the isomer with an axially arranged substituent (an up-field shift of δ 121.5 ppm) dominates. The latter isomer was obtained separately by preparative t.l.c. For the purpose of stabilization, technical grade amidophosphites were treated with elementary sulfur at 80°C. The resulting stable thioamidophosphates were isolated by column chromatography on silica gel. In this case two stereoisomeric 1,2-O-isopropylidene-α-D-xylofuranose N-(ethyl)-phenylamidophosphates (**16a,b**) were obtained, differing in their ^{31}P and ^{13}C n.m.r. chemical shifts and spin coupling constants:



15a, b **16a, b**
a: Ph(Et)N eq
b: Ph(Et)N ax

Isomer **16a** possesses a higher chromatographic mobility than **16b** and its ^{31}P n.m.r. chemical shift occurs at lower field (δ 64.7 ppm). Consequently, by analogy with 1,3,2-dioxaphosphorinan-2-ones and -2-thiones[7], **16a** can be assigned a configuration with an equatorial arrangement of the amid substituent. Accordingly, the second isomer (**16b**, ^{31}P n.m.r. δ 52.5 ppm) contains an axial amido group.

The observed ^{3}J P—C-4 constant in the ^{13}C n.m.r. spectrum for **16b** is 4.8 Hz lower than the same constant for **16a** (see Table I), which suggests an equatorial arrangement of the P=S group in **16b**[8] and, thus, agrees with the adopted configuration for phosphorus. Comparison of the ^{13}C n.m.r. spectra for **16a,b** and the original 1,2-O-isopropylidene-α-D-xylofuranose **14** shows a noticeable down-field shift for the C-3 and C-5 signals (by about 4–5 ppm), resulting from the electron-acceptor effect of the thioamidophosphate group. It is to be noted that the ^{13}C—P constants for **16b** are smaller that that for **16a** (see Table I).

Thus it turns out that in the case of xylose N-(ethyl) phenylamidophosphites an isomer with an axial rather than equatorial amidophosphite group is formed preponderantly (ax:eq = 2:1), which agrees with the data obtained earlier for diphenylamides and pyrrolides in the 1,3,2-dioxaphosphorinan series.[9]

It has been briefly stated by us earlier[10] that some of the carbohydrateamidophosphites can be used in the synthesis of complex palladium catalysts for nitrobenzene hydrogenation. This work presents results of studies of how it will be possible to use pentose amidophosphites as ligands of complex palladium catalysts for asymmetrical hydrogenation. Itaconic acid was used as the substrate.

We used for studies the compounds described in this paper, viz., 2,3-O-isopropylidene-α-methyl-D-ribofuranose 5-tetraethyldiamidophosphite **3**, xylitane 2; 3,5-triamidodiphosphite **11a** and previously synthesized[6] 1,2-O-isopropylidene-α-D-xylofuranose 3,5-diethylamidocyclophosphite **17**. The interaction of these pentose amidophosphites (L) with bis-(π-allyl palladium chloride) in dry benzene at 20°C afforded the synthesis of optically active palladium complexes $(C_3H_5)Pd(L)Cl$ (**18,19,20**) where L = **3, 11a** and **17,** respectively. The properties of the complexes are given in Table II. Subsequent reaction of **18** and **20** with $NaBH_4$ in an ethyl alcohol solution, as described elsewhere,[11] gave high-active catalysts for itaconic acid hydrogenation. Thus the times of the complete hydrogenation of $2.5.10^{-4}$ mole of itaconic acid were 5.0, 8.3 and 3.6 min for the catalysts obtained from **18, 19** and **20**, respectively.

The hydrogenation of itaconic acid gave 2-methyl-succinic acid which was isolated, purified by column chromatography and identified by the p.m.r. spectra and t.l.c. As follows from the results of Table II, the only way to obtain an optically active R-(+)-2-methyl-succinic acid is the use as the ligand of bidentate compound **11a.** The small optical yield in this case is probably due to a low stability of the intermediate active palladium complexes. This is substantiated by the formation of metallic palladium on hydrogenation and is consistent with the data reported elsewhere.[12]

EXPERIMENTAL

All the phosphorus-(III)-derivatives were handled dry argon. t.l.c. was carried out on the Silufol plates (Czechoslovakia) and also on silica gel L 100–250 and alumina of the second degree of activity in the systems:

A—benzene-dioxane, 3:1

B—benzene-dioxane, 5:1

C—chloroform-methanol, 9:1.

TABLE II

Physical, chemical and catalytic properties of palladium-pentose amidophosphite complexes

Complex	Ligand (L)	Color	M.p. (dec.), °C	R_f (Al_2O_3, system B)	^{31}P n.m.r. (DMFA), ppm	I.r. spectrum, cm^{-1}	$[\alpha]_D^{17}$ (c in CH_2Cl_2)	Elementary analysis: General formula; Found, %: C, H, P; Calc., %: C, H, P	Properties of $C_3H_5Pd(L)Cl$-based catalytic systems: H_2 mole/Pd mole.min	Optical yield, %
18	**3**	light-yellow	(over 103)	0.64	131.6	ν (P=N) 950–960, ν (P=OC) 1020–1040	−35.0° (5.43)	$C_{20}H_{40}O_5N_2PClPd$ 43.1; 7.3; 5.2 42.8; 7.1; 5.5	5.0	0
19	**11a**	bright-yellow	45–48	0	132.7 132.4	ν (P=N) 950–960, ν (P—OC) 1020–1070	+3.0° (1.19)	$C_{20}H_{42}O_4N_3P_2ClPd$ 40.1; 7.0; 10.2 40.6; 7.1; 10.5	8.3	4.6
20	**17**	light-yellow	(over 110)	0.20	133.3	ν (P=N) 950–970, ν (P=OC) 1030–1040	+8.4 (0.72)	$C_{15}H_{27}O_4NPClPd$ 38.3; 5.9; 6.1 38.0; 5.7; 6.5	3.6	0

^{1}H n.m.r. spectra were measured on a JNM-100 spectrometer, ^{13}C spectra—on a Brucker WP-80 (20.1 MHz) spectrometer, ^{31}P n.m.r. spectra—on a Brucker HX-90E (36.43 MHz) spectrometer (with 85% phosphoric acid as the external standard). Optical rotation was recorded on a Perkin-Elmer 141 polarimeter.

1-O-Methyl-2,3-O-isopropylidene-β-D-ribofuranoside 5-tetraethyldiamidophosphite ***3.***

A mixture of 4 g of **1** and 8 g of **2** was heated at 120–130°C for 4–5 h under argon until the calculated amount of diethylamine was distilled off. The excess of the phosphorylating agent was removed under reduced pressure, the residue distilled in high vacuum to afford compound **3,** a syrup; yield 5.7 g (77%), b.p. 110–115°C/10^{-3} mm, n_D^{20} 1.4690, d_4^{20} 1.0706, R_f 0.72 in the system A, R_f 0.9 in the system B, δ_P 138 ppm. Found for $C_{17}H_{35}O_5N_2P$, %: C, 53.44; H, 9.17; P, 8.42. Calc., %: C, 53.95; H, 9.32; P, 8.18.

1-O-Methyl-2,3-O-isopropylidene-β-D-ribofuranoside 5-tetraethyldiamidophosphate ***4.***

Nitrogen oxides were passed through a solution of 2 g of **3** in 5 ml of abs. dioxane for 4 h, then the dioxane was removed under reduced pressure in vacuo, the residue passed through an alumina column to afford compound **4,** a syrup; yield 1.94 g (83%), n_D^{20} 1.4600, R_f 0.27 in the system B. Found for $C_{17}H_{35}O_6N_2P$, %:C, 51.96%; H, 9.28; P, 7.66. Calc., %:C, 51.76; H, 8.94; P, 7.85.

1-O-Methyl-2,3-O-isopropylidene-β-D-ribofuranoside 5-tetraethyldiamidothiophosphate ***5.***

To a solution of 2 g of **3** in 5 ml of abs. dioxane was added 0.17 g of sulfur and the mixture was stored overnight at 22°. The dioxane was distilled off, the residue washed with hexane, and recrystallization from a hexane-(abs.)-ether mixture gave compound **5**; yield 1.9 g (90%), m.p. 80°C, R_f 0.54 (100% of chloroform). Found for $C_{17}H_{35}O_5N_2P$, %:C, 49.74; H, 8.59; P, 7.54, S, 7.81. Calc., %:C, 49.53; H, 8.75; P, 7.70; S, 8.06.

3,5-O-Isopropylidene-xylitane 2-tetraethyldiamidophosphite ***7.***

15 g of 3,5-O-isopropylidenexylitane **6** and 45 g (3 mol. equiv.) of hexaethyltriamidophosphite were heated to 110–120°C for 3 h under argon. The reaction was monitored by the amount of the diethylamine liberated and by t.l.c. The excess of the phosphorylating agent was removed under reduced pressure and the residue distilled in high vacuum; yield 20.7 g (69%), b.p. 113–118°C/10^{-4} mm, d_4^{20} 1.0705, n_D^{20} 1.4790, R_f 0.74 in the system A,R_f 0.85 in the system B, δ_P 137 ppm. ^{1}H n.m.r. spectrum (δ, ppm, benzene): H-2, H-3, and H-4, 3.78–4.06, narrow multiplet; 2 × H-1, 2 × H-5, narrow multiplet centered at 3.54; CH_2N, multiplet centered at 2.70; $(CH_3)_2C$, 1.10, 1.18, two singlets; CH_3CH_2N, multiplet centered at 0.92. Found for $C_{16}H_{33}O_4N_2P$, %:C, 55.45; H, 9.78; P, 9.17. Calc., %:C, 55.15; H, 9.54; P, 8.89.

3,5-O-Isopropylidene-xylitane 2-tetraethyldiamidophosphate ***8.***

Nitrogen oxides were passed through a solution of 15 g of 3,5-O-isopropylidene-xylitane 2-tetraethyldiamidophosphite **7** in 75 ml of abs. dioxane for 7 h at room temperature. The reaction was monitored by t.l.c. and ^{31}P n.m.r. method. The product was distilled in vacuo; yield 2.7 g (86%), b.p. 126°C/10^{-3} mm, n_D^{20} 1.4680, R_f 0.48 in the system A, R_f 0.27 in the system B, δ_p 16.8 ppm. Found for $C_{16}H_{33}O_5N_2P$, %: C, 53.20; H, 8.98; P, 8.41. Calc., %:C, 52.73; H, 9.13; P, 8.50.

3,5-O-Isopropylidenexylitane 2-tetraethyldiamidothiophosphate ***9.***

To a solution of 3 g of **7** in 8 ml of abs. dioxane was added 0.5 g of sulfur, the reaction proceeding at room temperature with slight self-heating. The dioxane was removed in vacuo, the residue treated with cold hexane to afford a crystalline product; yield 2.9 g (88%) after recrystallization from hexane(abs)-ether mixture, m.p. 49°C, R_f 0.85 in the system B, δ_P 78.8 ppm. ^{1}H n.m.r. spectrum (δ, ppm. J, Hz, benzene): H-1_{exo}, 3.75, singlet; H-2, 4.73, double doublets, J_{2-1} 10.5, J_{2-P} 3.0; H-3, 4.13, broadened singlet, J_{3-P} 0.4; H-4, 4.0, double doublets, J_{4-5} 9.2, $J_{4-5'}$ 3.0; 2 × H-5 and H-1_{endo}, 3.69–3.45, overlapping multiplets; CH_2N, multiplet centered at 2.81; $(CH_3)_2C$, 1.12, 1.06, two singlets; CH_3CH_2N, multiplet centered at 0.98. Found for $C_{16}H_{33}O_4N_2PS$, %:C, 50.14; H, 8.88; P, 7.94; S, 8.40. Calc., %:C, 50.51; H, 8.74; P, 8.14; S, 8.42.

Xylitane 2-tetraethyldiamidophosphite-3,5-diethylamidophosphite ***11***.

A mixture of 6.7 g of xylitane and 24.7 g (2 mol. equiv.) of **2** was heated at 110–120°C for 4 h, the calculated amount of diethylamine being distilled off. The residue was distilled in vacuo; yield 8.6 g (42%), b.p. 133–135°C/10^{-4} mm, n_D^{20} 1.4910, R_f 0.73 in the system A, R_f 0.85 in the system B, δ_P 134, 141.5 and 130.8 ppm. Found for $C_{17}H_{37}O_4N_3P_2$, %: C, 50.18; H, 9.15; P, 14.87. Calc., %: C, 49.87; H, 9.11; P, 15.13.

Xylitane 2-tetraethylamidothiophosphate-3.5-cyclodiethylamidothiophosphate ***12***.

To a solution of 2 g of **11** in 5 ml of abs. dioxane was added 0.18 g of sulfur, and the mixture was stored overnight at room temperature. The dioxane was distilled off, the residue treated with hexane to afford compound **12**; yield 2.1 g (90%), a syrup, R_f0.75 in the system B, δ_P 77.7, 68.6 and 66.2 ppm. Found for $C_{17}H_{37}O_4N_3P_2S_2$, %: C, 42.98; H, 8.03; P, 13.21; S, 13.14. Calc., %: C, 43.12; H, 7.81; P, 13.08; S, 13.54.

1,2-O-Isopropylidene-α-D-xylofuranose 3,5-N-ethyl-N-phenylamidophosphite ***15a,b***.

To a solution of 8.25 g (0.06 mole) of phosphorus trichloride in 60 ml of abs. benzene were added gradually with stirring 3.75 g (0.03 mole) of N-ethylaniline and 3.03 g (0.03 mole) of triethylamine in 50 ml of abs. benzene. The mixture was stored for 2 h. Then the triethylamine chlorohydrate was filtered off, the excess of the phosphorus trichloride and the solvent were removed in vacuo at 30°C, and N-ethyl-N-phenylamidodichlorophosphite **13** was distilled; yield 5.7 g (83%), b.p. 110–117°C/7 mm, n_D^{20} 1.5065. To a mixture of 4.1 g (0.02 mole) of 1,2-O-isopropylidenexylose and 2.8 ml (0.02 mole) of triethylamine in 60 ml of abs. dioxane was added dropwise with stirring a solution of 4.44 g (0.02 mole) of N-ethyl-N-phenylamidodichlorophosphite in 50 ml of abs. dioxane. The mixture was then stirred at room temperature for 5 h, the triethylamine chlorohydrate filtered off, its precipitate washed with abs. dioxane and the solvent evaporated, the residue obtained having δ_P 137.8, 121.5 ppm. The residue was purified by preparative t.l.c. on alkaline Al_2O_3, and 15 b was washed out with a benzene-dioxane mixture (9:1); yield 0.67 g (10%), a sirup, n_D^{20} 1.4363, R_f 0.76 in benzene-dioxane (9:1), δ_P 121.6 ppm. Found for $C_{16}H_{22}O_5NP$, %: C, 57.01; H, 6.22; P, 8.86. Calc., %: C, 56.63; H, 6.53; P, 9.13.

1,2-O-Isopropylidene-α-D-xylofuranose 3,5-N-ethyl-N-phenylamidothiocyclophosphate ***16a,b***.

To a mixture of 4.1 g (0.02 mole) of 1,2-O-isopropylidenexylose, 2.8 ml (0.02 mole) of triethylamine and 4.44 g (0.02 mole) of **13** obtained as described above (at about 22°C for 5 h), after separation of triethylamine chlorohydrate, was addded 0.7 g of finely ground sulfur. The suspension obtained was heated at 80°C for 3 h, and the solvent distilled off. The residue was chromatographed on a silica gel column, the compounds eluated successively with mixtures of benzene-dioxane (9:1, 5:1, 3:1) and benzene-dioxane-methanol (3:1:0.2) to afford an equatorial isomer 3,5-cyclothiophosphate **16a**, a dark syrup; yield 1.5 g (23%), $[\alpha]_D^{20}$ −75° (c 0.3, benzene), R_f 0.85 in the system A, R_f 0.72 in the system B, δ_P 64.7 ppm. Found for $C_{16}H_{22}NO_5PS$, %: C, 52.12; H, 6.27; P, 8.41. Calc., %: C, 51.74; H, 5.97; P, 8.34. Then the axial isomer 16b was eluated as a syrup; yield 3.4 g (44%), R_f 0.22 in the system A, R_f 0.32 in the system B, $[\alpha]_D^{20}$ −102° (c 0.4, benzene), δ_P 52.5 ppm. Found for $C_{16}H_{22}NO_5PS$, %: C, 52.21; H, 5.87; P, 8.12. Calc., %: C, 51.74; H, 5.97; P, 8.34.

Synthesis of complexes $C_3H_5Pd(L)Cl$ ***18–20***.

To a solution of 10^{-3} mole of $(C_3H_5PdCl)_2$ in 10 ml of dry benzene was gradually added a solution of 2.10^{-10} mole of **3**, or **11a**, or **17** in 10 ml of benzene. The solvent was distilled off at 30°C. Complex compounds **18** and **20** were purified by column chromatography (Al_2O_3, system B), and **19**—by its twice reprecipitation from benzene with hexane.

Synthesis of $C_3H_5Pd(L)Cl$*-based catalytic systems and methods of itaconic acid hydrogenation.*

10 ml of a solution of 5.10^{-5} mole of the $C_5H_5Pd(L)Cl$ complex in 99.5% ethylalcohol was introduced into a reactor for hydrogenation and treated with a 10-fold volume of oxygen. Then sodium borohydrate (0.004g) was introduced in a slow oxygen current. The reaction mixture was shaken at 30°C for 20 min. In this case the solution changed its color from light-yellow to dark-brown. Then the reactor was successively ventilated with 10-fold excesses of nitrogen and hydrogen. 10 ml of a solution of $2.5.10^{-4}$ mole of itaconic acid (recrystallized from methanol) in 99.5% ethylalcohol were introduced through the reac-

tor silicon membrane. The hydrogenation was taken to begin at the instant the reactor was set in motion (700–800 roc/min). The reaction was monitored by hydrogen absorption. The hydrogenation process took place at 30°C and $P_{H_2} = 1$ atm.

Isolation and purification of 2-methyl-succinic acid.

After hydrogenation the reaction mixtures were centrifuged, the metallic palladium residue removed (found 96% of Pd), the colorless clear solution evaporated to a minimum volume and passed through a column with a silica gel 40/100μm, eluent—benzene:dioxane-acetic acid (90:25:4), to afford 2-methyl-succinic acid. The optical yield of the itaconic acid hydrogenation was found from the optical rotation value (+)-2-methyl-succinic acid, $[\alpha]_D^{20}$ +17.09° (alcohol).[12]

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