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Synthesis and evaluation in asymmetric hydrogenation of carbohydrate-derived 1,3-bisphosphines*

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ABSTRACT

1,3-Bisphosphines and 1,3-phosphine sulfides have been prepared from 1,6-anhydro-β-D-glucopyranose in view of their application as bidentate ligands in transition-metal-catalyzed asymmetric hydrogenation. Reaction of 1,6:3,4-dianhydro-2-*O*-(*p*-toluenesulfonyl)-β-D-galactopyranose (**1**) with Ph_2PH in the presence of $AlMe_3$ gave 1,6:2,3-dianhydro-4-deoxy-4-(diphenylphosphino)-β-D-mannopyranose (**6**) which, upon treatment with $LiPPh_2$, led to 1,6-anhydro-2,4-dideoxy-2,4-bis(diphenylphosphino)-β-D-glucopyranose (**9**). Esterification of **9** with 1-naphthoyl chloride yielded the naphthoate **11**. Upon exposure to air, **9** and **11** were oxidized to the corresponding bisphosphine dioxides **10** and **12**. Treatment of **6** with PhSH and DBU led to 1,6-anhydro-2,4-dideoxy-4-(diphenylphosphino)-2-phenylthio-β-D-glucopyranose (**13**) and, after oxidation with air, to the corresponding phosphine oxide **14**. Similarly, **1** was transformed into 1,6-anhydro-2,4-dideoxy-2-(diphenylphosphino)-4-phenylthio-β-D-glucopyranose (**16**) and its oxide **17**. Attempted ring opening of **1** by Ph_2PH/KOH or by $Ph_2PH/AlMe_3$ and oxidative work-up gave 1,6-anhydro-3,4-dideoxy-4-(diphenylphosphoryl)-β-D-*threo*-hex-3-enopyranose (**3**). In the presence of HCl, both **3** and **7** (obtained by air oxidation of **6**) were transformed into 1,6-anhydro-2-chloro-2,4-dideoxy-4-(diphenylphosphoryl)-β-D-glucopyranose (**8**). The structure of **8** was established by an X-ray analysis. ^1H-, ^{13}C-, and ^{31}P-n.m.r. spectroscopy showed that the phosphines (**9, 11, 13**, and **16**) prefer a $^1C_4$ and the phosphine oxides (**8, 10, 12, 14,** and **17**) a $B_{3,O}$ conformation. The results of the rhodium- or ruthenium-catalyzed asymmetric hydrogenation with the phosphines **9, 11, 13,** and **16** as ligands are presented. In the hydrogenation of olefins (geraniol or the α-acetamidoacrylic acid **19**), low enantioselectivety is observed. Better enantiomeric excesses were obtained in the hydrogenation of α- and β-ketoesters (ketopantolactone, e.e. < 48%; methyl 3-oxotetradecanoate, e.e. < 55%).

INTRODUCTION

Homogeneous asymmetric catalysis by transition metal complexes with chelating bisphosphines has provided practical syntheses of many enantiomerically pure substances. The commonly used ligands are 1,2- 1,3-, and 1,4-bisphosphines, giving rise to chelates possessing five-, six-, and seven-membered rings[1,2]. Most of the research has focused on 1,2- and 1,4-bisphosphines, and this has led to the industrial application of

* Dedicated to Professor Grant Buchanan on the occasion of his 65th birthday.
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some bisphosphines such as BINAP[3,4]. There are only a few reports on the use of enantiomerically pure 1,3-bisphosphines as ligands[5-8].

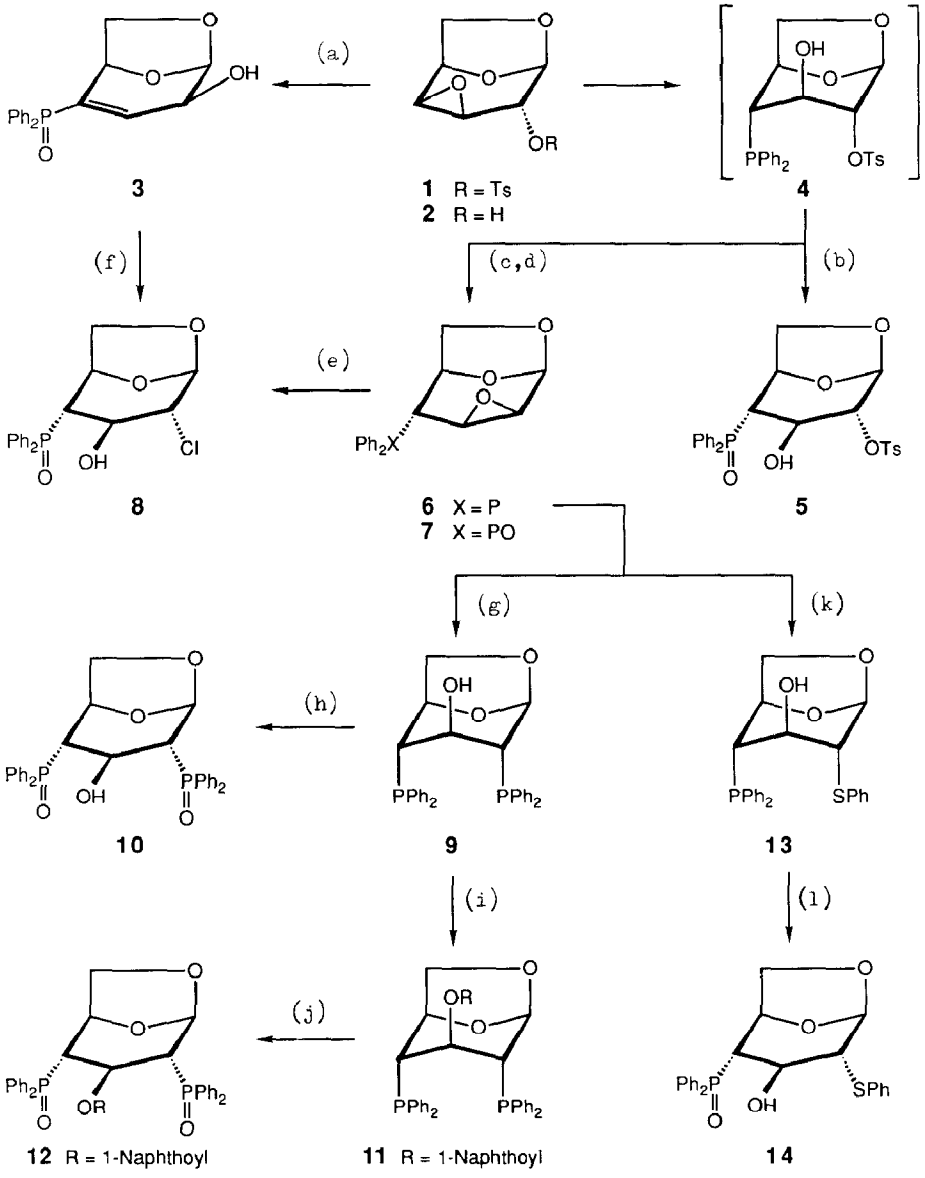
Two methods for the synthesis of 1,3-bisphosphines have been described. The first is based on the reaction of 1,3-ditosylates with alkali diphenylphosphides[2]. Almost all 1,3-bisphosphines were prepared by this method. 1,3-Bisphosphines were also obtained by the reaction of 2,3-epoxytosylates[5] or 2,3-epiminotosylates[9] with alkali diphenylphosphides. Unless the ring opening of such epoxides at position 3 is facilitated by an appropriate substituent such as a phenyl group, mixtures of 1,3- and 1,2-bisphosphines were obtained.

Diphosphorus derivatives of carbohydrates, such as protected 2,3-bis-*O*-(diphenylphosphino)-D-glucopyranosides[10] and 1,3- and 1,5-bisphosphines derived from glucose and galactose[11,12], have been used in enantioselective hydrogenation. Our approach to 1,3-bidentate phosphines makes use of the well established sequence of regioselective epoxide-ring opening and closing[13,14] from **1**, which has been prepared from 1,6-anhydro-*β*-D-glucopyranose (levoglucosan) in two steps and in a moderate overall yield[15].

RESULTS AND DISCUSSION

Whereas treatment of the epoxytosylate **1** (Scheme 1) with lithium diphenylphosphide from −90° to room temperature gave the known alcohol **2** (ref. 16), which was retransformed into **1**, reaction with diphenylphosphine in the presence of potassium hydroxide (aqueous Me_2SO, Ar) led, after work-up in the presence of air[17], to the unsaturated phosphine oxide **3**. The i.r. spectrum of **3** shows a band of a carbon–carbon double bond at 1625 cm^{-1} and an OH band at 3560 cm^{-1}. The presence of the diphenylphosphoryl group was indicated by u.v. absorptions at 240 (ε 3065), 266 (ε 1797), and 273 nm (ε 1457). In the ^1H-n.m.r. spectrum, H-3 at 6.00 p.p.m. couples with P-4 (17.85 Hz). The ^{13}C-n.m.r. spectrum shows signals for the anomeric carbon at 100.5 and for two olefinic carbons at 137.0 (C-4) and 141.9 p.p.m. (C-3). These two signals each exhibit a phosphorus coupling, 95.8 Hz for C-4 and 5.0 Hz for C-3, characteristic for α,β-unsaturated phosphine oxides[18]. The positive shift value of the ^{31}P signal (34.23 p.p.m. relative to phosphoric acid) indicates the presence of a phosphine oxide. The $J_{1,2}$ value of 2.3 Hz indicates a *cis* rather than a *trans* arrangement of H-1 and H-2. This interpretation is backed by a long-range coupling of 0.7 Hz between H-2 and H-6exo. The D-*threo* configuration is rationalized by a reaction mechanism that assumes opening of the epoxide ring followed by formation of the 2,3-anhydro ring, oxidation of the phosphine to the phosphine oxide, and *β*-elimination[14].

In the presence of trimethylaluminium[19], however, diphenylphosphine reacted with **1** to give the desired phosphine **4**, which was rapidly oxidized by air to the oxide **5** (87% yield). In order to avoid purification of the air-sensitive phosphine intermediates, we tried to obtain the bisphosphine in a one-pot reaction from **1** by adding various amounts of butyl-lithium to crude **4**. This reaction gave complex mixtures. However, a one-pot conversion of **1** into the epoxyphosphine **6** (70%) was realized by *in situ*



Scheme 1. (a) Ph_2PH, aq. KOH, Me_2SO, r.t.; AcOH, 22% *or* Ph_2PH, $AlMe_3$, CH_2Cl_2, $-38°$; NaOMe, $-20°$, 16%. (b) Ph_2PH, $AlEt_3$, benzene, r.t.; AcOH, 24% *or* Ph_2PH, $AlMe_3$, CH_2Cl_2, $-38°$; H_2O_2, $CHCl_3$–acetone–AcOH, 87%. (c) Ph_2PH, $AlMe_3$, CH_2Cl_2 $-38°$; NaOMe, $-20°$, 70%. (d) Air, 1:1:1 Et_2O–acetone–$CHCl_3$, 82%. (e) $CHCl_3$. (f) Conc. HCl, $CHCl_3$. (g) Ph_2PH, BuLi, tetrahydrofuran, 57%. (h) H_2O_2, AcOH, 2:1 $CHCl_3$–acetone, 0°, 71%. (i) 4-dimethylaminopyridine, pyridine, naphthoyl chloride, CH_2Cl_2, 84%. (j) as (h), 84%. (k) PhSH, DBU, benzene, 47%. (l) as (d), 85%.

treatment of **4** with a large excess of NaOMe at −20°. It was important to evaporate the solvent at a low temperature (≤ 20°), in order to avoid oxidation of **6** and β-elimination to the phosphine oxide **3**. Oxidation of **6** by air gave the epoxyphosphine oxide **7** which, upon dissolution in chloroform (containing traces of HCl), was transformed into the chlorohydrin **8** (82%). Stronger acidic conditions (conc. HCl in $CHCl_3$) were necessary for the conversion of **3** into **8**. The postulated *gluco* configuration of **8** requires inversion of configuration at C-2 of **3**, indicating that **3** is in equilibrium with the corresponding oxirane by intramolecular β-addition. Acid-catalyzed opening of the oxirane ring would then form **8**. Treatment of **6** with diphenylphosphine in the presence of trimethylaluminium gave complex mixtures, while the reaction between **6** and lithium diphenylphosphide in the presence of a small excess of diphenylphosphine[20] afforded the desired bisphosphine **9** (57%), which was oxidized (air) to the crystalline bisphosphine dioxide **10** (71%). In order to change the polarity of the ligand and to shield the bisphosphine from the top face (relative to the plane through the pyran ring), **9** was esterified with 1-naphthoyl chloride to give **11** (84%), which was oxidized to **12** (84%) using hydrogen peroxide at low temperature.

The structures of the products are deduced from their analytical data. In the ^{31}P-n.m.r. spectra (Table III), negative shift values show the presence of phosphines (**6**, **9**, and **11**), and positive ones the presence of phosphine oxides (**5**, **8**, **10**, and **12**). Characteristic $^1J_{C,P}$ coupling values[21] are observed in the ^{13}C-n.m.r. spectra of the phosphines ($^1J_{C,P}$ 15–19 Hz) and phosphine oxides ($^1J_{C,P}$ 66–70 Hz). The heteronuclear coupling constants $J_{H,P}$ and $J_{C,P}$ (Tables II and IV) show that the phosphinyl moiety of **6** is attached at C-4. The upfield shifts for H-2, H-3, C-2, and C-3 (3.40, 3.03, 48.3, and 33.3 p.p.m., respectively) indicate the 2,3-epoxy function. The comparison of vicinal $J_{H,H}$ of **6** and **1** (Table II) reveals the configurational and conformational similarity of the C-2 to C-4 fragment. Thus, the value of 0 Hz for $J_{1,2}$ and $J_{2,3}$ of **1** and for $J_{3,4}$ and $J_{4,5}$ of **6** indicates a *trans*-relation of the corresponding hydrogens, while values between 3.2 and 4.8 Hz for $J_{3,4}$ and $J_{4,5}$ of **1** and for $J_{1,2}$ and $J_{2,3}$ of **6** indicate a *cis*-relation. The *cis* arrangement of H-3 and H-5 in **6** is indicated by long-range coupling ($J_{3,5}$ 1.0 Hz). Thus, **6** must have the *manno* configuration. This is in keeping with the expected *trans*-diaxial opening of the epoxide ring of **1** (ref. 13). The structure of **7** is supported by its elementary analysis, the signal for $[M + 1]^+$ at *m/z* 329 in its mass spectrum, and the absence of OH bands in its i.r. spectrum.

The small vicinal coupling constants $J_{2,3}$ and $J_{3,4}$ in the ^1H-n.m.r. spectra of **9** and **11** (Table II) indicate the *gluco* configuration and the $^1C_4$ conformation of the pyranose ring. All derivatives of levoglucosan, except 3-amino-3-deoxy derivatives[22], 2,4-diammonium-2,4-dideoxy salts[23], and 2,4-diadeninyl-2,4-dideoxy derivatives[24], adopt this conformation*. The monophosphine oxides **5** and **8** exhibit large $J_{3,4}$ (9.4–9.5 Hz) and

* MM2 calculations favour the $^1C_4$ over the $B_{3,O}$ conformation of levoglucosan by 1.4 kcal/mol (ref. 25). According to Alchemy calculations, the pyran rings in both conformations are flattened (dihedral angles R_{ax}-2/R_{ax}-3 and R_{ax}-3/R_{ax}-4, 150°–160°). The calculated chair conformation of levoglucosan is very close to its conformation in the crystalline state[26].

TABLE I

^{1}H-N.m.r. chemical shifts (p.p.m.) for compounds **1**, **3**, **5**, **6**, and **8**–**17** (400 MHz, $CDCl_3$)[a]

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6endo*	*H-6exo*	*OH*	*Arom. H*	*Me*
1	5.17	4.40	3.14	3.61	4.83	3.95	3.50	-	7.87–7.36	2.46
3	5.55	4.42	6.00	-	4.96	3.89	3.76	2.26	7.83 7.27	-
6	5.75	3.40	3.03	2.91	4.25	3.81	3.71	-	7.65–7.38	-
15	5.76	3.48	3.28	3.52	4.57	3.80	3.80	-	7.52–7.28	-
9	5.37	2.84	3.66	2.89	4.38	4.22	3.70	3.00	7.74–8.18	-
11	5.49	3.09[b]	5.31	2.90[b]	4.44	4.34	3.80	-	8.20–7.29	-
13	5.78	3.33	3.98	2.82	4.34	4.20	3.75	2.90	7.67–7.17	-
16	5.36	2.89	3.93	3.40	4.80	4.23	3.77	3.14	7.62–7.18	-
5	5.38	4.27	4.06	2.50	4.71	3.69	3.58	3.88	7.87–7.31	2.43
8	5.50	3.77	4.13	2.62	4.72	3.75	3.63	-	7.89–7.48	-
10	5.55	2.85	4.04	2.67	5.13	3.79	3.74	4.66	7.99–7.39	-
12	5.69	3.55	5.95	3.44	4.93	4.04	3.71	-	7.94 6.73, 8.71	-
14	5.59	3.17	3.96	2.69	4.68	3.75	3.64	4.08	7.86–7.22	-
17	5.50	2.85	4.05	3.13	4.68	3.82	3.71	4.41	7.85–7.23	-

[a] The unambiguous assignment is based upon decoupling experiments for compounds **3**, **5**, **6**, **8**, **9**, **11**, **12**, **15**, and **17**. [b] Attributions may be interchanged.

TABLE II

$J_{H,H}$ and $J_{H,P}$ Values (Hz) for compounds **1**, **3**, **5**, **6**, and **8–17**

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5a,5b}$	$J_{6a,6b}$	*Other* $J_{H,H}$
1	0	0	3.9	4.8	4.9	6.5	$J_{1,5}$ 1.5
3	2.4	2.2	-	-	4.2	7.2	$J_{1,5}$ 2.2, $J_{5,6a}$ 0.7, $J_{5,OH}$ 11.8
6	3.2	4.0	0	0	6.2	6.8	$J_{1,5}$ 1.0, $J_{5,6a}$ 1.4
15	3.1	3.6	0	0	5.9	7.2	$J_{1,5}$ 0.8, $J_{5,6a}$ 2.1
9	[a]	[a]	[a]	0	5.0	7.1	$J_{5,OH}$ 7.0
11	0	0.9	0.9	0	5.4	6.9	-
13	[a]	[a]	[a]	0	5.9	7.0	-
16	[a]	[a]	[a]	0	5.0	7.5	$J_{5,OH}$ 7.1
5	0	6.0	9.0	2.3	4.1	7.2	$J_{5,OH}$ 2.3
8	0	6.8	9.1	2.5	4.2	7.1	-
10	0	9.5	9.8	2.4	4.4	7.3	-
12	0	9.4	10.2	2.0	4.4	7.4	-
14	0	8.0	9.0	2.4	4.3	7.2	-
17	0.5	9.2	8.3	1.1	5.2	7.6	$J_{6a,6b}$ 0.6, $J_{5,OH}$ 1.8

Compound	$^2J_{3,P-4}$	$^2J_{4,P-4}$	$^3J_{5,P-4}$	$^4J_{6a,6b,P-4}$	$^2J_{1,P-2}$	$^3J_{2,P-2}$	$^3J_{3,P-2}$	*Other* $J_{H,P}$
1	-	-	-	-	-	-	-	-
3	18.0	-	4.6	0	-	-	-	$^3J_{1,P-4}$ 2.4
6	4.4	1.2	7.6	0	-	-	-	-
15	-	-	-	-	-	-	-	-
9	[a]	[a]	6.6	2.1	[a]	[a]	[a]	-
11	0	[a]	6.0	1.9	2.3	[a]	0	-
13	[a]	[a]	5.9	2.0	-	-	-	-
16	-	-	-	-	[a]	[a]	[a]	-
5	14.5	12.7	15.7	1.6	-	-	-	-
8	13.2	12.3	15.1	1.5	-	-	-	-
10	13.0	10.4	15.8	1.4	8.9	13.3	13.0	-
12	11.9	9.8	15.6	1.0	9.5	8.2	11.9	-
14	13.0	12.2	15.5	1.9	-	-	-	-
17	-	-	-	-	8.6	14.0	12.8	-

[a] Small coupling of < 2 Hz (corresponding signals appear as s with $W_{1/2} \sim 5$ Hz).

TABLE III

^{13}C-N.m.r. and ^{31}P-n.m.r. chemical shifts (p.p.m.) for compounds **3, 5, 6,** and **8–17** (50 or 81 MHz, $CDCl_3$)

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Me*	*Arom. C*	*C=O*	*P-2*	*P-4*
3	100.64	68.62	141.88	137.01	71.45	71.71	-	132.56–128.34	-	-	34.23
6	98.31	54.14	48.33	39.29	69.00	69.59	-	135.21–128.63	-	-	−14.19
15	98.19	54.15	49.34[a]	47.47[a]	71.94	68.51	-	133.26, 132.03, 129.39, 129.31	-	-	-
9	102.20	47.51[a]	67.53	45.74[a]	73.07	69.58	-	135.91–128.48	-	−16.15[b]	−20.12[b]
11	101.58	44.85[a]	69.07	43.75[a]	72.81	69.46	-	135.86–124.52	165.23	−15.57[b]	−18.75[b]
13	102.60	54.14	69.81	44.55	72.68	69.50	-	136.54–120.60	-	-	−15.38
16	102.17	46.50	69.96	53.58	76.12	68.27	-	136.06–127.22	-	−18.69	-
5	101.33	84.37	65.69	44.53	69.80	70.94	21.64	132.87–128.07, 145.10	-	-	36.98
8	104.07	63.86	69.04	46.17	70.06	71.04	-	132.65–128.24	-	-	36.65
10	97.80	50.20[a]	61.20	44.52[a]	69.65	70.13	-	132.61–128.19	-	34.52[b]	32.62[b]
12[c]	97.88	47.80[a]	69.66	44.85[a]	62.06	69.88	-	132.53–123.03	162.91	31.27[b]	29.32[b]
14	104.15	56.35	65.48	47.56	69.84	71.00	-	133.53–127.01	-	-	37.07
17	98.18	49.88	65.48	56.02	77.14	69.73	-	133.53–127.01	-	35.28	-

[a,b] Attributions may be interchanged. [c] $(CD_3)_2SO$ at 100°. Broad s of P-2 and P-4 (W_{50} 20.3 Hz).

TABLE IV

$J_{C,P}$ and $J_{P,P}$ Values (Hz) for compounds **3**, **5**, **6**, **8**–**14**, **16**, and **17**

Compound	$^2J_{1,P-2}$	$^2J_{2,P-3}$	$^2J_{3,P-4}$	$^3J_{1,P-3}$	$^2J_{3,P-4}$	$^3J_{3,P-4}$	$^1J_{4,1-4}$	$^3J_{1,P-4}$	$^3J_{5,P-4}$	$^3J_{P-2,P-4}$
3	-	-	-	-	11.7	5.0	95.8	15.0	0	-
6	-	-	-	-	0	27.0	15.3	13.6	6.5	-
9	14.5	17.6[a]	21.7	0	0	21.7	16.2[a]	11.4	4.8	101.5
11	13.9	19.1[a]	24.6	0	0	24.6	17.7[a]	10.1	4.0	98.7
13	-	-	-	-	0	19.3	17.6	12.1	4.7	-
16	15.5	19.2	17.9	0	-	-	-	-	-	-
5	-	-	-	-	12.8	0	68.5	0	11.1	-
8	-	-	-	-	12.3	0	67.9	0	11.0	-
10	3.9	66.5[a]	0	11.1[a]	10.0[a]	0	68.6[a]	0	11.1	4.1
12	0	65.7[a]					69.7[a]	0	-	
14	-	-	-	-	10.0	0	67.9	0	11.2	-
17	5.9	65.2	0	12.0	-	-	-	-	-	-

[a] Attributions may be interchanged. - Not defined (broad signals).

medium $J_{2,3}$ values (**5**, 6.0; **8**, 6.8 Hz). Dreiding models show that the pyran ring conformation in such a dioxa[3.2.1]bicyclo-octane system is restricted to a $^2C_1$ or a $B_{3,0}$ conformation, which implies that the value of the dihedral angle between H-3 and H-2 is similar to that between H-3 and H-4. The different values of $J_{3,4}$ and $J_{2,3}$ must therefore be caused mainly by different group-electronegativities of the substituents. According to the program Gandour[27], the value of $J_{3,4}$ (phosphoryl group) should be ~ 20% larger than that of $J_{2,3}$ (mesyloxy or chloro group). Irrespective of this factor, these coupling constants indicate the presence of either a chair–boat equilibrium or of a flattened $B_{3,0}$ conformation for **5** and **8**. No conformational equilibrium could be detected for a solution of **5** in CD_2Cl_2 at temperatures above 198 K. Since the chair–chair interconversion of tetrahydropyrans is frozen below 220 K (ref. 28), a flattened $B_{3,0}$ conformation with dihedral angles of ~ 150° for H-3,4 and H-2,3, is probable. Calculations by the Alchemy program also point towards a flattened $B_{3,0}$ form as the most stable conformation. This conformation has been postulated[29] for the 2,4-diammonium derivatives of levoglucan. The structure of **8** was established by an X-ray analysis (Fig. 1 and Tables V–VIII) that confirmed the flattened $B_{3,0}$ conformation of the pyran ring. The dihedral angles between H-2 and H-3 (159°) and between H-3 and H-4 (164°) correspond well to the above-mentioned coupling constants. The P–O bond is synclinal to the C-3/C-4 and the C-4/C-5 bonds. An intermolecular hydrogen bond between HO-3 and the oxygen atom of the phosphoryl group is observed (d = 1.85 Å; bond angle O–H–O' 173°, H–O'–P' 158°). The values of $J_{2,3}$ and $J_{3,4}$ (9.4–10.2 Hz) of the bisphosphine dioxides **10** and **12** agree well with a flattened $B_{3,0}$ form and indicate that the conformation of **10** is not influenced by an intramolecular hydrogen bond. The different conformations of the phosphines and phosphine oxides reflect the much larger steric demand of the diphenylphosphoryl group (A-value 2.74 kcal/mol, ref. 29) than of the

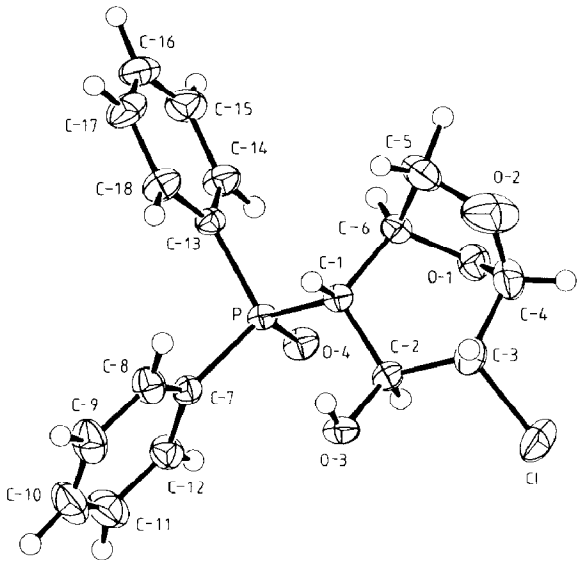


Fig. 1. A view of the molecule of 1,6-anhydro-2-chloro-2,4-dideoxy-4-(diphenylphosphoryl)-β-D-glucopyranose (**8**).

TABLE V

Crystal data and experimental conditions for the X-ray analysis of **8**

Molecular formula	$C_{18}H_{18}ClO_4P$
Formula weight	364.76
Crystal system	Monoclinic, non-centrosymmetric
Space group	$P2_1$
a	8.831 (1) Å
b	5.879 (1) Å
c	16.603 (2) Å
β	93.903 (9)°
Z	2
Volume	860.0 (2) Å^3
Calculated density	1.409 g.cm^{-3}
Radiation	Mo-K_α
λ (graphite-monochromated)	0.70926 Å
μ (Mo-K_α)	3.291 cm^{-1}
$F(000)$	380
Collection mode	Wyckoff ω-scans
Scan speed	Variable, 2.5–19.3°/min
Diffractometer	Nicolet-R3
Temperature of data collection	−60°
No. of measured reflections	3042
Unique total	2595 (R_{int} = 0.011)
Observed reflections [$I > 3\sigma(I)$]	2244
$2\Phi_{(max)}$	55°
Least-squares parameters	288
R	0.0297
wR (w = $[\sigma^2(F)]^{-1}$)	0.0307
Goodness-of-fit	1.597
Maximal and minimal residual electron density	0.31, −0.16 e.Å^{-3}

TABLE VI

Selected interatomic distances for **8** with e.s.d.s in parentheses

Bond	*Distance (Å)*	*Bond*	*Distance (Å)*
Cl C-3	1.797 (3)	O-2 C-5	1.417 (4)
P O-4	1.487 (2)	O-3 C-2	1.411 (3)
P C-1	1.818 (3)	C-1 C-2	1.552 (3)
P C-7	1.811 (3)	C-1 C-6	1.558 (9)
P C-13	1.813 (2)	C-2 C-3	1.529 (4)
O-1 C-4	1.403 (4)	C-3 C-4	1.529 (5)
O-1 C-6	1.433 (3)	C-5 C-6	1.515 (4)
O-2 C-9	1.405 (4)		

TABLE VII

Selected bond angles for **8** with e.s.d.s in parentheses

Bond angle	*Value (°)*	*Bond angle*	*Value (°)*
O-4 P C-1	111.9 (1)	Cl C-3 C-2	108.2 (2)
O-4 P C-7	111.3 (1)	Cl C-3 C-4	109.4 (2)
O-4 P C-13	111.0 (1)	C-2 C-3 C-4	112.1 (3)
C-1 P C-7	110.3 (1)	O-1 C-9 O-2	106.4 (3)
C-1 P C-13	104.4 (1)	O-1 C-9 C-3	109.7 (3)
C-7 P C-13	107.6 (1)	O-2 C-4 C-3	109.4 (3)
C-4 O-1 C-6	101.6 (2)	O-2 C-5 C-6	103.3 (3)
C-4 O-2 C-5	107.5 (3)	O-1 C-6 C-1	109.1 (2)
P C-1 C-2	111.3 (2)	O-1 C-6 C-5	101.3 (2)
P C-1 C-6	109.3 (2)	C-1 C-6 C-5	112.6 (2)
C-2 C-1 C-6	111.1 (2)	P C-7 C-8	123.4 (2)
O-3 C-2 C-1	111.6 (2)	P C-7 C-12	117.0 (2)
O-3 C-2 C-3	112.0 (2)	P C-13 C-14	117.3 (2)
C-1 C-2 C-3	112.1 (2)	P C-13 C-18	123.7 (2)

diphenylphosphino group (A-value unknown; A-value of PMe_2, 1.5 kcal/mol, ref. 30).

Phosphorus sulfur bidentate ligands are also useful in asymmetric catalysis[31], and both **13** (Scheme 1) and **16** (Scheme 2) should be available from **1**. Refluxing of a mixture of **6**, thiophenol, and DBU[32] gave slightly impure **13** in 93% yield. The contaminant could not be removed by chromatography or crystallization, but was preferentially oxidized and then removed by chromatography. Pure **13** was obtained in 47% yield and oxidized to **14** (85%). In order to obtain **16**, **1** was treated with thiophenol according to Vegh and Hardegger[33], to yield **15***. The reaction between **14** and lithium diphenylphosphide led to the crystalline phosphine **16**. In contact with air, **16** was transformed into **17**.

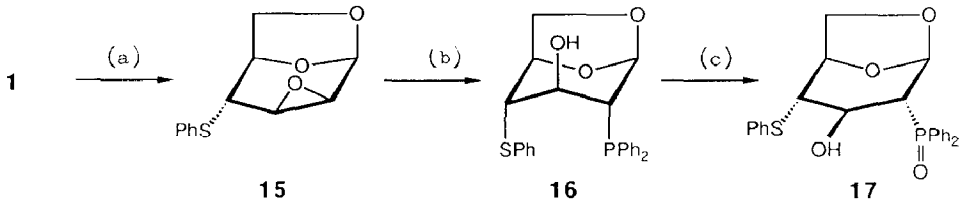
The vicinal $J_{H,H}$ values for **15** are very similar to those of **6** and indicate the *manno*

* In contrast to ref. 33, we found a positive $[\alpha]_D^{25}$ value (+15° instead of −13°).

TABLE VIII

Selected torsion angles for **8** with e.s.d.s in parentheses

Torsion angle	*Value (Å)*	*Torsion angle*	*Value (Å)*
O-4–P–C-1–C-2	−61.3 (2)	C-4–O-2–C-5–C-6	6.6 (3)
O-4–P–C-1–C-6	61.7 (2)	C-5–O-2–C-4–O-1	21.1 (3)
O-4–P–C-7–C-8	172.1 (2)	C-5–O-2–C-4–C-3	−97.3 (3)
O-4–P–C-7–C-12	−9.7 (2)	P–C-1–C-2–O-3	−75.4 (2)
O-4–P–C-13–C-14	−8.4 (2)	P–C-1–C-2–C-3	158.0 (2)
O-4–P–C-13–C-18	173.4 (2)	P–C-1–C-6–O-1	−105.3 (2)
C-1–P–C-7–C-8	47.3 (3)	P–C-1–C-6–C-5	143.1 (2)
C-1–P–C-7–C-12	−134.5 (2)	C-2–C-1–C-6–O-1	17.9 (2)
C-7–P–C-1–C-2	63.2 (2)	C-2–C-1–C-6–C-5	−93.7 (2)
C-7–P–C-1–C-6	−173.8 (2)	C-6–C-1–C-2–O-3	162.5 (2)
C-1–P–C-13–C-14	112.3 (2)	C-6–C-1–C-2–C-3	36.0 (3)
C-1–P–C-13–C-18	−65.9 (2)	O-3–C-2–C-3–Cl	77.3 (2)
C-13–P–C-1–C-2	178.5 (2)	O-3–C-2–C-3–C-4	−162.0 (2)
C-13–P–C-1–C-6	−58.4 (2)	C-1–C-2–C-3–Cl	−156.3 (1)
C-7–P–C-13–C-14	−130.5 (2)	C-1–C-2–C-3–C-4	−35.6 (3)
C-7–P–C-13–C-18	51.3 (2)	Cl–C-3–C-4–O-1	100.0 (2)
C-13–P–C-7–C-8	−66.0 (2)	Cl–C-3–C-4–O-2	−143.7 (2)
C-13–P–C-7–C-12	112.3 (2)	C-2–C-3–C-4–O-1	−20.1 (3)
C-4–O-1–C-6–C-1	−75.4 (2)	C-2–C-3–C-4–O-2	96.3 (3)
C-4–O-1–C-6–C-5	43.5 (2)	O-2–C-5–C-6–O-1	−31.0 (2)
C-6–O-1–C-4–O-2	−41.1 (3)	O-2–C-5–C-6–C-1	85.4 (2)
C-6–O-1–C-4–C-3	77.1 (3)		



Scheme 2. (a) PhSH, NaOMe, 67%. (b) Ph_2PH, BuLi, THF, 83%. (c) Air, 1:1:1 Et_2O–acetone–$CHCl_3$, 91%.

configuration of **15**. The i.r. spectra of **13, 14, 16**, and **17** are characterised by OH bands between 3400 and 3570 cm^{-1}. The ^1H-n.m.r. spectra of the monophosphines **13** and **16** and of the monophosphine oxides **14** and **17** exhibit similar coupling constants as the spectra of the corresponding bisphosphines and bisphosphine oxides, respectively, indicating their *gluco* configuration, a $^1C_4$ conformation for the phosphines, and a $B_{3,O}$ conformation for the phosphine oxides.

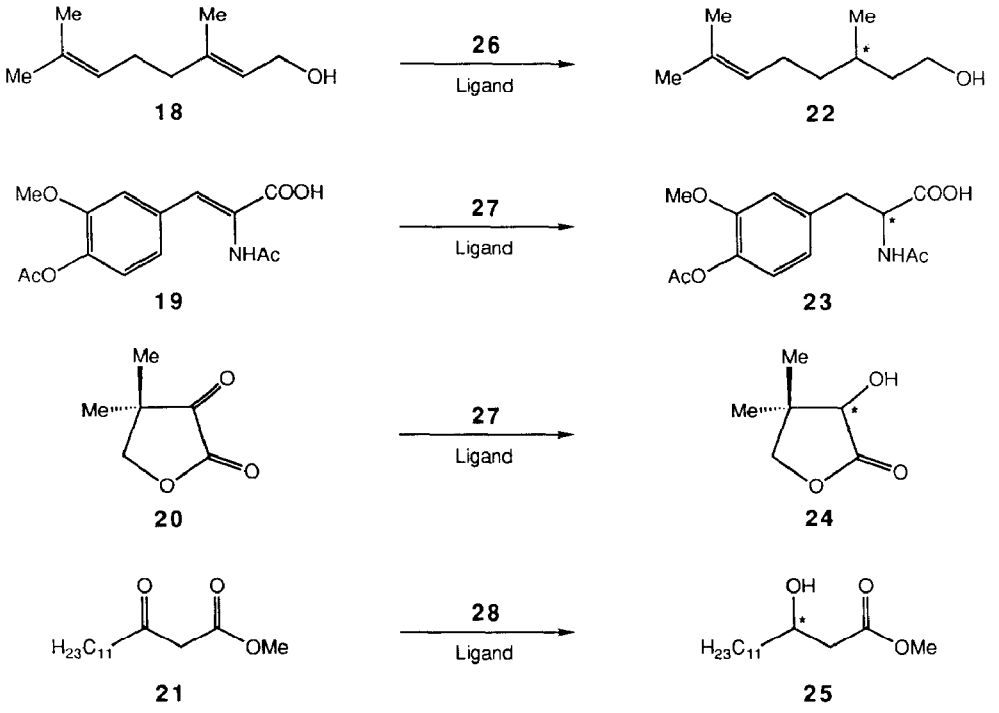
Additional information about the conformation of the mono- and bis-phosphines and phosphine oxides was obtained from the homo- and hetero-nuclear couplings of phosphorus[34,35] (Tables II and IV). The values for $^3J_{P,C}$ and $^3J_{P,H}$ of phosphine oxides depend strongly on the dihedral angle. Values of 10–13 Hz for the vicinal couplings of ^{31}P with C-2, C-4, and C-6 of the phosphine oxides **5, 8, 10, 12, 14,** and **17**

correspond to dihedral angles of about 150–170°, as realized in a $B_{3,O}$ conformation. The values of $^3J_{P,H}$ of 8.5–14.5 Hz for these phosphine oxides are compatible with a dihedral angle of 30° between the C–P and the C–H bonds. A small $^4J_{P,H}$ (W-coupling) is observed between P-4 and H-6exo of the phosphine oxides **5**, **8**, **10**, **12**, and **14** and also of the phosphines **9**, **11**, and **13**. This coupling confirms the configuration at C-4 and is independent of the ($^1C_4$ or $B_{3,O}$) conformation. The values of $^3J_{P,H}$ and $^3J_{P,C}$ of phosphines depend strongly both upon the dihedral angle and upon the orientation of the lone pair, whereas $^2J_{P,H}$ and $^2J_{P,C}$ depend strongly only upon the orientation of the lone pair[34,35,36]. Small values were observed for $^2J_{P,H}$ (< 2 Hz for **9**, **11**, **13**, and **16**), and large values for $^2J_{P,2,C\text{-}1}$ (13.9–15.5 Hz for **9**, **11**, and **16**), $^2J_{P,2,C\text{-}3}$ (17.9–24.6 Hz for **9**, **11**, and **16**), $^2J_{P,4,C\text{-}3}$ (19.3–24.6 Hz for **9**, **11**, and **13**), and $^2J_{P,4,C\text{-}5}$ (10.1–11.4 Hz for **9**, **11**, and **13**). These data show a preferred antiperiplanar arrangement of the P-2 lone pair with H-2 and of the P-4 lone pair with H-4 on the one hand, and a synclinal arrangement of the P-2 lone pair with C-3 and C-1 and of the P-4 lone pair with C-3 and C-5 on the other hand. The larger values of $^2J_{P,C\text{-}3}$ than $^2J_{P,C\text{-}1}$ or $^2J_{P,C\text{-}5}$ suggest that the corresponding lone pairs are closer to C-3 than to C-1 or C-5.

Only small $^4J_{P,P}$ values (< 2 Hz) are observed in acyclic 1,3-diphosphorus compounds[37,38]. As expected from the W-arrangement of the PCCCP fragment, the $^4J_{P,P}$ value of 4.1 Hz for the bisphosphine dioxide **10** is somewhat larger than the usual values. Extremely large $^4J_{P,P}$ values are observed in the spectra of the bisphosphines **9** (101.3 Hz) and **11** (98.7 Hz). They are about half as large as $^1J_{P,P}$ in diphosphines (160–212 Hz, ref. 39) and correlate with the unusual close proximity of the P atoms and the orientation of their lone pairs. Except for 1,8-naphthalenediyl-bis(dimethylphosphane), for which a large $^4J_{P,P}$ is postulated[40], this is the first case where large $^4J_{P,P}$ coupling constants are directly observed. A similar situation is encountered in 1,3-difluorides, which exhibit large values for the $^4J_{F,F}$ coupling constants when the F atoms are in close proximity[41]. Alchemy calculations show that the bisphosphine **9** adopts a flattened chair conformation where the P atoms are separated by 3.52 Å. The same P···P distance is obtained when HO-2 and HO-4 in the X-ray structure of levoglucosan[26] are substituted by phosphino groups, using a C–P bond length of 1.84 Å. The calculated distance is smaller than the sum of the van der Waals radii (P/P 3.8 Å), but considerably larger than the P–P bond length (2.22 Å).

In order to test the four bidentate ligands **9**, **11**, **13**, and **16** in catalytic hydrogenation, rhodium and ruthenium complexes were prepared from the transition-metal precursor complexes **26** (ref. 42), **27**, and **28** (ref. 43). The phosphine complexes were used *in situ* as catalysts for the asymmetric hydrogenation of the olefinic bond of the allylic alcohol system in geraniol (**18**, ref. 44) and of the α-acetamidoacrylic acid **19** (refs. 4 and 45), and of the carbonyl groups of the α-ketolactone **20** (ketopantolactone, ref. 46) and the β-ketoester **21** (ref. 42), respectively (Scheme 3 and Table IX).

The activity of the phosphine complexes in these hydrogenations was poor for the sulfur–phosphorus bidentate ligands **13** and **16** and moderate for the bisphosphines **9** and **11**. Only poor enantioselectivities were observed in the ruthenium- or rhodium-catalyzed hydrogenation of the olefins **18** and **19**. The presence of NEt_3 did not enhance



Precursor complexes: **26** $Ru_2(\mu\text{-}CF_3CO_2)_4(COD)_2$,
27 $[Rh(\mu\text{-}Cl)(COD)]_2$,
28 $Ru_2Cl(\mu\text{-}Cl)_3(COD)_2(CH_3CN)$
(COD: *cis,cis*-1,5 cyclooctadiene)

Ligand: **9** *or* **11** *or* **13** *or* **16**

Scheme 3.

the enantioselectivity in the hydrogenation of **19**, in contrast to the results obtained from an analogous hydrogenation using the BPPM-rhodium complex[45]. Somewhat higher e.e. values were observed in the rhodium-catalyzed hydrogenation of ketopantolactone (**20**), but only the less active complexes gave higher selectivities. The best results were obtained in the reduction of the β-ketoester **21**, with e.e. values of 54 (**9**) and 49% (**16**), but only the complex of the bisphosphine **9** converted **21** in good yield (80%) into the β-hydroxyester **25**. To the best of our knowledge, this is the first example where non-atropisomeric bisphosphine complexes of ruthenium give an appreciable e.e. in the hydrogenation of a β-ketoester. The atropisomeric BINAP complexes give the β-hydroxyesters with e.e. >97% (ref. 47).

EXPERIMENTAL

General methods. — See ref. 48. All reactions involving phosphines and organometallic compounds were performed under an Ar atmosphere, using standard vacu-

TABLE IX

Asymmetric hydrogenation with rhodium and ruthenium complexes of **9**, **11**, **13**, and **16**: reaction conditions and results

Substrate	*Metal precursor complex*	*Ligand*	*Molar ratio ligand/metal*	*Molar ratio substrate/catalyst*	*Solvent*	*Concentration of substrate (% w/w)*	T (°)	*p (bar)*	*Time (h)*	*Conversion (%)*	*Selectivity (%)*	*E.e. (%)*	*Configuration of main enantiomer*
18	**26**	**9**	1	200	MeOH	1.0	20	60	19	97.2	92.0[a]	0.2	*S*
18	**26**	**11**	1	200	MeOH	1.0	20	60	19	64.8	96.8[a]	0.7	*R*
18	**26**	**13**	1	200	MeOH	1.0	20	60	19	16.2	80.9[a]	0	
18	**26**	**16**	1	200	MeOH	1.0	20	60	18	19.7	89.3[a]	1.3	*R*
18	**26**	**16**	2	200	MeOH	1.0	20	60	19	0.8	100		
19	**27**	**9**	1	100	EtOH	2.4	60	50	48	100	100	3.2[b]	*S*
19	**27**	**11**	1	100	EtOH	2.4	30	50	99	100	100	0[b]	
20	**27**	**9**	1	100	Toluene	1.0	50	60	41	68.0	100	14.5	*R*
20	**27**	**11**	1	100	Toluene	1.0	50	60	46	32.5	100	37.8	*R*
20	**27**	**16**	1	100	Toluene	1.0	30	60	92	8.7	100	47.4	*R*
20	**27**	**16**	2	100	Toluene	1.0	30	60	45	1.1	100		
21	**28**	**9**	1	200	MeOH[c]	1.6	80	35	19	100	79.8[d]	54.3	*R*
21	**28**	**11**	1	200	MeOH[c]	1.6	80	35	19	96.4	73.8[d]	24.8	*R*
21	**28**	**13**	1	200	MeOH[c]	1.6	80	35	19	57.8	24.2[d]	2.3	*R*
21	**28**	**16**	1	200	MeOH[c]	1.6	80	35	18	68.2	27.1[d]	49.4	*R*
21	**28**	**16**	2	200	MeOH[c]	1.6	80	35	18	61.4	12.4[d]	12.4	*R*

[a] The rest: dihydrocitronellol. [b] Optical purity. [c] With ~ 7% (v/v) CH_2Cl_2. [d] The rest: enol ether and acetal.

um-line techniques and round-bottom flasks having a sidearm with a stopcock[49]. All transfers of liquids and solutions of air- or moisture-sensitive materials were carried out with Ar-purged syringes fitted with stainless steel needles or with steel tubing. Ar was purified by successive passage through self-indicating silica gel and BTS catalyst. Tetrahydrofuran was distilled from Na and benzophenone, MeOH from Mg, and CH_2Cl_2 from P_2O_5 under a stream of deoxygenated (BTS) and dried (silica gel) N_2. Isolation of air-sensitive products was carried out by adding degassed silica gel in an Ar-purged round-bottom flask to the reaction mixture, removing the solvents at 0.08 mbar to give the silica-gel-absorbed products, and column chromatography. Before transferring degassed eluents to the reservoir, the silica gel in the column was washed with acetone and the eluent in turn, and purged with N_2 for 3 cycles. All the solvents for flash chromatography (f.c.) were degassed using the freeze–pump–thaw method with N_2 (3 cycles). F.c. was carried out on silica gel (Merck 60, 0.015–0.040 mm) under N_2 pressure, and fractions were collected in Ar-purged round-bottom flasks having a sidearm with a stopcock connected to a N_2 balloon as a pressure equalizer. Solvents were distilled on a vacuum line using an oil pump.

*1,6-Anhydro-3,4-dideoxy-4-(diphenylphosphoryl)-β-*D-threo*-hex-3-enopyranose* (**3**). — (*a*) Ph_2PH (0.807 mL, 4.66 mmol) and 50% aqueous KOH (567 mg, 5.06 mmol) were added in turn to a solution of **1** (630 mg, 2.11 mmol) in Me_2SO (21 mL, dried over CaH_2) at room temperature. The mixture was stirred thereat for 38 min until the disappearance of **1**. After addition of 0.5 mL of AcOH, normal work-up, and f.c. (AcOEt), crystallization from $CHCl_3$–EtO_2 gave **3** (152 mg, 22%, not optimized) as white needles.

(*b*) $AlMe_3$ (4.32 mL, 36 mmol) and Ph_2PH (4.17 mL, 24 mmol) were added in turn to cooled (−38°) CH_2Cl_2 (30 mL). This mixture was stirred for 40 min and added in one portion to a cooled (−38°) solution of **1** (1.78 g, 6 mmol) in CH_2Cl_2 (100 mL). The mixture was stirred at −38° for 10 h, treated with a solution of NaOMe (210 mmol) in MeOH (65 mL), warmed up to −20°, and kept at −20° for 3 h. After addition of the mixture to silica gel, the solvent was removed at room temperature using an oil pump. T.l.c. showed that the product (R_F 0.92, 5:1 $CHCl_3$–AcOEt) was transformed into a slower moving one (R_F 0.87) during evaporation of the solvent. Further work-up was done without an Ar atmosphere. Elution of the silica gel with $CHCl_3$, drying ($MgSO_4$) and concentration of the eluent, and crystallization (3 times) from $CHCl_3$–EtO_2 gave **3** as white needles (310 mg, 16%, not optimized), R_F 0.33 (2:1 $CHCl_3$–acetone), m.p. 197–198°, $[\alpha]_D^{25}$ −124° (*c* 0.5, chloroform); $\lambda_{max}^{CHCl_3}$ 240 (ε 3065), 266 (ε 1797), 273 (ε 1457) nm; ν_{max} 3560 m, 3330 m (br), 3064 m, 3083 w, 2998 s, 2902 m, 1625 m, 1593 m, 1487 m, 1440 s, 1392 s, 1350 s, 1262 s, 1175 s, 1138 s, 1123 s, 1105 s, 1075 s, 1050 s, 1030 s, 1000 s, 980 s, 945 m, 930 m, 890 s, 870 s, 695 s cm^{-1}. C.i.-mass spectrum: *m/z* 329 (100, $[M + 1]^+$), 311 (3), 269 (10), 241 (4), 81 (3).

Anal. Calc. for $C_{18}H_{17}O_4P$ (328.27): C, 65.85; H, 5.22; P, 9.43. Found: C, 65.56; H, 5.22; P, 9.59.

*1,6-Anhydro-4-deoxy-4-(diphenylphosphoryl)-2-*O-(p-*toluenesulfonyl)-β-*D-*glucopyranose* (**5**). — (*a*) $AlEt_3$ (1.2 mL, 5.7 mmol in toluene) was added to a solution of

Ph_2PH (0.02 mL, 0.5 mmol) in benzene (5 mL). The mixture was stirred for 5 min at room temperature and added to a solution of **1** (149 mg, 0.5 mmol) in benzene (15 mL). The mixture was stirred for 75 min at room temperature and treated with AcOH (50 mL). Usual work-up for air-stable compounds, preparative t.l.c. (10:3 $CHCl_3$–AcOEt, R_f 0.22), and crystallization from $CHCl_3$ gave **5** (57 mg, 24%, not optimized) as white needles.

(*b*) Ph_2PH (1.39 mL, 6 mmol) and $AlMe_3$ (5.03 mL, 12 mmol) were added to CH_2Cl_2 (15 mL). The mixture was stirred for 1 h at −38° and added to a cooled (−38°) solution of **1** (596 mg, 2 mmol) in CH_2Cl_2 (40 mL). Stirring was continued at −38° for 6 h. The mixture was neutralized with saturated aqueous NH_4Cl (6 mL). A solution of the crude product, obtained by the normal work-up for air-sensitive compounds, in 2:1 $CHCl_3$–acetone (30 mL) was treated with AcOH (5 mL) and H_2O_2 (38%, 5 mL) with stirring in an ice bath for 40 min. Normal work-up, f.c. (10:1.5 $CHCl_3$–acetone), and crystallization from $CHCl_3$–Et_2O gave **5** (869 mg, 87%) as white needles. R_f 0.42 (AcOEt), m.p. 165–168°, $[\alpha]_D^{20}$ −41° (*c* 0.1, chloroform); $\lambda_{max}^{CHCl_3}$ 239 (*ε* 2663), 266 (*ε* 2234), 273 (*ε* 1835) nm; ν_{max} 3400 m (br), 3030 w (sh), 2995 m, 2900 w, 1600 m, 1449 m, 1365 s, 1175 s, 1122 s, 1098 s, 1012 s, 985 s, 902 s, 865 m cm^{-1}. C.i.-mass spectrum: *m/z* 365 (5), 329 (7), 299 (19), 297 (100), 266 (12), 252 (9), 241 (28), 225 (16), 219 (21), 204 (11), 203 (60), 173 (25), 135 (61), 111 (38), 88 (53), 79 (10), 67 (10), 65 (10).

Anal. Calc. for $C_{23}H_{23}O_3PS$ (500.51): C, 59.99; H, 5.03; P, 6.18. Found: C, 59.75; H, 5.22; P, 6.05.

*1,6:2,3-Dianhydro-4-deoxy-4-(diphenylphosphino)-β-*D*-mannopyranose* (**6**). $AlMe_3$ (4.33 mL, 36 mmol) and Ph_2PH (4.17 mL, 24 mmol) were added to CH_2Cl_2 (30 mL). The solution was stirred for 40 min at −38° and added to a cooled (−38°) solution of **1** (1.788 g, 6 mmol) in CH_2Cl_2 (100 mL). Stirring was continued at −38° for 10 h, when the mixture was treated with NaOMe (210 mmol) in MeOH (56 mL), warmed up to −20°, kept at −20° for 3 h, and treated with AcOH (18 mL). Isolation according to the general procedure for air-sensitive compounds, f.c. (1:2 AcOEt–hexane), and evaporation of the solvent at −20° gave **6** (1.311 g, 70%) as a colourless syrup. R_f 0.47; $\lambda_{max}^{CHCl_3}$ 250 (*ε* 5688) nm; ν_{max} 3060 m (sh), 2960 s, 2902 m, 2858 w, 1600 w, 1470 m, 1435 m, 1350 m, 1260 s, 1165 s, 1140 s, 1100 s, 1010 s, 980 s, 938 s, 915 s, 870 m, 750 s cm^{-1}.

*1,6:2,3-Dianhydro-4-deoxy-4-(diphenylphosphoryl)-β-*D*-mannopyranose* (**7**) *and 1,6-anhydro-2-chloro-2,4-dideoxy-4-(diphenylphosphoryl)-β-*D*-glucopyranose* (**8**). Air was blown through a solution of **6** (50 mg) in 1:1:1 Et_2O–acetone–$CHCl_3$ (100 mL). Et_2O and acetone were added regularly to maintain the solvent ratio. When t.l.c. showed completion of the oxidation (48 h), evaporation of the solvent and crystallization from $CHCl_3$–Et_2O gave **7** (43 mg, 82%) as white needles. Upon dissolution in $CDCl_3$, **7** was transformed completely into **8**.

Data for **7**: R_f 0.52 (2:1 $CHCl_3$–acetone), m.p. 195–197°; ν_{max} 3030 m (sh), 2990 s, 2900 m, 1600 w, 1480 w, 1438 m, 1350 m, 1312 w, 1165 s, 1148 s, 1118 s, 1072 m, 1010 s, 1000 s, 982 s, 938 m, 915 s, 848 s cm^{-1}. C.i.-mass spectrum: *m/z* 330 (13, $[M + 2]^+$), 329 (66, $[M + 1]^+$), 219 (10), 261 (5), 58 (7), 57 (100), 56 (7), 43 (57), 42 (7), 41 (13).

Anal. Calc. for $C_{18}H_{17}O_4P$ (328.31): C, 65.85; H, 5.22; P, 9.43. Found: C, 65.61; H, 5.32; P, 9.34.

Data for **8**: R_F 0.50 (AcOEt), m.p. 153°, $[\alpha]_D^{25}$ −32° (*c* 0.6, chloroform); $\lambda_{max}^{CHCl_3}$ 239 (ε 1974), 266 (ε 2419), 273 (ε 2002) nm; ν_{max} 3480–3180 br m, 2995 s, 2905 m, 1590 w, 1485 w, 1440 m, 1330 w, 1312 w, 1260 w, 1165 s, 1148 s, 1120 s, 1100 s, 1072 m (sh), 1010 s, 1000 s, 982 m, 945 w, 900 m, 915 m, 872 m, 690 m, 645 w cm^{-1}. C.i.-mass spectrum: *m/z* 367 (37, $[M + 3]^+$), 365 (100, $[M + 1]^+$), 330 (14), 329 (78, $[M - Cl]^+$), 243 (22), 241 (9), 203 (42).

Anal. Calc. for $C_{18}H_{18}O_4ClP$ (364.75): C, 59.27; H, 4.97; Cl, 9.71. Found: C, 59.19; H, 4.74; Cl, 9.57.

Transformation of **3** *into* **8**: A mixture of **3** (7 mg), molecular sieves (3 Å), and conc. HCl (10 μL) in $CHCl_3$ (2 mL) was stirred at room temperature for 48 h. Normal work-up followed by t.l.c. (2:1 $CHCl_3$–acetone) gave **8** (2 mg). The R_F and the ^{1}H-n.m.r. spectrum were identical to those of **8** obtained from **7**.

*1,6-Anhydro-2,4-dideoxy-2,4-bis(diphenylphosphino)-β-*D*-glucopyranose* (**9**). — BuLi (2.1 mL, 3.4 mmol) was added to a solution of Ph_2PH (0.70 mL, 4 mmol) in tetrahydrofuran (5 mL). The mixture was stirred for 40 min at room temperature and added to a solution of **6** (530 mg, 1.69 mmol) in tetrahydrofuran (26 mL). T.l.c. showed completion of the reaction within 15 min. The solution was filtered through a mixture of NH_4Cl (0.3 g) and silica gel (20 g), and the adsorbent washed with tetrahydrofuran. F.c. (1:2 AcOEt–hexane) of the crude product gave **9** (480 mg, 57%) as a white amorphous solid, R_F 0.41 (2:3 AcOEt–hexane); $\lambda_{max}^{CHCl_3}$ 255 (12 287) nm; ν_{max} 3552 m, 3060 m, 3000 m, 2960 s, 2928 m, 2900 m, 2858 m, 1588 w, 1480 s, 1432 s, 1291 m, 1259 s, 1118 s, 1093 s, 1070 w, 1055 m, 1048 m, 1028 m, 1000 s, 975 m, 940 m, 888 m, 692 s cm^{-1}.

*1,6-Anhydro-2,4-dideoxy-2,4-bis(diphenylphosphoryl)-β-*D*-glucopyranose* (**10**). — AcOH (2 mL) and H_2O_2 (38%, 1 mL) were added to an ice-cooled solution of **9** (120 mg) in 2:1 $CHCl_3$–acetone (30 mL). The solution was stirred until completion of the oxidation (3 h). Usual work-up gave 112 mg of crude product, which, upon crystallization from MeOH, gave **10** (90 mg, 71%) as white needles, R_F 0.38 (1:1 $CHCl_3$–acetone), m.p. 236° (dec.), $[\alpha]_D^{25}$ +27° (*c* 1, chloroform); $\lambda_{max}^{CHCl_3}$ 273 (ε 3284), 266 (ε 3918), 239 (ε 2479) nm; ν_{max} 3400 s (br), 3064 w, 2998 s, 2930 m, 2905 m, 1595 m, 1485 w, 1440 s, 1315 m, 1210 s, 1160 s, 1120 s, 1098 s, 1055 s, 1030 s, 1010 s, 1000 s, 985 m, 895m cm^{-1}. C.i.-mass spectrum: *m/z* 532 (35, $[M + 2]^+$), 531 (100, $[M + 1]^+$), 335 (10), 334 (45), 287 (17), 276 (12), 259 (11), 245 (30), 243 (11), 219 (21), 203 (20).

Anal. Calc. for $C_{30}H_{28}O_5P_2$ (530.50): C, 67.92; H, 5.32; P, 11.67. Found: C, 67.72; H, 5.32; P, 11.42.

*1,6-Anhydro-2,4-dideoxy-2,4-bis(diphenylphosphino)-3-*O*-(1-naphthoyl)-β-*D*-glucopyranose* (**11**). — A solution of **9** (642 mg, 1.29 mmol), pyridine (0.17 mL, 2.32 mmol, dried over KOH), 4-dimethylaminopyridine (15 mg), and 1-naphthoyl chloride (0.27 mL, 1.80 mmol) in CH_2Cl_2 (30 mL) was stirred for 2.5 h (t.l.c.: completion of the reaction) at room temperature. Work-up according to the usual procedure for air-sensitive compounds and f.c. (10:2 toluene–$CHCl_3$) gave **11** (705 mg, 84%) as a white foam, R_F 0.37 (8:2 toluene–$CHCl_3$); $\lambda_{max}^{CHCl_3}$ 246 (ε 19 768) nm; ν_{max} 3060 s, 3010 s, 2968 s, 2930 s, 2900 m, 2860 m, 1715 s, 1595 m, 1580 s, 1510 m, 1480 m, 1435 s, 1378 w, 1278 w, 1136 s, 1130 s, 1095 m, 1075 m, 1064 m, 1025 s, 1010 s, 950 s, 920 m, 898 m, 865 w, 693 s cm^{-1}.

1,6-Anhydro-2,4-dideoxy-2,4-bis(diphenylphosphoryl)-3-O-(1-naphthoyl)-β-D-glucopyranose (**12**). — Oxidation of **11** (40 mg) and isolation of **12** were performed as described for the preparation of **9**. Preparative t.l.c. (1:1 $CHCl_3$–acetone) gave **12** (35 mg, 84%) as a white solid, R_f 0.44 (1:1 $CHCl_3$–acetone), $[\alpha]_D^{25}$ −71° (*c* 0.33, chloroform); $\lambda_{max}^{CHCl_3}$ 243 (ε 21 130), 309 (ε 7695) nm; ν_{max} (1.5% in $CHCl_3$) 3060 w, 2998 s, 2970 s, 2938 m, 2960 w, 1730 s, 1598 m, 1514 w, 1488 w, 1442 s, 1280 m, 1263 s, 1188 s, 1150 w, 1122 s, 1102 s, 1010 s, 965 w, 945 w, 900 w, 695 m cm^{-1}. C.i.-mass spectrum: *m/z* 513 (7), 438 (12), 437 (43), 419 (12), 296 (10), 295 (54), 294 (20), 220 (13), 219 (100), 173 (56), 172 (49), 155 (37).

Anal. Calc. for $C_{41}H_{34}O_6P_2$ (684.66): C, 71.92; H, 5.00; P, 9.04. Found: C, 71.85; H, 5.22; P, 8.86.

1,6-Anhydro-2,4-dideoxy-4-(diphenylphosphino)-2-phenylthio-β-D-glucopyranose (**13**). — PhSH (1.53 mL, 15 mmol, freshly distilled) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.1 mL, 7.5 mmol) were added to a solution of **6** (559 mg, 7.5 mmol) in benzene (20 mL). The solution was heated under reflux for 12 h. T.l.c. (3:10 AcOEt–hexane) gave 700 mg of slightly impure **13** (93%). A solution of **13** (465 mg) in 1:1 Et_2O–$CHCl_3$ (30 mL) was exposed to air for 4 h. Evaporation of the solvent and fractionation of the product by t.l.c. (10:1 $CHCl_3$–AcOEt, R_f 0.47–0.70) conducted in an AtmosBag under N_2 gave pure **13** (237 mg; total yield, 47%). R_f (hexane–AcOEt, 10:3) 0.17; $\lambda_{max}^{CHCl_3}$ 257 (ε 13 556) nm; ν_{max} 3570 m (br), 3060 w, 3010 m, 2960 s, 2930 s, 2860 m, 1588 w, 1482 m, 1435 m, 1375 w, 1292 w, 1262 s, 1200 s, 1122 s, 1095 s, 1060 m, 1010 s, 980 m, 940 w, 910 w, 887 w, 660 m cm^{-1}.

1,6-Anhydro-2,4-dideoxy-4-(diphenylphosphoryl)-2-phenylthio-β-D-glucopyranose (**14**). — Compound **13** (38 mg) was oxidized to **14** within 20 h, as described for the oxidation of **6** to **7**. T.l.c. (1:1 $CHCl_3$–AcOEt) and crystallization from acetone–hexane gave **13** (33 mg, 85%), R_f 0.13 (10:1 $CHCl_3$–AcOEt), m.p. 172–173°, $[\alpha]_D^{25}$ −26 (*c* 1, chloroform); $\lambda_{max}^{CHCl_3}$ 240 (ε 5227, sh), 257 (ε 7749) nm; ν_{max} 3400 s, 3060 w, 3000 s, 2973 s, 2900 w, 1585 w, 1480 m, 1440 s, 1315 w, 1260 s, 1155 m, 1100 s, 1015 s, 980 m, 940 w, 890 m, 870 cm^{-1}. C.i.-mass spectrum: *m/z* 440 (25, $[M + 2]^+$), 439 (100, $[M + 1]^+$), 293 (19) 57 (12).

Anal. Calc. for $C_{24}H_{23}O_4PS$ (438.49): C, 65.74; H, 5.29; P, 7.06; S, 7.31. Found: C, 65.60; H, 5.25; P, 6.85; S, 7.30.

1,6:2,3-Dianhydro-4-deoxy-4-phenylthio-β-D-mannopyranose (**15**). — Compound **15**, prepared according to ref. 33, had R_f 0.73 (2:3 AcOEt–hexane), $[\alpha]_D^{25}$ +15 (*c* 1, chloroform); ν_{max} 3070 m, 3010 m, 2986 s, 2910 m, 1580 s, 1480 s, 1442 s, 1420 w, 1350 s, 1285 w, 1253 s, 1150 s, 1120 s, 1072 w, 1060 w, 1028 m, 1000 s, 980 s, 940 s, 872 m, 848 s cm^{-1}.

1,6-Anhydro-2,4-dideoxy-2-(diphenylphosphino)-4-phenylthio-β-D-glucopyranose (**16**). — BuLi (1.9 mL, 3.1 mmol) was added to a solution of Ph_2PH (0.6 mL, 3.6 mmol) in tetrahydrofuran (20 mL). The mixture was stirred for 40 min at room temperature and then added to a solution of **15** (472 mg, 2 mmol) in tetrahydrofuran (20 mL). Stirring was continued at room temperature for 20 min (t.l.c.: **15** had disappeared) when AcOH (0.12 mL) was added. Normal isolation as described for air-sensitive compounds

and f.c. (1:2 AcOEt–hexane) gave **16** (832 mg, 99%). Crystallization from CH_2Cl_2–MeOH at $-10°$ to $-15°$ gave fine white needles (700 mg, 83%), R_F 0.43 (4:6 AcOEt–hexane), m.p. 149–151° (in a sealed tube under N_2); $\lambda_{max}^{CHCl_3}$ 258 (ε 17958) nm; ν_{max} 3560 m, 3060 m, 3010 m, 2962 s, 2930 s, 2908 s, 2878 m, 1585 m, 1482 s, 1435 s, 1403 w, 1293 w, 1263 s, 1188 m, 1120 s, 1096 s, 1062 m, 1028 m, 1010 s, 978 m, 940 m, 888 m, 694 s cm^{-1}.

*1,6-Anhydro-2,4-dideoxy-2-(diphenylphosphoryl)-4-phenylthio-β-*D*-glucopyranose* (**17**). — Compound **16** (55 mg) was oxidized to **17**, as described for the oxidation of **6** to **7**. Preparative t.l.c. (10:3 $CHCl_3$–acetone) gave **17** (52 mg, 91%). Long, fine needles were obtained by crystallization from acetone; R_F 0.73 (10:7 $CHCl_3$–AcOEt), m.p. 194–196°, $[\alpha]_D^{25}$ −25° (*c* 1, chloroform); $\lambda_{max}^{CHCl_3}$ 238 (ε 4648), 259 (ε 8361) nm; ν_{max} 3400 s (br), 3070 m, 3010 s, 2938 m, 2908 m, 2860 m, 1595 w, 1585 w, 1480 m, 1440 s, 1315 w, 1265 w, 1150 s, 1110 s, 1073 w, 1028 w, 982 w, 949 w, 890 m cm^{-1}. C.i.-mass spectrum: *m/z* 440 (27, $[M + 2]^+$), 439 (100, $[M + 1]^+$), 329 (5), 273 (9).

Anal. Calc. for $C_{24}H_{23}O_4PS$ (438.49): C, 65.74; H, 5.29; P, 7.06; S, 7.31. Found: C, 65.52; H, 5.45; P, 7.19; S, 7.51.

X-Ray analysis of **8**. — Structure solution was performed using the direct methods routine of SHELXS86 (ref. 50). Data reduction and structure refinement were performed with the TEXSAN program package[51]. All non-hydrogen atoms were located by direct methods. No absorption corrections were applied. All of the hydrogen atoms could be located in a difference Fourier map and their positions were allowed to refine. The positions of the non-hydrogen atoms were refined with anisotropic thermal parameters; for the hydrogen atoms, individual isotropic temperature factors were refined. One reflection was omitted from the final cycles of refinement because of suspected extinction. The final difference Fourier maps were featuresless.*

General procedure for the in situ *preparation of the catalysts and for the hydrogenations* (data in Table IX): — In a glove box (Ar, < 1 p.p.m. O_2), a solution of the chiral ligand (**9, 11, 13,** or **17**; 0.02–0.1 mmol) in 20 mL of the mentioned solvent (except for reactions with **26** where 6 mL of CH_2Cl_2 were used) was added to a solution of the calculated amount of the metal complex (**26** or **27** or **28**) in the same solvent (20 mL). The resulting solution was stirred at room temperature for 30 min (**27**) or 90 min (**26** and **28**). The solution of the complex of **27** in EtOH was treated with 6 mol. equiv. of NEt_3.

In the glove box, a 500-mL stainless-stell autoclave equipped with a magnetically driven stirrer and a glass vessel was charged successively with the substrate, the solvent, the catalyst solution, and 10 bar of Ar. Before connecting the autoclave to the H_2 source (99.9999%), the lines were carefully flushed with H_2. The Ar was replaced by three cycles of pressurizing with 20 bar of H_2 and venting.

Determination of the enantiomeric excesses of the hydrogenation products: The e.e. of **23** was deduced from the optical rotation[45], whereas that of **24** was determined by g.l.c. on a column of permethylated β-cyclodextrin (home made, commercially available

* Lists of atomic co-ordinates and temperature factors have been deposited with, and may be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/466/*Carbohydr. Res.*, 216 (1991) 149–169.

from Machery-Nagel). Both **22** and **25** were transformed into the (*S*)-methyltrolox ester[52] (reagent available from Fluka) and the ratios of these derivatives determined by g.l.c.

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