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Approaches to new water-soluble phosphines

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Abstract

Approaches to water-soluble phosphines are described which involve conversion of ethylene glycol derivatives and sugar diacetonides into monoallyl ethers, and hydrophosphorylation of the latter. In the case of the sugars, water-solubility is conferred by a subsequent hydrolysis.

Introduction

The continuing environmental discussion with its vehement criticism of chemists and chemistry presents a variety of problems. One of these is the reduction in the amount of organic solvents used in laboratories and in industry, and one obvious way to overcome this problem is to synthesise water-soluble reagents or catalysts. The outstanding example is the replacement of triphenylphosphine (TPP) as a ligand by the sodium salt of the corresponding sulfonic acid (TPPTS) in the Veba–Rhone Poulenc process, as discussed by Kuntz [1]. A recent review by Sinou [2] shows that few other successful approaches to water-soluble phosphines had been described prior to 1987. Although several relevant papers have appeared since then [3–7], it appeared worthwhile to try other approaches. The present paper describes two synthetic strategies, one based on ethylene glycols (in analogy to Breslow's water-soluble triorganotin hydride [8]) and the other on sugar chemistry.

Results and discussion

The ethylene glycol approach

The conversion of ethylene glycols into their monoallyl ethers has been described previously in detail [9,10]. Addition of the P–H bonds of phenyl- or diphenylphosphine to such an ether is expected to occur regioselectively with

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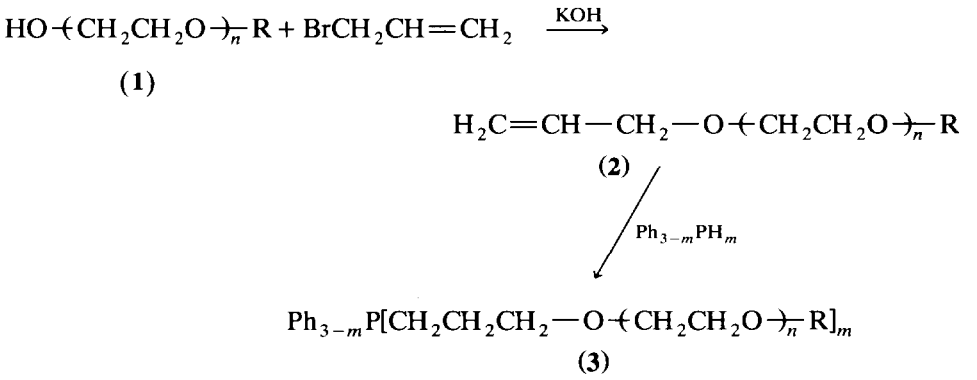


1a	$n = 1$, R = Me	**3a**	$n = 1$,	R = Me, $m = 1$
1b	$n = 2$, R = Me	**3b**	$n = 1$,	R = Me, $m = 2$
1c	$n = 1$, R = H	**3c**	$n = 2$,	R = Me, $m = 1$
1d	$n = 2$, R = H	**3d**	$n = 2$,	R = Me, $m = 2$
1e	$n = 3$, R = H	**3e**	$n = 1$,	R = H, $m = 1$
		3f	$n = 1$,	R = H, $m = 2$
		3g	$n = 2$,	R = H, $m = 1$
		3h	$n = 2$,	R = H, $m = 2$
		3i	$n = 3$,	R = H, $m = 1$
		3j	$n = 3$,	R = H, $m = 2$

Scheme 1.

bonding of the phosphorus atom to the terminal carbon atom, thus providing modified phosphorus-containing ethylene glycols, which should possess some degree of water-solubility. This methodology (Scheme 1) was applied successfully to a series of ethylene glycol derivatives, whereby the allyl ethers (**2**) were prepared in analogy to the methods in ref. 11 rather than by the earlier routes [9,10] since these require the use of sodium metal. The structures of the phosphines (**3**) thus prepared are given in Table 1. The preparation of one of the compounds (**3b**) has been described previously but by a somewhat different method [12] (see below).

To avoid the necessity of working with phosphine itself, we attempted to prepare compounds containing three ethylene glycol residues by first carrying out an anti-Markovnikoff addition of HBr to the allyl ethers (addition of borane/THF followed by bromination [25]), treating the bromides thus obtained with magnesium to give the corresponding Grignard reagents, and subsequently treating these with PBr_3, by analogy with the procedure previously described in ref. 13 (although product yields for the corresponding step to give **5a** were not given there). However, the results were very disappointing (yields 3–30%) and this route (Scheme 2) was not pursued further. Products **5** and **6** are listed in Table 1.

A third related approach involved the use of glycerine monoallyl ether rather than allyl ethers derived from ethylene glycol. The corresponding sequence (Scheme 3) was successful in both cases attempted; the products (**8**) are included in Table 1.

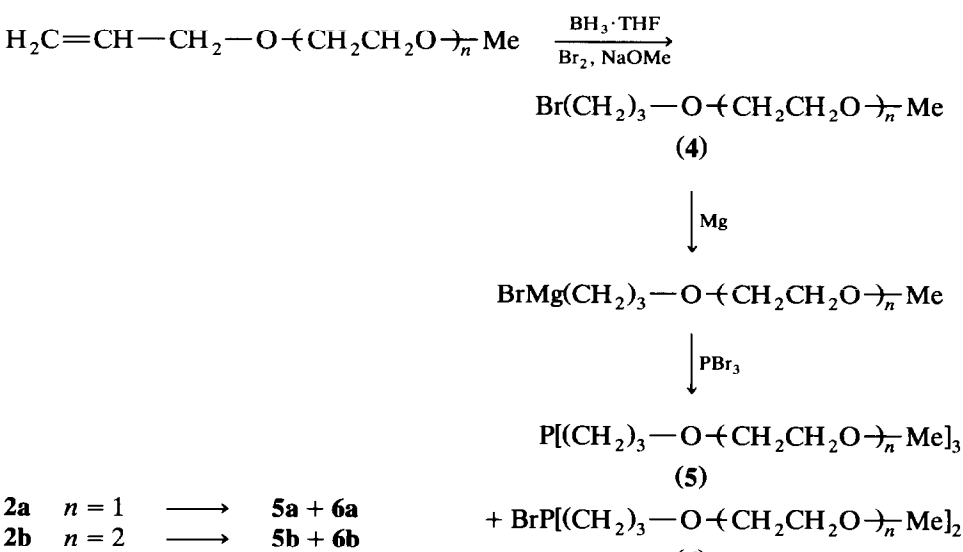
The purity of the phosphines was checked by ^{31}P NMR spectroscopy, since no other spectroscopic method is as clearly indicative. Complete ^{13}C and proton NMR

Table 1

Reactant consumption and yields for compounds **3** ($m = 1, 2$) and **5**, **6** ($m = 3$) of the type $Ph_{3-m}P[CH_2CH_2CH_2O(CH_2CH_2O)_nR]_m$ ($n = 1$–3) and **8** of the type $Ph_{3-m}P[CH_2CH_2CH_2OCH_2CH(OH)CH_2OH]_m$

Compound	R	n	m	Phosphine consumption (%)	NMR yield (%) [a]		Method A/B [d]	Time (days)
					1:1 [b]	2:1 [c]		
3a	Me	1	1	80	75	–	A	6
3a	Me	1	1	100	90 [e]	–	B	6
3b	Me	1	2	100	5	90	A	7
3b	Me	1	2	100	5	85	B	2
3c	Me	2	1	90	85 [f]	–	B	5
3d	Me	2	2	100	5	40	B	2.5
3e	H	1	1	100	95	–	B	3
3f	H	1	2	100	–	98	B	3
3g	H	2	1	100	95	–	B	8
3h	H	2	2	100	–	95	B	8
3i	H	2	2	100	95	–	B	7
3j	H	3	2	100	98	–	B	7
5a/6a	Me	1	3	100	30 [h]	55 [g]	–	–
5b/6b	Me	2	3	100	3 [h]	5 [g]	–	–
8a	–	–	1	95	95	–	A	8
8b	–	–	2	100	5	95	A	8

[a] As determined by ^{31}P NMR; [b] Refers in the case of diphenylphosphine to an adduct of type $Ph_2P(OCH_2CH_2CH_2R)_2$, in the case of phenylphosphine to an adduct of the type $PhP(H)OCH_2CH_2CH_2R$. [c] Refers in the case of phenylphosphine to the adduct $PhP(OCH_2CH_2CH_2R)_2$. [d] Method A: heating at 80°C in the presence of a catalytic amount of AIBN, method B: UV-irradiation. [e] Isolated yield 43%, b.p. 185°C/0.04 mmHg; [f] Isolated yield 31%, b.p. 164°C/0.001 mmHg. [g] Compound of the type $BrP[CH_2CH_2CH_2O(CH_2CH_2O)_nMe]_2$. [h] Compound of the type $P[CH_2CH_2CH_2O(CH_2CH_2O)_nMe]_3$.



2a $n = 1$ ⟶ **5a + 6a**
2b $n = 2$ ⟶ **5b + 6b**

Scheme 2.

$$H_2C{=}CH{-}CH_2{-}O{-}CH_2{-}CH(OH){-}CH_2OH$$

(7)

$$\downarrow Ph_{3-m}PH_m$$

$$Ph_{3-m}P[CH_2CH_2CH_2{-}O{-}CH_2{-}CH(OH){-}CH_2OH]_m$$

(8) ($m = 1, 2$)

Scheme 3.

spectra were also recorded, but because of the close similarity of most of the parameters, only directly structure-relevant NMR parameters are given in Table 2.

While the water-solubility of the glycol-derived phosphines thus prepared was close to zero, the glycerine derivatives **8a** and **8b** were soluble to the extent of approx. 50 and 130 mmol/L, respectively.

The sugar approach

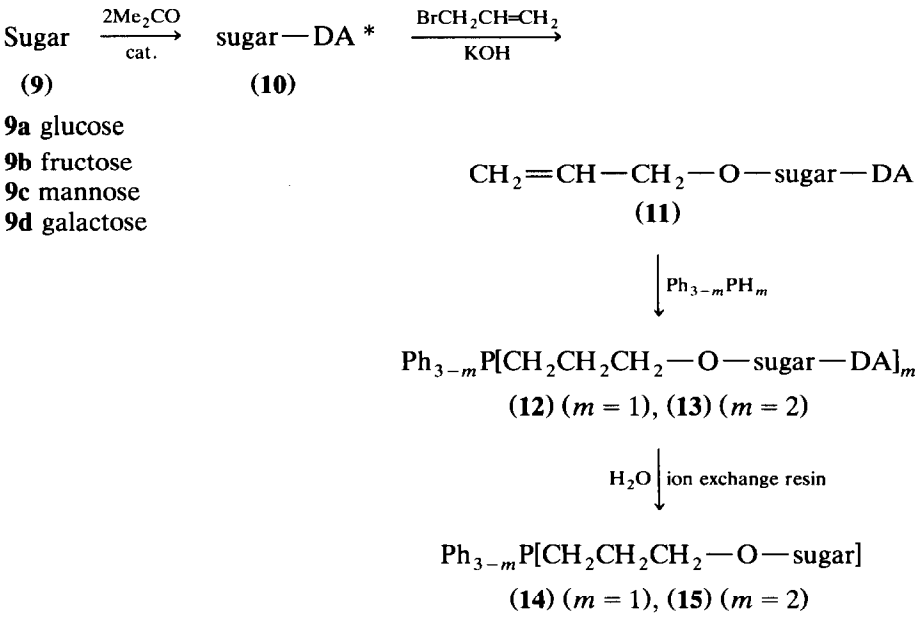
The concept of incorporating a diphenylphosphino moiety into sugar derivatives has been used by a number of authors, the phosphorus atom being linked to the carbohydrate skeleton via oxygen [14–16] or (at various distances from the ring) via carbon [17–21]. The phosphines thus obtained were also shown in a number of cases to be active as ligands in catalytic processes [14,15,20,22]. However, to our knowledge the hydroxyl functions were in each case at least partially protected and not free. Our approach involves the formation of an allyl ether of a (partially protected) sugar followed by hydrophosphorylation of the allyl group; subsequent

Table 2

^{31}P and ^{13}C chemical shifts and coupling constants $^xJ(P, C)$ ($x = 1$–3) for compounds **3** ($m = 1, 2$) and **5**, **6** ($m = 3$) of the type $Ph_{3-m}P[C^{\alpha}H_2C^{\beta}H_2C^{\gamma}H_2O(CH_2CH_2O)_nR]_m$ ($n = 1$–3) and **8** of the type $Ph_{3-m}P[C^{\alpha}H_2C^{\beta}H_2C^{\gamma}H_2OCH_2CH(OH)CH_2OH]_m$ ($m = 1, 2$)

Compound	R	n	m	$\delta(^{31}P)$	$\delta(C^{\alpha})/{}^1J(P, C)$	$\delta(C^{\beta})/{}^2J(P, C)$	$\delta(C^{\gamma})/{}^3J(P, C)$
3a	Me	1	1	−18.2	25.3/16.2	23.5/11.6	70.7/13.9
3b	Me	1	2	−26.8	25.2/13.9	23.6/11.7	71.0/10.5
3c	Me	2	1	−18.1	25.7/16.5	24.0/11.4	71.3/14.0
3d	Me	2	2	−26.9	25.0/13.2	23.2/11.4	70.5/12.6
3e	H	1	1	−18.0	25.9/16.0	24.1/10.6	71.3/12.7
3f	H	1	2	−26.7	25.7/13.8	24.1/12.0	71.7/9.8
3g	H	2	1	−18.1	25.6/16.0	23.9/11.3	71.2/14.1
3h	H	2	2	−26.7	25.8/13.9	24.2/11.2	71.6/12.5
3i	H	2	2	−18.2	25.6/16.5	23.8/11.4	71.1/14.0
3j	H	3	2	−26.8	25.3/13.4	23.7/11.2	71.1/12.3
5a	Me	1	3	−32.7	21.1/16.5	21.1/8.9	69.6/12.7
5b	Me	2	3	−33.3	– [a]	– [a]	– [a]
8a	–	–	1	−18.2	25.6/15.7	23.9/11.2	71.5/14.0
8b	–	–	2	−27.0	25.7/13.0	24.1/11.0	71.6/12.2

Chemical shifts in ppm *versus* external 85% H_3PO_4 and internal TMS, respectively; coupling constants $^xJ(^{31}P, ^{13}C)$ in Hz. [a] Not determined.



* sugar–DA = sugar diacetonide = diisopropylidene ketal of sugar

Scheme 4.

hydrolysis of the protecting groups (in our case acetonide residues) should lead to the free phosphorylated sugar (Scheme 4).

Glucose (**9a**) [23], fructose (**9b**) [23], mannose (**9c**) [23] and galactose (**9d**) [24] were converted into the diacetonides by published procedures. The protected sugars **10** were then converted into their monoallyl ethers **11** by treatment with KOH and allyl bromide [25–28]; yields were between 61 and 91%.

The allyl ethers **11** were allowed to react with phenyl- and diphenylphosphine either at 80°C in the presence of AIBN as a radical initiator or under UV irradiation; reaction conditions and yields for the hydrophosphorylation to **12** (products from diphenylphosphine) and **13** (products from phenylphosphine) are given in Table 3. Only terminal attack of the phosphorus moiety was observed. Compounds **12a** (from **11a**) and **12c** (from **11c**) were isolated as crystalline solids; all other products/mixtures were obtained as viscous oils. The structures of compounds **12** (as determined by NMR spectroscopy) are given in Scheme 5.

It was hoped that phenylphosphine would react with two equivalents of the protected sugar ether to give products **13** of the type PhP (sugar ether)$_2$, but this behaviour was observed only in the case of **9a** (glucose) and **9c** (mannose). The ethers derived from fructose and galactose gave mixtures of **13** and a product of the type PhPH (sugar ether); the latter species could not be separated but were shown to be present by their ^{31}P NMR signals, which appeared at relatively high field (-54 ± 0.5 ppm). Product yields are given in Table 3. The purity of the products **12** and **13** was again determined by ^{31}P NMR spectroscopy. ^{13}C and ^{1}H NMR spectra were also recorded; because of the complexity of the proton spectra,

Table 3

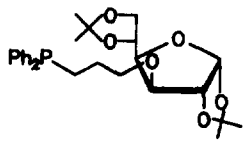
Reactant consumption and yields for compounds **12** ($m = 1, 2$) of the type $Ph_{3-m}P[CH_2CH_2CH_2O$-sugar diacetonide$]_m$

Compound	sugar	m	Phosphine consumption (%)	NMR yield (%) [a]		Method A/B [d]	Time (days)
				1:1 [b]	2:1 [c]		
12a	Glucose	1	100	95 [e]	–	A [f]	7
12b	Fructose	1	45	45	–	A	4.5
12c	Mannose	1	65	65 [g]	–	A	6.5
12d	Galactose	1	60	55	–	B	6
13a	Glucose	2	100	–	90	A	4.5
13b	Fructose	2	90	45	40	A	4.5
13c	Mannose	2	100	5	95	A	6.5
13d	Galactose	2	90	60	30	A	6.5

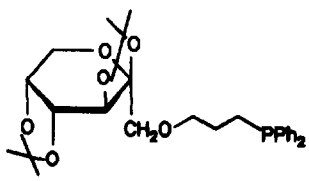
[a] As determined by ^{31}P NMR. [b] Refers in the case of diphenylphosphine to an adduct of type $Ph_2P(CH_2CH_2CH_2O$-sugar), in the case of phenylphosphine to an adduct of the type $PhP(H)CH_2$-CH_2CH_2O-sugar. [c] Refers in the case of phenylphosphine to the adduct $PhP(CH_2CH_2CH_2O$-sugar$)_2$. [d] Method A: heating to 80°C in the presence of a catalytic amount of AIBN; method B: UV-irradiation. [e] Isolated yield 54%, m.p. 105°C. [f] In the presence of methanol as hydrogen donor. [g] Isolated yield 50%, m.p. 80–82°C.

the proton data are not included here, and only the directly structure-relevant ^{13}C data are included (Tables 4, 5).

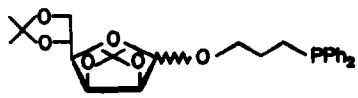
Hydrolysis was carried out as follows: the protected sugar phosphines **12a–d, 13a–d** were heated for 6 h under reflux with deoxygenated water and Amberlite



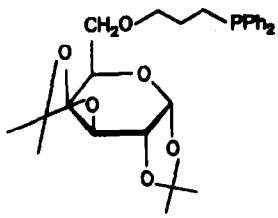
^3O-(3-diphenylphosphinopropyl)
$^1O,^2O:{}^5O,^6O$-diisopropylideneglucofuranose
(12a)



^1O-(3-diphenylphosphinopropyl)
$^2O,^3O:{}^4O,^5O$-diisopropylidenefructopyranose
(12b)



^1O-(3-diphenylphosphinopropyl)
$^2O,^3O:{}^5O,^6O$-diisopropylidenemannofuranose
(12c)



^6O-(3-diphenylphosphinopropyl)
$^1O,^2O:{}^3O,^4O$-diisopropylidenegalactopyranose
(12d)

Scheme 5.

Table 4

^{31}P and ^{13}C NMR chemical shifts (alkyl chain) with coupling constants $^{x}J(P, C)$ ($x = 1-3$) for compounds **12** of the type $Ph_{3-m}P[C^{\alpha}H_2C^{\beta}H_2C^{\gamma}H_2O$–sugar diacetonide$]_m$ ($m = 1, 2$)

Compound	Sugar	m	$\delta(^{31}P)$	$\delta(C^{\alpha})/{}^{1}J(P, C)$	$\delta(C^{\beta})/{}^{2}J(P, C)$	$\delta(C^{\gamma})/{}^{3}J(P, C)$
12a	Glucose	1	−19.2	25.5/16.5	23.9/11.4	70.3/14.0
12b	Fructose	1	−18.0	25.6/16.5	24.0/10.2	71.6/14.0
12c	Mannose	1	−18.5	25.8/17.9	24.2/11.4	67.3/13.7
12d	Galactose	1	−18.1	25.9/14.0	24.2/10.2	68.3/15.4
13a	Glucose	2	−27.5	19.3/11.4	28.1/7.6	70.3/11.4
13b	Fructose	2	−26.2	19.3/11.4	28.2/7.6	70.3/11.4
13c	Mannose	2	−28.0	– [a]	– [a]	66.1/10.0
13d	Galactose	2	−26.5	19.6/11.4	28.5/8.0	71.9/12.7

Chemical shifts in ppm with respect to external 85% H_3PO_4 and internal TMS respectively; coupling constants in Hz. [a] Hidden.

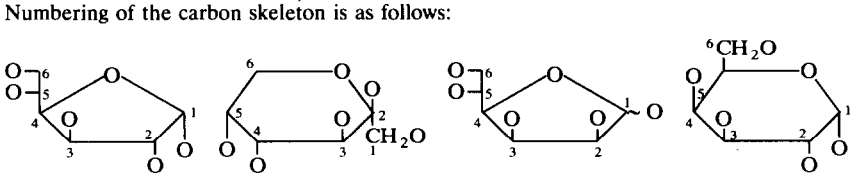
IR 120 ion-exchange resin; removal of the water *in vacuo* yielded the deprotected sugar phosphines as extremely viscous oils; attempts to crystallize them have so far been unsuccessful. A multinuclear NMR analysis (for data, see Experimental section) indicated that hydrolysis of **12a** gave **14a** in the pyranose form (α/β = 40:60) while that of **13b** gave solely **15b** as a 70:30 mixture of the β-pyranose and β-furanose forms. The ^{13}P NMR signals from **14a, 15b** were shifted very far to low field (**14a**, ~42 ppm; **15b**, ~52 ppm), so that we initially feared that the hydrolysis had been accompanied by oxidation of the phosphine to the phosphine oxide. However, this possibility was ruled out on the basis of two experiments. Thus the diacetonide **12a** and the deprotected product **15b** were subjected to

Table 5

^{13}C NMR chemical shifts (α-carbon of phenyl residues, sugar residues) with coupling constants $^{1}J(P, C)$ for compounds **12** of the type $Ph_{3-m}P[CH_2CH_2CH_2O$–sugar diacetonide$]_m$ ($m = 1, 2$)

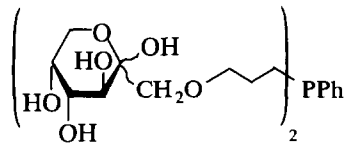
Compound	Sugar	m	$\delta(C_a^{Ph})/{}^{1}J(P, C)$ [a]	$\delta(C_1)$	$\delta(C_2)$	$\delta(C_3)$	$\delta(C_4)$	$\delta(C_5)$	$\delta(C_6)$
12a	Glucose	1	138.2/12.7	104.9	85.0	80.9	81.8	72.1	66.9
12b	Fructose	1	138.1/14.0	64.0	102.1	70.4	69.3	69.6	60.4
12c	Mannose	1	138.2/13.5	105.8	84.6	79.9	79.9	72.7	66.5
12d	Galactose	1	138.2/14.0	95.9	70.8	70.1	70.2	68.0	61.3
13a	Glucose	2	134.9/11.4	104.8	84.9	80.8	82.0	72.0	66.8
13b	Fructose	2	134.7/10.2	64.2	102.1	70.5	69.4	69.7	60.4
13c	Mannose	2	137.0/14.0	105.4	84.3	79.6	78.7	72.6	67.0
13d	Galactose	2	134.5/15.3	96.2	71.0	70.4	70.4	66.5	61.9

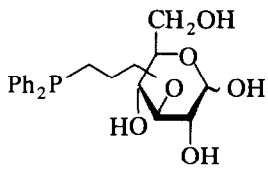
Chemical shifts in ppm with respect to internal TMS, coupling constants in Hz. [a] C_{β}: $d = 132.5 \pm 1$ ppm, $^{2}J(P, C) = 18 \pm 1$ Hz. C_{γ}: δ 128 ± 0.5 ppm, $^{3}J(P, C)$ 6.2 ± 0.2 Hz. C_{δ}: $\delta = 128.0 \pm 0.1$ ppm. Numbering of the carbon skeleton is as follows:



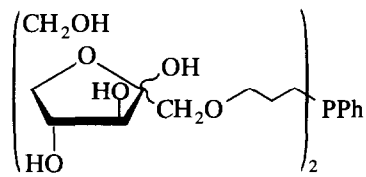
Glucofuranose Fructopyranose Mannofuranose Galactopyranose

oxidation with H_2O_2 in acetone. The ^{31}P chemical shifts of the phosphine oxides thus obtained were 32.3 and 58.8 ppm, respectively. The deprotected product **14a** was then reconverted to the extent of 50% to the diacetonide under oxygen-free conditions and the product shown by NMR spectroscopy to be **12a** and not its oxidized form.





(14a)



(15b)

In all other cases the products of hydrolysis were not uniform but consisted of intractable mixtures that were not subjected to further purification; hydrolysis had apparently affected not only the acetonide groups but also the linkage between the sugar moiety and the propyl chain. The water-solubility of the acetonides was as expected extremely low; however, that of the free sugar phosphines was much greater than that of the glycol and glycerine derivatives. The following values were determined: **14a** ~ 200 mmol/L; **15b** ~ 800 mmol/L. The product mixtures obtained by hydrolysis of **12b–12d, 13a, 13c** and **13d** were also extremely water-soluble, but their unclear structure renders a solubility estimate of only doubtful value. The values determined in fact lie in the same range (~ 100–500 mmol/L).

Experimental

All experiments involving phosphorus-containing materials were carried out under argon in order to preclude oxidation. Ethylene glycol derivatives (**1**), glycerine monoallyl ether (**7**) and sugars (**9**) were commercial products.

Preparation of monoallyl ethers 2 from glycol derivatives 1

Compounds **1** were converted into **2** by the procedure described by Allen and Gates [9]. KOH (16.8 g, 300 mmol) was introduced into a 500 mL three-necked flask equipped with a reflux condenser and a dropping funnel and **1** (300 mmol) was added; the mixture became warm. Allyl bromide (36.3 g, 330 mmol for **1a, 1b**; 300 mmol for **1c–e**) was added dropwise with ice-cooling if required. The mixture was then heated at 60°C for 3 h, allowed to cool to room temperature, treated with ether (200 mL), and dried over $MgSO_4$. Ether was distilled off, and the residue

subjected to distillation at reduced pressure to give **2a** (84%, b.p. 56°C/60 mmHg), **2b** [11] (84%, b.p. 86°C/15 mmHg, lit. 49°C/1.5 mmHg), **2c** [10] (60%, b.p. 60°C/15 mmHg, lit. 159°C/761 mmHg); **2d** [10] (63%, b.p. 102°C/15 mmHg, lit. 106°C/10 mmHg) and **2e** [10] (49%, b.p. 135°C/15 mmHg, lit. 92–93°C/0.4 mmHg).

Hydrophosporylation of monoallyl ethers 2

A mixture of the phosphine Ph_2PH or $PhPH_2$ (7.5 mmol) and the allyl ether (1 or 2 equiv., respectively) was either heated at 80°C in the presence of a catalytic amount of AIBN (method A) or irradiated (with stirring) in a quarz Schlenk tube with a TQ150 UV lamp (Heraeus, Hanau) (method B). Reaction times and yields are given in Table 1.

Indirect addition of HBr to monoallyl ethers 2

Compounds **2** were converted into **4** by method A, described by Brown and Lane [13]. Yields and boiling points were as follows: $MeOCH_2CH_2OCH_2CH_2$-CH_2Br: 58%, b.p. 56–62°C/1 mmHg; $MeOCH_2CH_2OCH_2CH_2OCH_2CH_2CH_2Br$: 53%, b.p. 79–81°C/0.2 mmHg.

Reaction of 4 with magnesium and PBr_3

Compounds **4** were converted into the corresponding Grignard reagents by conventional treatment with magnesium metal in THF as solvent. The molarity of the Grignard reagent solutions was determined by titration. A solution containing 30 mmol of the Grignard reagent ($\sim 0.63\ M$) was cooled to -15°C and a solution of PBr_3 2.7 g, 10 mmol) in THF (50 mL) was added dropwise with stirring. The mixture was allowed to warm to room temperature, stirred for 30 min, and treated with $\sim$ 1 mL of deoxygenated water to hydrolyse any remaining Grignard reagent. Filtration through a plug of glass wool gave a yellow solution, which was dried over $MgSO_4$. The THF was subsequently removed at the water pump to leave a yellow viscous oil, consisting of a mixture of **5** and **6**. Analysis was carried out by NMR spectroscopy.

Hydrophosphorylation of glycerine monoallyl ether 7

The hydrophosphorylation was carried out as for ethers **2**; details are given in Table 1.

Conversion of sugars 9 to their diacetonides 10

The sugar diacetonides (diisopropylidene derivatives) were prepared by previously described procedures as follows: glucose (**9a/10a**) [23]; fructose (**9b/10b**) [23]; mannose (**9c/10c**) [23]; galactose (**9d/10d**) [24].

Preparation of monoallyl ethers 11 from 10 [27]

The sugar diacetonides **9a–9d** (50 mmol) and KOH (2.8 g, 50 mmol) were suspended in acetone (100 mL) in a 250 mL two-necked flask fitted with a reflux condenser and a dropping funnel. Allyl bromide (7.3 g, 60 mmol) was added, and the mixture heated for 3 h under reflux. The mixture was dried over $MgSO_4$, the solvent removed under reduced pressure and the residue distilled to give the ethers derived from the following sugars: glucose (**11a** [25], 61%, b.p. 93°C/0.001

mmHg, lit. 88°C/0.08 mmHg [26]), fructose (**11b**, 91%, b.p. 80°C/0.001 mmHg), mannose (**11c** [27], 65%, b.p. 80°C/0.001 mmHg, no lit. value), galactose (**11d** [28], 90%, b.p. 90°C/0.001 mmHg, lit. 86°C/0.03 mmHg).

Hydrophosphorylation of ethers 11 to give products 12 and 13

The hydrophosphorylation was carried out as for ethers **2** by methods A and B. For product composition, see Table 3; for structure-relevant NMR data, see Tables 4, 5. Compounds **12a** and **12c** were obtained as crystalline solids: **12a** (54%), m.p. 105°C; **12c** (50%), m.p. 80–82°C: satisfactory elemental analyses (C, H) were obtained for both compounds. **12a** was also characterized by mass spectrometry, the molecular ion (19.6%) being detected at the calculated m/e value of 486. The following values for the optical rotation were obtained: **12a**, $[\alpha]_D^{20}$ −16.8; **12b**, $[\alpha]_D^{20}$ −20.8; **12c**, $[\alpha]_D^{20}$ +25.3 ($CHCl_3$, $c = 2$).

Hydrolysis of protected sugar phosphines 12 and 13

A mixture of compound **12** or **13** (7.5 mmol), deoxygenated water (10 mL), and Amberlite IR 120 ion exchange resin (1 g) was heated with stirring in a 25 mL two-necked flask fitted with a reflux condenser for 6 h under reflux. The ion exchange resin was filtered off under argon and washed with deoxygenated water. The combined aqueous solutions were heated to 50°C at the water pump to remove the water, leaving yellow viscous oils that were characterized by multinuclear NMR spectroscopy.

The structure-relevant NMR data of compounds **14a** and **15b** (for structures, see text) are as follows: **14a**: $\delta(^{31}P)$ 41.66 (α-form), 41.73 (β-form); $\delta(C^{\alpha})$ 24.0 ($^1J(P, C) = 3.8$); $\delta(C^{\beta})$ 26.7 ($^2J(P, C) = 76.3$); $\delta(C^{\gamma})$ 74.2 (α-form) ($^3J(P, C) = 14.3$), 74.8 (β-form) ($^3J(P, C) = 13.6$). Sugar skeleton: $\delta(C_1)$ 94.3(α), 98.1(β), $\delta(C_2)$ 73.4(α), 76.0(β), $\delta(C_3)$ 83.9(α), 86.6(β), $\delta(C_4)$ 71.8(α), 71.4(β), $\delta(C_5)$ 73.8(α), 78.0(β), δ (C_6) 62.9 (α, β). **15b**: $\delta(^{31}P)$ 51.8; $\delta(C^{\alpha})$ 22.8 ($^1J(P, C) = 5.0$); $\delta(C^{\beta})$ 26.0 ($^2J(P, C) = 53.2$); $\delta(C^{\gamma})$ 64.6 (pyranose) ($^3J(P, C) = 20.3$), 63.9 (furanose) ($^3J(P, C) = 17.8$). Sugar skeleton: $\delta(C_1)$ 66.0(p), 64.6(f), $\delta(C_2)$ 100.2(p), 103.3(f), $\delta(C_3)$ 71.3(p), 78.1(f), $\delta(C_4)$ 71.8(p), 82.8(f), $\delta(C_5$, 69.7(p), 76.6(f), $\delta(C_6)$ 65.5, 64.5 (p, f).

Determination of water solubility

A known amount of the phosphine was weighed into a 250 mL flask. Deoxygenated water was added with stirring until a clear solution was obtained.

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