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Unexpected Reactions of (*1R*)2,3,4,6-Tetra-O-acetyl-1-azido-D-galactopyranosyl Cyanide and the Derived Carboxamide with Triphenylphosphine

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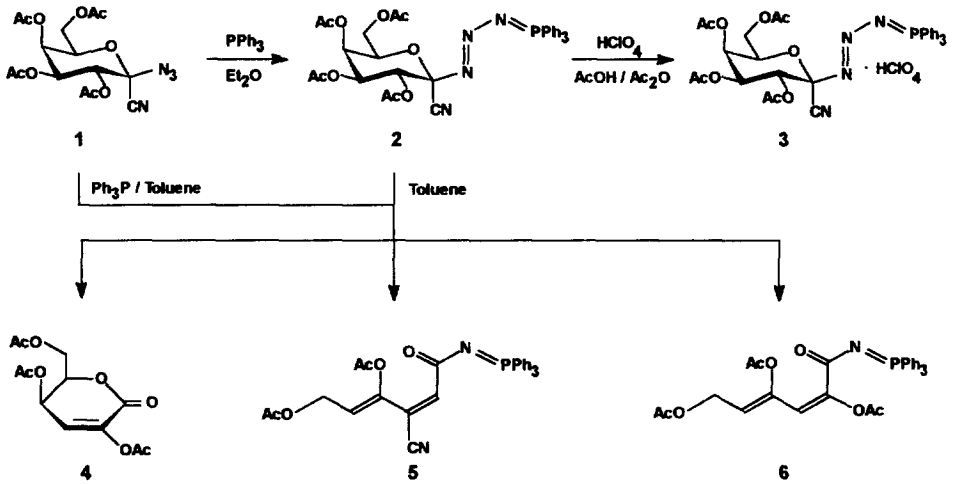
Abstract: Staudinger reaction of acetylated (*1R*)-1-azido-D-galactopyranosyl cyanide (**1**) with triphenylphosphine in diethyl ether led to the isolation of a crystalline phosphazide (**2**), unprecedented in carbohydrate chemistry. Spontaneous decomposition of **2** in toluene furnished the mixture of the unsaturated lactone **4**, as minor product, and two major products: the triphenylphosphoranylidene derivatives of (*2Z,4Z*)-3-cyano-4,6-diacetoxy-2,4-hexadienoic amide (**5**), and (*2E,4Z*)-triacetoxy-2,4-hexadienoic amide (**6**), respectively, owing to an unusual pyranoid ring opening between C-5 and the pyranose oxygen. The carboxamide analogue (**10**) of **1** underwent a regular phosphinimine formation affording the equilibrium mixture of both anomers **11** and **12**.

The Staudinger reaction[1] - transformation of organic azides with tertiary phosphines to produce iminophosphoranes (phosphinimines) - is a versatile tool in organic syntheses.[2] The use of the phosphinimine method in the carbohydrate field provides an easy access to various N-containing sugars (carbodiimides, cyclic carbamates, epimines, ureido- and guanidino derivatives e.t.c.).[3] In the course of our studies on the synthesis and transformation of sugar phosphinimines, recently, a particular interest has been aimed at the Staudinger reaction of glycosyl azides bearing an additional functional group at the anomeric carbon. First, we described the reaction of tetra-O-acetyl-D-glucopyranosylidene 1,1-diazide[4] with triphenylphosphine to give a fused *v*-triazolo-pyranosyl phosphinimine.[5]

Now we report on the anomalous Staudinger reaction of (*1R*)2,3,4,6-tetra-O-acetyl-1-azido-D-galactopyranosyl cyanide[6] (**1**) and its carboxamide analogue[6b] **10**, respectively. Reaction of **1** with triphenylphosphine in molar ratio 1:1 in dry diethyl ether did not give the expected phosphinimine but the phosphazide **2** which precipitated from the reaction mixture in 80% yield. Phosphazides, as primary adducts of the Staudinger reaction, were isolated in several cases,[7] however, to our best knowledge **2** is the first one isolated in the sugar field. ^{1}H-NMR data of **2** exhibited signals of the peracetylated galactopyranose moiety (Table 1). The ^{31}P-NMR spectrum of **2** displayed a signal at δ 25.92 (Table 2) which is in good agreement with previously reported values of phosphazides.[7,8] Unlike sugar phosphinimines,[3c,d,5] the anomeric carbon of **2** (δ 94.27, Table 2) has no coupling with the phosphorus atom, as a consequence of the four bonds sequence between them.

The outcome of the reaction is practically not influenced by the molar ratio of the reactants; both with 2 and 0.5 equiv triphenylphosphine the yield of **2** (calculated for **1**) was 74% and 33%, respectively, while the



reactant used in excess was not consumed. Formation of **2** from **1** accords well with the anomalous Staudinger reaction of α-azidodiphenylacetonitrile which furnished a phosphazide with *Z* configuration[7]. Similar geometry of the phosphazide moiety of **2** might be assumed, but in the lack of suitable crystals for X-ray analysis it could not be proved.

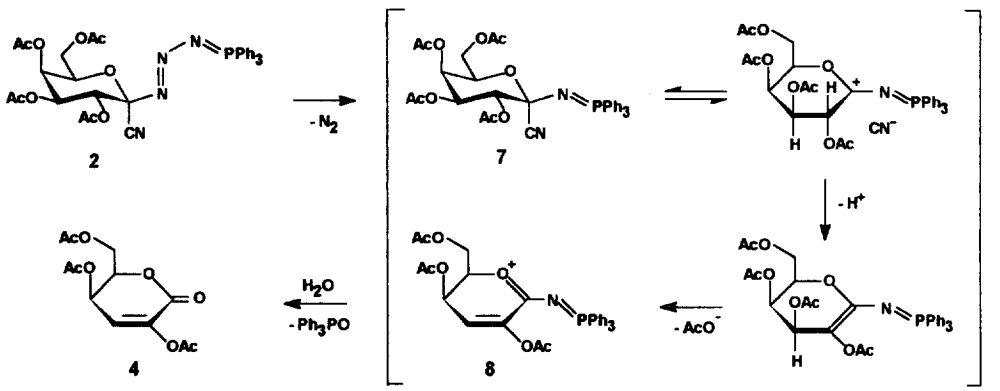
On treatment with perchloric acid in acetic anhydride **2** was transformed into the protonated salt **3**, pro-viding evidence for the phosphazide structure of the molecule. Both **2** and its perchlorate salt (**3**) are stable in solid state, however in chloroform solution they decompose to give multicomponent mixtures.

Attempts to transform **2** into the corresponding phosphinimine by heating in toluene led to a dark comp-lex mixture with tarry precipitation. However, when a solution of **2** in toluene was left to stand at room temperature for 3 d, tlc showed the disappearance of the phosphazide and formation of several products. The main components of the reaction mixture could be separated by column chromatography to give the unsaturated lactone **4**[9,10] (9%), the crystalline (*2Z,4Z*)-3-cyano-4,6-diacetoxy-*N*-(triphenylphosphoranylidene)-2,4-hexadienoic amide (**5**, 44 %) and (*2E,4Z*)-2,4,6-triacetoxy-*N*-(triphenylphosphoranylidene)-2,4-hexadienoic amide (**6**, 18%), besides triphenylphosphine oxide (15%).

^{1}H-, ^{13}C- and ^{31}P-NMR spectra of the unsaturated aliphatic phosphinimines **5** and **6** revealed the constitution of both molecules and pointed to the close analogy of their structure (Tables 1 and 2). The exact structure of **5** was proved by X-ray diffraction.[12] In the case of **6** *Z* configuration of the C-4 = C-5 double bond was corroborated by NOE measurement, indicating the closeness of H-3 and H-5. Otherwise, the large value of the coupling $^{3}J_{CO,H\text{-}3}$ =7.8 Hz, determined by selective 2D INEPT measurement[13], proved the *trans* relationship of H-3 and the imide carbonyl, which corresponds to the *2E* configuration. Thus, disregarding the CN-substituent in **5**, the iminophosphoranes **5** and **6** contain the same carbon skeleton.

When the reaction of **1** with triphenylphosphine (molar ratio 1:1.05) was performed in dry toluene the same products were obtained as from the isolated phosphazide, but in this case the triacetate **6** was formed predominantly. The hexadienoic phosphinimines **5** and **6** are quite stable compounds. In contrast to sugar phosphinimines they do not react with carbon dioxide, owing to their resonance-stabilized structure.

As for the reaction mechanism, transformation of the phosphazide (**2**) in solution may proceed in two different ways. The side-reaction (Scheme 1) leading to the unsaturated lactone **4** involves the formation of 1-cyano-1-phosphinimine **7** which can be stabilized by releasing the cyanide anion and eliminating acetic acid to give an unsaturated lactone-imino phosphonium salt (**8**). Formation of the enollacton **4** is attributed to the hydrolysis of **8** during the reaction or chromatographic separation.

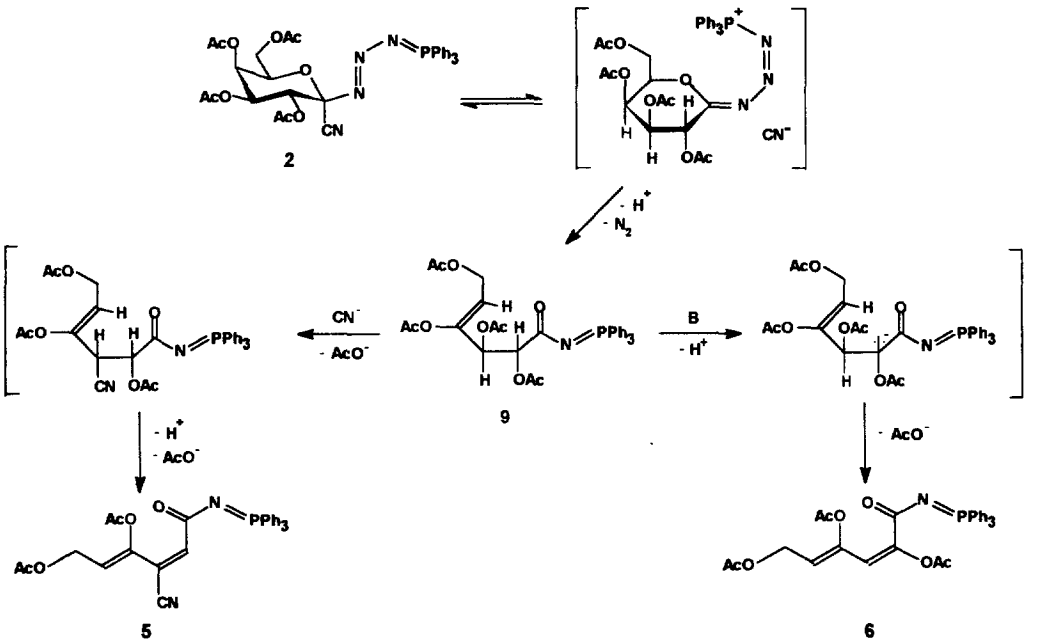


Scheme 1

The main pathway (Scheme 2) resulting in the formation of acyclic unsaturated iminophosphoranes **5** and **6** requires an unusual ring opening between C-5 and the pyranose oxygen. The reason for this might be the relative stability of the phosphazide system in the *Z* configuration which allows an interaction between the pyranose oxygen and the positively charged phosphorus atom. This anchimeric effect may help on the pyranose ring opening. Subsequent deprotonation at C-4 and splitting of nitrogen make the reaction irreversible furnishing a 4,5-unsaturated aldonyl phosphinimine (**9**) which may serve as a key intermediate for both final products. On one hand, replacement of AcO-3 by the cyanide anion (S_N2 reaction) followed by release of H-3 and subsequent β-elimination of the acetate anion from C-2 leads to the product **5**. Alternatively, **9** may be stabilized by deprotonation from C-2 and β-elimination of AcO-3 to give the triacetate **6**. The influence of the reaction conditions on the yields of the products is being investigated.

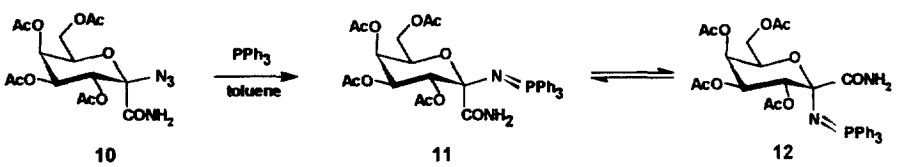
A similar acetoxy-group elimination process affording heterocycles with penta-dienyl side chain was observed[14] in the anomalous Wittig reaction of aldonic thioamide derivatives.

In contrast to the very fast transformation of **1** with triphenylphosphine, the carboxamide analogue **10**[6b] reacts very slowly under the same conditions. With 1.1 equiv triphenylphosphine in diethyl ether at room



Scheme 2

temperature the reaction was not complete even in two weeks. Therefore, 2 equiv triphenylphosphine was used in toluene at 80° C for 10 h and the reaction mixture was chromatographed to give 3,4,5,7-tetra-O-acetyl-2-deoxy-2-(triphenylphosphoranylideneamino)-β-D-*galacto*-hept-2-ulopyranosonamide (**11**) and its α-anomer (**12**) in 36% and 21% yield, respectively. Both anomers are stable in neat form, however, during six weeks in chloroform solution they anomerize to give a 15:85 mixture of **11** and **12** as shown by NMR measurements. The preponderance of **12** in the equilibrium mixture - indicated also by tlc and the change of optical rotation - may be explained by the strong anomeric effect of the phosphinimino-group[15] and the reverse anomeric effect of the carbamoyl group.[16]



The ^{1}H-NMR spectra (Table 1) of both **11** and **12** indicated the acetylated galactopyranose moieties to be in the $^4C_1$ conformation. The theoretically possible ring closure between the phosphinimine function and the carbamoyl group to form a spirobicycle could be ruled out by the heterocorrelated 2D ^{1}H-^{15}N NMR spectrum of the equilibrium mixture of **11** and **12** which proved that in both anomers the two NH protons belong to the same nitrogen atom. Selective ^{1}H-{^{1}H} NOE measurements helped to assign the stereochemistry of **11** and **12**.

Table 1. ^{1}H-NMR data[a] measured for $CDCl_3$ solutions at 400 MHz (δ [ppm], *J* [Hz])

	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{6a,6b}$)	H-6b ($J_{5,6b}$)	Phenyl H_{ortho}	Phenyl H_{para}	Phenyl H_{meta}	Acetyl	NH ($J_{NH,NH}$)
2	5.73 (10.5)	5.29 (3.2)	5.52 (1.3)	4.42 (6.8)	4.20 (11.2)	4.13 (6.2)	7.72	7.64	7.52	2.14, 2.02, 1.97, 1.67	--
3	5.47 (10.5)	5.22 (3.2)	5.51 (1.3)	4.38 (6.3)	4.15 (11.3)	4.12 (6.5)	7.7-7.8	7.89	7.7-7.8	2.17, 2.04, 1.97, 1.81	--
4	--	6.64 (6.3)	5.43 (2.6)	4.92 (6.0)	4.37 (11.6)	4.35 (6.5)	--			2.28, 2.12, 2.11	--
5	6.91	--	--	6.05 (6.5)	4.51	4.51 (6.5)	7.74	7.61	7.50	2.01, 1.61	--
6	--	6.10[b]	--	5.64 (6.9)	4.53	4.53 (6.9)	7.76	7.56	7.47	2.21, 1.97, 1.71	--
11	5.12 (10.7)	5.95 (3.6)	5.38 (2.0)	5.03 (6.4)	3.69 (10.9)	3.66 (6.8)	7.69	7.49	7.43	2.11, 1.90, 1.88, 1.84	8.03, 5.70 (6.0)
12	5.41[c] (10.2)	5.83 (3.5)	5.59 (1.5)	4.78 (5.6)	4.12 (11.2)	4.00 (7.3)	7.76	7.46	7.39	2.12, 2.00, 1.98, 1.91	6.20, 4.67 (4.0)

[a]Listed according to parent sugar numbering. [b]$J_{3,5} \approx 1$ Hz, $J_{3,6} \approx 1$ Hz. [c]$J_{H\text{-}2,P} = 5.0$ Hz.

Table 2. ^{13}C- and ^{31}P-NMR data[a,b,c] for $CDCl_3$ solutions[d]

	C-1	C-2	C-3	C-4	C-5	C-6	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	$CH_3\underline{C}O$	$\underline{C}H_3CO$	CN	$CONH_2$	P
2	94.27	68.21	70.28	66.80	71.55	61.05	125.90 (95.9)	133.67 (9.2)	128.98 (12.0)	133.10 (2.9)	170.26 170.20 169.90 168.26	20.67 20.62 20.57 20.30	114.49	--	25.92
3	92.85	66.13[e]	69.47	66.79[e]	72.68	60.58	117.06 (102)	134.34 (11.7)	130.40 (13.9)	136.23 (3.0)	170.19 169.92 169.61 168.25	20.62 20.60 20.44 20.16	112.13	--	39.00
4	157.53	141.85	124.42	62.97	76.13	61.27	--	--	--	--	170.39 169.76 168.08	20.67 20.51 20.35	--	--	--
5	172.10 (7.4)	144.19 (23.6)	111.17 (2.6)	142.41	119.25	58.65	126.96 (99.5)	133.21 (10.3)	128.88 (12.5)	132.77 (2.9)	170.53 167.72	20.75 19.92	117.07	--	20.91
6	169.88 (7.0)	148.15 (25.3)	116.82 (1.4)	144.47	117.35	58.99	127.48 (99.7)	133.21 (10.1)	128.68 (12.5)	132.41 (2.7)	170.71 169.34 168.26	20.84 20.81 20.19	--	--	22.08
11	90.65 (8.7)	74.13 (2.6)	69.49	68.31	70.80	62.02	132.70 (101.8)	132.84 (10.1)	128.10 (12.2)	131.27 (2.7)	170.49 170.27 169.97 169.92	21.16 20.90 20.75 20.73	--	174.52	5.20
12	91.15 (1.9)	71.01 (16.8)	69.92	69.22	67.14	62.73	132.70 (102.1)	132.81 (9.8)	128.00 (12.1)	131.09 (2.7)	170.54 170.47 170.44 170.39	20.88 20.87 20.81 20.67	--	172.58	8.68

[a]Listed according to parent sugar numbering. [b]Chemical shifts (δ [ppm]). [c]Couplings [Hz] of ^{31}P with the corresponding ^{13}C in parenthesis. [d]Recorded at 101 MHz (^{13}C) and 162 MHz (^{31}P), respectively. [e]Assignments may be interchanged.

In **11** NOE-s were measured between H-2 and the *ortho* phenyl protons, while irradiation of H-3 resonance gave enhancement of the amide proton signals. On the contrary, spatial proximity was observed between H-2 and the amide protons, moreover, between H-3, H-5 and the phenyl protons in **12.** These results are in agreement with the vicinal coupling value between the amide carbonyl and H-2 which, knowing the conformation ($^4C_1$) of the pyranoid ring, allowed to establish the absolute configuration of the anomeric carbon in both anomers. Thus, $^3J_{CONH2,H\text{-}2}$ = 5.7 Hz measured in **11** corresponds to the antiperiplanar (*trans*) orientation of H-2 and the amide carbonyl (*S* configuration), while $^3J_{CONH,H\text{-}2}$ = 1.5 Hz for **12** indicates a *gauche* coupling (*R* configuration). These values accord well with the corresponding three bond couplings of the parent azido-amide **10** and those of other glycopyranosylidene derivatives having a C-substituent at the anomeric carbon.[6] Both C-1 and C-2 (according to parent sugar numbering) couple with phosphorus, however, a striking difference was found in the $^2J_{C\text{-}1,P}$ value for **11** (8.7 Hz) and that for **12** (1.9 Hz) and, especially, in the $^3J_{C\text{-}2,P}$ value for **11** (2.6 Hz) and that for **12** (16.8 Hz). On the basis of the stereospecificity of $^3J_{C,P}$ couplings[17] the latter large value indicates the γ-*anti* orientation of P-N and C-1 ÷ C-2 bonds in the molecule **12,** stabilized by the exo-anomeric effect.[18] In contrast, the small value of $^3J_{C\text{-}2,P}$ in **11** reflects a conformation in which the orientation of the P-N bond is γ-*gauche* related to the C-1 ÷ C-2 bond. The latter conformation being opposite to that measured in acetylated glycosyl phosphinimines[3c,d] might be stabilized by an interaction between phosphorus and the oxygen atom of the carbamoyl group. Of course, this stabilizing P-O interaction can also work in the case of the thermodynamically more stable anomer **12**. The ^{31}P-NMR spectra of **11** and **12** exhibited signals of phosphorus at very high field (δ 5.20 in **11** and δ 8.60 in **12**) in comparison to those of various imino-phosphoranes.[3c,d,7]. This may be the consequence of the special structural feature that in **11** and **12** the phosphinimino group is bonded to an electrondeficient quaternary carbon.

These sugar phosphinimines of new type have low reactivity, both **11** and **12** remained intact on treatment with methyl iodide as well as in the attempted aza-Wittig reaction with carbon dioxide. This latter reaction was unsuccessful, as reported very recently[19], even if the azido-amide **10** was treated with tri-n-butyl-phosphine in the presence of carbon dioxide. On the contrary, the phosphinimine method has been successfully applied to a D-*ribo* configurated, furanoid azido-amide providing a facile synthetic route to (+)hydantocidin.[20]

EXPERIMENTAL

Tlc was performed on DC-Alurolle, Kieselgel 60 F_{254} (Merck); detection by UV light and charring with H_2SO_4. For column chromatography Kieselgel 60 (Merck) was used. Melting points were measured in open capillary tubes in a Büchi apparatus or on a Koffler hot-stage and are uncorrected. Optical rotations were determined with a Zeiss Polamat A polarimeter at 25 °C. Ir spectra were taken with a Nicolet FT 205 spectrometer. The Raman spectra were recorded on a Nicolet 950 FT Raman spectrometer. NMR spectra were recorded on a Varian VXR-400 spectrometer. Chemical shifts refer to signals of tetramethylsilane in the case of ^{1}H- and ^{13}C spectra and to 85 % aqueous phosphoric acid in the case of ^{31}P spectra. Fast-atom bombardment (FAB) mass spectra were obtained with a VG ZAB-2SEQ mass spectrometer (using 3-nitro-benzylalcohol matrix). Microanalyses were performed in the Microanalytical Laboratory of the Institute

(1R)-2,3,4,6-Tetra-O-acetyl-1-(3-triphenylphosphazido)-D-galactopyranosyl cyanide [*3,4,5,7-tetra-O-acetyl-2-deoxy-2-(3-triphenylphosphazido)-β-D*-galacto-*hept-2-ulopyranosono-nitrile*] **2.** (a) To a stirred solution of **1**[6] (159 mg, 0.4 mmol) in dry diethyl ether (3 ml) was added a solution of triphenylphosphine (110 mg, 0.42 mmol) in the same solvent (4 ml). A white solid precipitated within 1 min. After stirring for 10 min at room temperature the product was collected and washed with dry ether to give practically pure **2** (211 mg, 80 %), mp 92-93 °C; $[\alpha]_D$ +99 (c1.5, $CHCl_3$); IR (KBr): ν 1756 (OAc), 1430, 1113, 723, 694 cm^{-1} (Ph); Raman (solid): ν 2235 (CN), 1756 (OAc), 1586, 1103, 1027, 997 cm^{-1} (Ph); MS: 661 $[M+H]^+$. Anal. Calcd for $C_{33}H_{33}N_4O_9P$ (660.64): C, 60.00; H, 5.04; N, 8.48. Found:C, 59.83; H, 4.89; N, 8.13.

(b) When the reaction was carried out in the same way but using 2 equiv triphenylphosphine, **2** was obtained in 74 % yield, identical with the product in (a). Excess of PPh_3 was detected (tlc) in the mother liquor.

(c) Using 0.5 equiv PPh_3 in the same reaction afforded **2** in 33 % yield (calculated for **1**), identical with the product in (a). Concentration of the filtrate and crystallization of the residue from EtOH gave unreacted **1** (37 %).

Perchlorate salt (**3**) *of phosphazide* **2.** To a solution of **2** (0.33 g, 0.5 mmol) in an ice-cold mixture of aqueous 70 % perchloric acid (0.2 ml) and acetic anhydride (2 ml) was added diethyl ether (25 ml) to give crude **3** (0.34 g, 89 %), mp 129-133 °C. Precipitation with diethyl ether from dichloromethane solution afforded the pure salt (0.25 g, 66 %) mp 138 °C; $[\alpha]_D$ + 44 (c2, $CHCl_3$); IR (KBr): ν 1761 (OAc), 1439, 1119, 732 (Ph), 1100, 623 cm^{-1} (ClO_4^-). Anal. Calcd for $C_{33}H_{34}ClN_4O_{13}P$ (761.10): C, 52.08; H, 4.50; N, 7.36. Found: C, 51.94; H, 4.33; N, 7.26.

Transformation of **2** *in toluene.* (a) A solution of **2** (0.4 g, 0.6 mmol) in dry toluene (8 ml) was stored at room temperature for 3 d. The brown solution was decanted from the tarry residue and concentrated in *vacuo* to give a complex mixture. Column chromatography on silica gel (eluent: dichloromethane-acetone 9:1) afforded *(5R,6R)-3,5-bis(acetoxy)-6-(acetoxymethyl)-5,6-dihydro-2H-pyran-2-one*[9,10] **4** (15 mg, 9 %) as a colourless oil, the crystalline *(2Z,4Z)-3-cyano-4,6-diacetoxy-*N*-(triphenylphosphoranylidene)-2,4-hexadienoic amide* **5** (136 mg, 44 %) and *(2E,4Z)-2,4,6-triacetoxy-*N*-(triphenylphosphoranylidene)-2,4-hexadienoic amide* **6** (60 mg, 18 %) as a colourless solid and triphenylphosphine oxide (25 mg, 15 %), respectively.

For **4**: $[\alpha]_D$ -150 (c0.5, $CHCl_3$). Anal. Calcd for $C_{12}H_{14}O_8$ (286.24): C, 50.35; H, 4.93. Found: C, 50.58; H, 4.99.

For **5**: mp 137 °C (from diethyl ether); IR (KBr): ν 2227 (CN), 1769, 1741 (OAc), 1593 (CO), 1440, 1114, 723 cm^{-1} (Ph); Raman (solid): ν 2232 (CN), 1671, 1609 1590 (C=C), 1027, 999 cm^{-1} (Ph); MS: 513 $[M+H]^+$. Anal. Calcd for $C_{29}H_{25}N_2O_5P$ (512.51): C, 67.96; H, 4.92; N, 5.47. Found: C, 67.90; H, 5.03; N, 5.60.

For **6**: mp 128-129 °C (from diethyl ether); IR (KBr): ν 1763, 1737 (OAc), 1598 (CO), 1439, 1116, 723 cm^{-1} (Ph); Raman (solid): ν 1656, 1590 (C=C), 1029, 1000 cm^{-1} (Ph); MS: 546 $[M+H]^+$. Anal. Calcd for $C_{30}H_{28}NO_7P$ (545.54): C, 66.05; H, 5.17; N, 2.57. Found: C, 66.09; H, 5.26; N, 2.74.

(b) To a solution of **1** (219 mg, 0.55 mmol) in dry toluene (5 ml) was added dropwise a solution of triphenylphosphine (152 mg, 0.58 mmol) in the same solvent (5 ml) during 15 min and the mixture was stored at room temperature for 3 d. Work-up according to (a) furnished **4** (9 mg, 6 %) and **5** (54 mg, 19 %) and **6** (88 mg, 29 %) and triphenylphosphine oxide (32 mg, 21 %), respectively, identical with the products in (a).

3,4,5,7-Tetra-O-acetyl-2-deoxy-2-(triphenylphosphoranylideneamino)-β- (**11**) *and -α-D*-galacto-*hept-2-ulopyranosonamide* (**12**). To a solution of **10** (416 mg, 1 mmol) in dry toluene (25 ml) was added triphenylphosphine (0.52 g, 2 mmol) and the mixture was heated at 80 °C for 10 h. After removal of the solvent in *vacuo*, the residue was chromatographed on a silica gel column using diethyl ether as eluent. First, unreacted triphenylphosphine (239 mg, 46 %) was recovered then the anomeric mixture of **11** and **12** (483 mg, 75 %) was obtained. Repeated column chromatography of the raw product using dichloromethane/acetone 3:1 as eluent gave the syrupy **11** (237 mg, 36 %) and **12** (134 mg, 21 %), respectively.

For **11**: $[\alpha]_D$ -12.9 → +79.4 (c3.1, $CHCl_3$); IR (film): ν 1749 (OAc), 1685 ($CONH_2$), 1438, 1109, 715, 696 cm^{-1} (Ph). Anal. Calcd for $C_{23}H_{35}N_2O_{10}P$ (650.63): C, 60.92; H, 5.42; N, 4.31. Found: C, 60.59; H, 5.27; N, 4.19.

For **12**: $[\alpha]_D$ + 95 → + 79.8 (c3.2, $CHCl_3$); IR(film): ν 1749 (OAc), 1700 ($CONH_2$), 1438, 1110, 716, 695 cm^{-1} (Ph). Anal. Calcd for $C_{33}H_{35}N_2O_{10}P$ (650.63): C, 60.92; H, 5.42; N, 4.31. Found: C, 60.74; H, 5.19; N, 4.21.

Solutions of both **11** and **12** in $CDCl_3$ were proved by NMR to transform into anomeric mixtures of **11** and **12** with the equilibrium ratio of 15:85 within 6 weeks, in accord with the change of the optical rotations.

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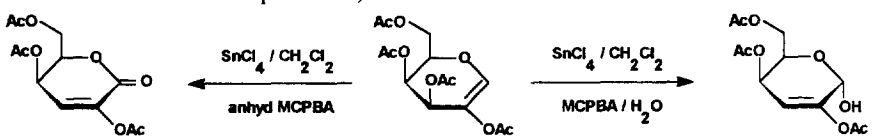
REFERENCES AND NOTES

1. Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635-646.
2. a) Gololobov, Yu. G. *Tetrahedron* **1992**, *48*, 1353-1406; b) Molina, P.; Vilaplana, M. J. *Synthesis* **1994**, 1197-1218.
3. a) Messmer, A.; Pintér, I.; Szegõ, F. *Angew. Chem.* **1964**, *76*, 227-228; b) Pintér, I.; Kovács, J.; Messmer, A.; Kálmán, A.; Tóth, G.; Lindberg, B. K. *Carbohydr. Res.* **1979**, *72*, 289-296, c) Kovács, J.; Pintér, I., Messmer, A.; Tóth, G.; *Carbohydr. Res.* **1985**, *141*, 57-65; d) Kovács, J.; Pintér,I.; Messmer, A.; Tóth, G.; Duddeck, H. *Carbohydr. Res.* **1987**, *166*, 101-111; e) Cano, F. H.; Foces-Foces, C.; Jiménez-Barbero, J.; Allemany, A.; Bernabé, M.; Martin-Lomas, M. *J. Org. Chem.* **1987**, *52*, 3367-3372; f) Rück, K.; Kunz, H. *Synthesis* **1993**, 1018-1028; g) Pintér, I.; Kovács, J.; Tóth, G. *Carbohydr. Res.* **1995**, *273*, 99-108; h) Mészáros, P.; Kovács, J.; Pintér, I. *Carbohydr. Lett.* (in press).
4. a) Praly, J-P.; El Kharraf, Z.; Descotes, G. *J. Chem. Soc., Chem. Commun.* **1990**, 431-432, b) Praly, J-P.; Péquery, F.; Di Stéfano, C.; Descotes, G. *Synthesis* **1996**, 577-579.
5. Kovács, J.; Pintér, I.; Kajtár-Peredy, M.; Praly, J-P.; Descotes, G. *Carbohydr. Res.* **1995**, *279*, C1-C3.
6. a) Praly, J-P.; Di Stéfano, C.; Descotes, G.; Faure, R.; Somsák, L.; Eperjesi, I. *Tetrahedron Lett.* **1995**, *36*, 3329-3332; b) Somsák, L.; Sós, E.; Györgydeák, Z.; Praly, J-P.; Descotes, G. *Tetrahedron* **1996**, *52*, 9121-9136, and refs. therein.
7. Molina, P.; López-Leonardo, C.; Llamas-Botía, J.; Foces-Foces, C.; Fernández-Castano, C. *Tetrahedron* **1996**, *52*, 9629-9642, and refs. therein.
8. Ponomarchuk, M. P.; Kasukhin, L. F.; Shevchenko, M. V.; Sologub, L. S.; Kukhar, V. P. *Zh. Obshch. Khim.* **1984**, *54*, 2468-2473.
9. Lichtenthaler, F. W.; Rönninger, S.; Jarglis, P. *Liebigs Ann.Chem.* **1989**, 1153-1161.
10. The physical and spectral data for the enollactone **4** are at variance with those reported for a product of stucture **4** with mp 159-161 °C and $[\alpha]_D$ -45 (c1, $CHCl_3$), obtained on $SnCl_4$ catalyzed 3-chloroperbenzoic acid (MCPBA)-oxidation of 3,4,6-tri-O-acetyl-2-deoxy-D-galactal[9] (**i**). These discrepancies were resolved by the finding[11] that $SnCl_4$-promoted peroxidation of (**i**) with anhydrous MCPBA indeed yields the enollactone **4** as colourless syrup of $[\alpha]_D$ - 151.5 (c1, $CHCl_3$), exhibiting the NMR data reported here (Tables 1 and 2). The crystalline product previously obtained and erroneously taken for enollacton **4**, proved to be[11] 2,4,6-tri-O-acetyl-3-deoxy-α-D-*threo*-hex-2-enopyranose (**ii**) of mp 160-161 °C and $[\alpha]_D$ -45 (c1, $CHCl_3$) ; ^{1}H-NMR ($CDCl_3$): δ 2.07, 2.09, 2.19 (3s, OAc), 4.17 (m, H-5), 4.32 (m, H_2-6), 5.26 (dd, H-4), 5.50 (s, H-1), 6.02 (d, H-3), $J_{3,4}$ =6.1, $J_{4,5}$ = 1.3 Hz.[11] Compound **ii** is formed instead of **4**, when the $SnCl_4$-induced MCPBA-oxidation is not performed under strictly anhydrous conditions (commercial MCPBA contains water up to 35 %).



4 **i** **ii**

11. Lichtenthaler, F. W. personal communication.
12. Argay, Gy.; Kálmán, A.; Kovács, J.; Pintér, I. in preparation.
13. Jippo, T.; Kamo, O.; Nagayama, K. *J. Magn. Reson.* **1986**, *66*, 344-348.

14. Somogyi, L.; Herczegh, P.; Batta, Gy. *Heterocycles* **1984**, *24*, 2735-2738.
15. Paulsen, H.; Györgydeák, Z.; Friedmann, M. *Chem. Ber.* **1974**, *107*, 1590-1613.
16. Chmielewski, M.; BeMiller, J. N.; Cerretti, D. P. *J. Org.Chem.* **1981**, *46*, 3903-3908.
17. a) Buchanan, G. W.; Morin, F. G. *Can J. Chem.* **1979**, *57*, 21-26; b) Quin, L. D.; Gallagher, M. J.; Cunkle, G. T.; Chesnut, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 3136-3143; c) Duncan, M.; Gallagher, M.J.; *Org. Magn. Reson.* **1981**, *15*, 37-42.
18. Juaristi, E.; Cuevas, G. *Tetrahedron* **1992**, *48*, 5019-5087, and refs. therein.
19. Õsz, E.; Sós, E.; Somsák, L.; Szilágyi, L.; Dinya, Z. *Tetrahedron* **1997**, *53*, 5813-5824.
20. Mio, S.; Kumagawa, Y.; Sugai, S. *Tetrahedron* **1991**, *47*, 2133-2144.

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