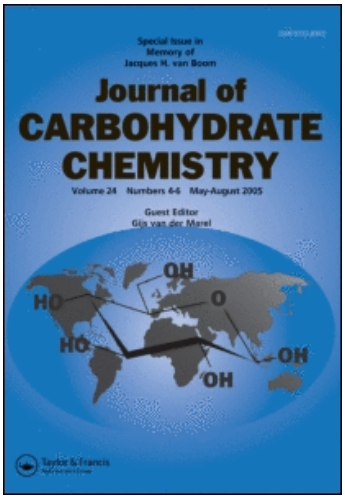

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Regioselective Benzoylation of N-Protected D-Glucosamine

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REGIOSELECTIVE BENZOYLATION OF N-PROTECTED D-GLUCOSAMINE

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ABSTRACT

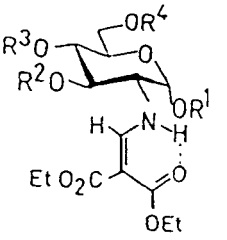
Regioselective benzoylations of 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (1) yielded 6-mono-*O*- (2) 3,6-di-*O*- (3), 4,6-di-*O*- (4) and 1,3,6-tri-*O*-benzoyl- (5) derivatives. The fully benzoylated compound 6 was the major product when excess of benzoyl chloride was used. The di-*O*-acetyl derivatives (7 and 8) of 3 and 4 respectively were also prepared. The structures of 2-8 are based on analytical and/or spectroscopic data. Some data on MS fragmentation pathways of the partially protected compounds 2 and 4 are also reported.

INTRODUCTION

Selectively esterified monosaccharide derivatives are useful precursors for specific functionalisation[1-2] and for oligosaccharide syntheses.[3] On the other hand, D-glucosamine is a frequent structural unit in natural oligo- and polysaccharides. Regioselective acylation of sugar derivatives has been performed by both chemical[1,2,4] and enzymatic[5-8] methods and regioselective benzoylation has been carried out on pentopyranosyl[9,10] and hexopyranosylamines.[2] This paper describes our findings regarding the regioselective benzoylations of 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose[11] (1), which is a D-glucosamine derivative suitable for *N*-deprotection.[2,11]

RESULTS AND DISCUSSION

The results from the treatment of 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (1) with 2-5.5 mol of benzoyl chloride in pyridine at different temperatures are shown in Table I. Although the work-up of these reactions involves a distribution between water and chloroform (see Experimental), TLC of the residue of the aqueous layer after concentration showed no presence of benzoyl derivatives **2-6**. Compounds **2-4** each have a free anomeric hydroxyl group. However, they do not mutarotate (see Experimental), and **3** and **4** on acetylation yield exclusively the α-acetates **7** and **8**, respectively. Additionally, the 1-*O*-benzoyl derivatives 5 and 6 have the α anomeric configuration (see below). These facts are in agreement with data reported for 2-(2-acylvinylamino)-2-deoxy-α-D-glucopyranose and their tetra-*O*-acetyl derivatives which indicate that the *N*-(2-acylvinyl) group reinforces the anomeric effect.[11] Moreover, it has also been described[12] that the catalytic de-*O*-acetylation at C-1 of 1,3,4,6-tetra-*O*-acetyl-2-(2-acylvinylamino-2-deoxy-α- and β-D-glucopyranoses yielded only 3,4,6-tri-*O*-acetyl-2-(2-acylvinylamino)-2-deoxy-α-D-glucopyranoses.



	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
R^1	H	H	H	H	Bz	Bz	Ac	Ac
R^2	H	H	Bz	H	Bz	Bz	Bz	Ac
R^3	H	H	H	Bz	H	Bz	Ac	Bz
R^4	H	Bz	Bz	Bz	Bz	Bz	Bz	Bz

The partially protected compounds which can be isolated with best yields are **2** (Table 1, entry 2), **3** and **5** (Table 1, entry 3). The experiments at low temperature (entries 1-3) indicate that the order of reactivity on benzoylation of **1** is OH-6>OH-3>OH-1≅OH-4. The experiments at r.t. and 45 °C (entries 4 and 5) show that no significant regioselectivity takes place over 0 °C. The primary hydroxyl group is esterified more readily than are secondary hydroxyl groups, as is described for hexopyranosylamines[2] and hexopyranosides.[13] The low reactivity of OH-4 has been observed in glucose,[14] α-glucosides[4] and glucosylenamines,[2] and may be due to steric hindrance through a *gauche* interaction with CH_2OBz (considering that HO-6 is esterified first) and BzO-3. The relatively low reactivity of the anomeric hydroxyl group is attributed to its axial position[2,9,11] and to the steric effect of the bulky enamino group on C-2. The HO-3 in **1** is less reactive than the same hydroxyl group in glucosylenamines,[2] which may be explained by the above mentioned steric effect of the enamino group.

The acetyl derivatives **7** and **8** were prepared in order to complete the structural study of **3** and **4** respectively.

The structures of **2-8** were based on UV, IR , ^1H and ^{13}C NMR, analytical and/or mass spectroscopic data.

Compounds **2-8** showed low stretching frequencies for NH (3230-3290 cm^{-1}) and C=O (1647-1674 cm^{-1}) groups, indicative of a chelated structure.[11,15] This fact was also confirmed by the chemical shifts (see Tables 2-4) for the resonances of the *NH* (9.08-9.32 ppm) and one *C*=O group (167.9-169.8 ppm) and by the high value for $J_{NH,=CH}$ (12.7-14.6 Hz, Table 3) which is indicative of antiperiplanar protons.

The values of $J_{1,2}$ (≅3.7 Hz), the high and positive optical rotation for **2-8** and the ^1H δ values for the 1-OAc signal (≅2.21 ppm) in **7-8** showed α(**D**) configuration for prepared compounds. The $^3J_{H,H}$ values for **3-8** indicated the

Table 1. Benzoylations of 1.

Entry	Temp. (°C)	[BzCl]/1 in mol	Benzoylated derivative and yield (%)					Benzoylated positions (%)			
			2	3	4	5	6	OH-6	OH-4	OH-3	OH-1
1	-40	2:1	31.0	1.2	0.5	---	---	32.7	0.5	1.2	---
2	-15	3:1	37.0	2.0	0.4	0.6	---	40.0	0.4	2.6	0.6
3	0	4:1	---	15.0	5.0	16.0	16.0	52.0	21.0	47.0	32.0
4	r.t.	9:2	---	---	---	3.0	80.0	83.0	80.0	83.0	83.0
5	45	11:2	---	---	---	---	92.0	92.0	92.0	92.0	92.0

Table 2. ^{1}H NMR chemical shifts (δ, ppm) of compounds **2-8** in $CDCl_3$.

Comp.	Sugar ring							Enamino group			
	H-1	H-2	H-3	H-4	H-5	H-6	H-6'	NH	=CH	CH_2	CH_3
2[a]	5.13dd	<-----3.50-3.10m----->			4.30-3.80m	4.53dd	4.40dd	9.08dd	8.00d	4.10q 4.04q	1.21t 1.19t
3[b]	5.47d	3.61td	5.64t	3.82t	4.38m	4.73dd	4.63dd	9.14dd	8.02d	4.14q 4.04q	1.25t 1.17t
4[b]	5.40bd	3.47td	4.20t	5.34t	4.53ddd	4.63dd	4.34dd	9.30dd	8.10d	4.19q 4.11q	1.30t 1.24t
5[b]	6.53d	3.85td	5.69t	3.88m	4.20m	4.88dd	4.51dd	9.21dd	8.00d	4.08q 4.05q	1.18t 1.17t
6[b]	6.61d	4.10-3.90m	6.03t	5.79t	<-----4.65-4.39m----->			9.23dd	7.96d	4.12q 4.10-3.90m	1.18t 1.15t
7[b]	6.24d	3.74td	5.59t	5.34t	4.21m	<-4.48-4.32m->		9.08dd	7.78d	4.15q 3.93q	1.12t 1.06t
8[b]	6.24d	3.67td	5.53t	5.43t	4.35m	<-4.57-4.40m->		9.15dd	7.93d	4.15q 4.10q	1.20t 1.17t

a. In $(CD_3)_2SO$.
b. In $CDCl_3$.

Table 3. ^{1}H NMR coupling constants (Hz) of compounds **2-8**.

Comp.	Sugar ring							Enamino group		
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{NH,=CH}$	$J_{2,NH}$	$^3J_{H,H}$ (Et)
2[a]	3.7	---	---	---	2.5	5.0	12.5	14.3	9.0	7.0
3[b]	3.5	10.0	10.0	10.0	3.5	2.3	12.3	14.3	10.0	7.1
4[b]	3.7	9.7	9.7	9.7	2.7	4.3	11.9	13.7	9.7	7.1
5[b]	3.7	10.0	10.0	---	3.5	2.2	12.3	12.7	9.2	7.1
6[b]	3.8	9.9	9.9	9.9	---	---	---	14.6	9.6	7.1
7[b]	3.7	9.8	9.8	9.8	---	---	---	13.3	9.8	7.1
8[b]	3.7	9.7	9.7	9.7	---	---	---	13.1	9.7	7.1

a. In $(CD_3)_2SO$.
b. In $CDCl_3$.

Table 4. ^{13}C NMR chemical shifts (δ, ppm) for the sugar rings of compounds 2-8.

Comp.	C-1	C-2	C-3	C-4	C-5	C-6
2[a]	90.7	63.4	71.6	69.7	70.2	64.2
3[b]	91.5	62.5	74.8	69.4	70.3	63.2
4[b]	91.4	63.9	71.6	70.6	67.7	62.9
5[b]	91.6	61.3	73.8	68.5	73.0	62.8
6[b]	91.4	61.4	71.2	68.4	70.0	62.1
7[b]	90.6	61.1	71.2	67.6	70.0	61.8
8[b]	90.3	60.7	70.6	68.5	69.9	62.2

a. In $(CD_3)_2SO$.

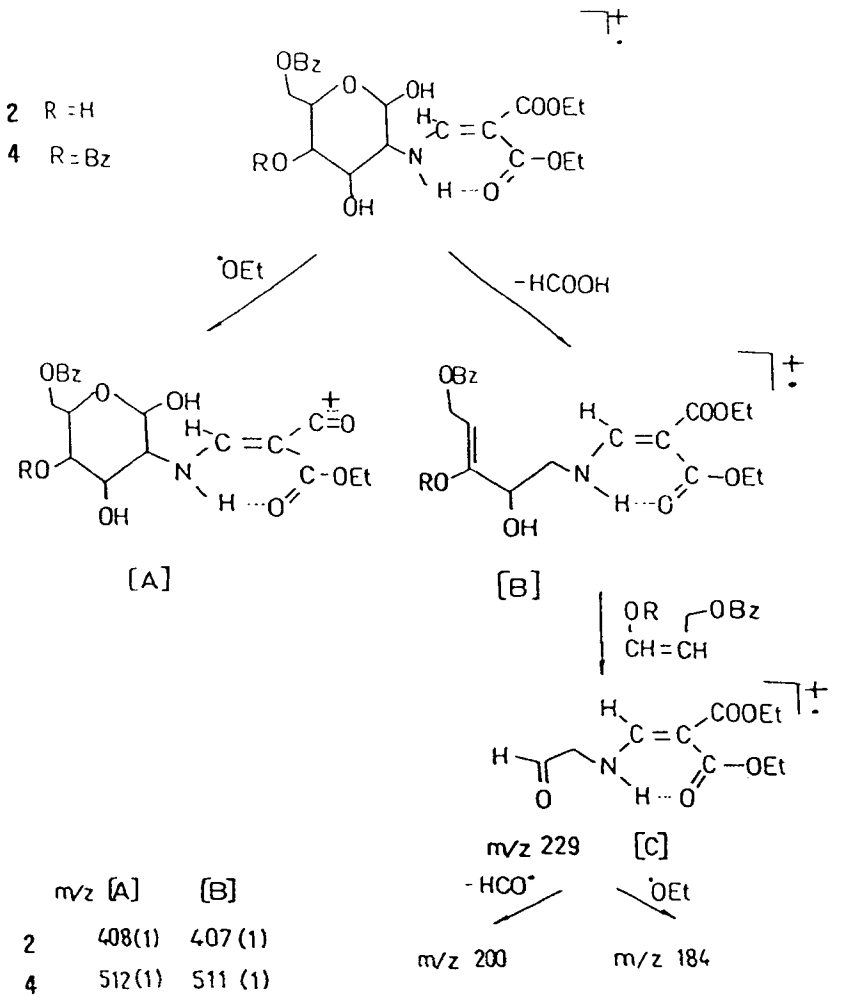
b. In $CDCl_3$.

presence of a $^4C_1$(D) conformation in chloroform-d_3 solutions.

No transbenzoylations were observed when solutions of **2** (methyl sulphoxide-d_6), and **3-5** (chloroform-d_3) were kept for ten days at room temperature.

The mass spectra of **2-4**, **7** and **8** showed molecular ions. The base peaks for **2-8** were always *m/z* 105 (Bz^+) and prominent fragments at *m/z* 122 ($BzOH^+$) and 77 (Ph^+) were observed. Scheme 1 summarises the primary fragments and the pathways of fragmentation for **2** and **4**. The spectrum of **4** was carried out with a resolution of 10,000 (10% valley definition) and the atomic composition of the fragments agrees with the indicated structures. The loss of EtO$^\bullet$ (peak A) is similar to that reported for

SCHEME 1



m/z	[A]	[B]
2	408(1)	407(1)
4	512(1)	511(1)

N-diethoxycarbonylvinyl glycosylamines.[9] Peak B is evidence of the free anomeric hydroxyl group, and its structure is similar to that described for acetylated aldopyranosylamines.[16] Peak C shows the presence of a hydroxyl group on C-3. Although no mass spectral data for acylated 2-deoxy-2-enamino aldoses are available, the results for **2-8** (see Experimental) agree with those reported for acetylated[16,17] and benzoylated[9] *N*-substituted glycosylamines.

EXPERIMENTAL

General procedures. Melting points are uncorrected. Optical rotations were measured at 20 ± 2 °C with a Perkin-Elmer 141 MC polarimeter, using 1 cm cell. UV spectra were recorded on a Beckman DU-7 spectrophotometer, IR spectra for KBr discs were measured with a Bomen Michelson MB-120 FT IR spectrophotometer. ^{1}H NMR (200.13 MHz) and ^{13}C NMR (50.33 MHz) were obtained with a Varian XL-200 spectrometer for solutions in $CDCl_3$ or DMSO-d_6. Assignments of ^{1}H signals were confirmed by decoupling and H/D exchange experiments. Proton-decoupled APT[18] (attached proton test) spectra were used to assist in the assignment of signals. EI mass spectra (70 eV) were recorded with a Kratos MS-80RFA instrument, with an ionising current of 100 μA, an accelerating voltage of 4 KV, and a resolution of 1000 (10% valley definition). The elemental compositions of the ions were determined with a resolution of 10000 (10% valley definition). Preparative chromatography was performed on Silica Gel 60 (Merck, 230 mesh), and TLC was carried out on silica gel 30 F_{254} (Merck) plates.

Benzoylation of 2-Deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (1). (a) To a stirred solution of **1** (3.0 g, 8.6 mmol) in pyridine (15 mL) at -40 °C was gradually added benzoyl chloride (2.42 g, 2 mL, 17 mmol) in pyridine (5 mL). The mixture was kept for 72 h at -40 °C, then poured into ice-water (≈300 mL) to give a colourless syrup which was extracted with chloroform (3×30 mL), and successively washed with 1M sulphuric acid (3×30 mL), saturated aqueous sodium hydrogencarbonate (3×30 mL) and water (3×30 mL). The organic layer was dried ($MgSO_4$) and concentrated to dryness to give a syrup. Column chromatography (carbon tetrachloride-acetone 4:1 to 1:1) of this syrup gave 4,6-di-*O*-benzoyl-2-deoxy-2[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (**4**; 25 mg, 0.5%), R_F (carbon tetrachloride-acetone 2:1), 0.61; 3,6-di-*O*-benzoyl-2-deoxy-2[(2,2-diethoxycarbonylvinyl)amino]-α-D-

glucopyranose (3, 58 mg, 1.2%), R_F=0.55; and 6-*O*-benzoyl-2-deoxy-2[(2,2-diethoxycarbonylvinyl)amino]-α-**D**-glucopyranose (2, 1.224 g, 31%), R_F=0.38.

Compound **2** had mp 148-150 °C (from dichloromethane); $[\alpha]_D^{21}$ +82.2° (*c* 1.0, dichloromethane), no mutarotation was observed after 24 h; UV (CH_2Cl_2) 232 and 280 nm (ε_{mM} 13.2 and 18.4); IR 3550 (OH), 3290 (NH), 1724 (C=O free), 1674 (C=O bonded), 1614 (C=C and NH),[11,15] and 1271 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6) Tables 2 and 3, and δ 8.12-7.50 (m, 5H, Bz), 7.10 (d, 1H, $J_{1,OH}$ 5.0 Hz, OH-1), 5.41, and 5.40 (2d, 2H, $J_{3,OH}$=$J_{4,OH}$= 6.0 Hz, OH-3, OH-4); ^{13}C NMR (DMSO-d_6) Table 4 and δ 168.4, 165.8, 165.3 (3C=O), 160.0 (=CH), 133.5-128.9 (6C, Ph), 88.3 (=C), 59.0, 58.9 ($2CH_2$), 14.6 and 14.5 ($2CH_3$). MS (scheme 1): *m/z* 453 (1, $M^{+\cdot}$), 408 (1, $M^{+\cdot}$-EtO$^\cdot$, [A]), 407 (2, $M^{+\cdot}$-HCOOH, [B]), 229 (17, [C]), 200 (40, [C]-HCO$^\cdot$), 184 (19, [C]-EtO$^\cdot$), 154 (73, 184-H_2CO), 122 (80, $BzOH^+$), 105 (100, Bz^+), and 77 (63, Ph^+).

Anal. Calcd for $C_{21}H_{27}O_{10}N$: C, 55.62; H, 6.00; N, 3.08. Found: C, 55.23; H, 5.96; N, 2.87.

Compound **3** was an amorphous and hygroscopic solid, and had $[\alpha]_D^{20}$ +120.3° (*c* 0.8, dichloromethane), no mutarotation was observed after 24 h; UV (CH_2Cl_2) 239.5 and 279.0 nm (ε_{mM} 11.9 and 12.7); IR 3364 (OH), 3280 (NH), 1723 (C=O free), 1661 (C=O bonded), and 1271 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$) Tables 2 and 3, and δ 8.04-7.40 (m, 10H, 2Bz), 5.2 (bs, 2H, 2OH), ^{13}C NMR ($CDCl_3$) Table 4 and δ 168.8, 167.3, 166.8, 165.4 (4C=O), 158.9 (=CH), 133.5-128.3 (12C, 2Ph), 90.9 (=C), 60.2, 59.6 ($2CH_2$), 14.2 and 14.0 ($2CH_3$). MS: *m/z* 557 (1, $M^{+\cdot}$), 226 (6, Bz_2O^+), 122 (78, $BzOH^+$), 105 (100, Bz^+), and 77 (32, Ph^+); Found $M^{+\cdot}$ 557.1907. $C_{28}H_{31}O_{11}N$ requires M, 557.1867.

Compound **4** was an amorphous and hygroscopic solid, and had $[\alpha]_D^{21}$ +26.2° (*c* 0.9, dichloromethane), no change in optical rotation was observed after 24 h; UV (CH_2Cl_2) 233 and 280 nm (ε_{mM} 15.4 and 11.3); IR 3356 (OH), 3260 (NH), 1724 (C=O free), 1661 (C=O bonded), 1603 (C=C and NH), and 1265 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$) Tables 2 and 3, and δ

8.12-7.25 (m, 10H, 2Bz), 4.51 (bs, 2H, 2OH); ^{13}C NMR ($CDCl_3$) Table 4 and δ 169.2, 166.1, 166.0, 165.9 (4C=O), 159.6 (=CH), 133.5-128.3 (12C, 2Ph), 90.4 (=C), 60.0, 59.7 ($2CH_2$), 14.3, and 14.1 ($2CH_3$). MS (scheme 1): *m/z* 557 (1, $M^{+\cdot}$), 512 (1, $M^{+\cdot}$-EtO$^{\cdot}$, [A]), 511 (1, $M^{+\cdot}$-HCOOH, [B]), 229 (8, [C]), 200 (18, [C]-HCO$^{\cdot}$), 184 (9, [C]-EtO$^{\cdot}$), 154 (28, 184-H_2CO), 122 (38, $BzOH^+$), 105 (100, Bz^+), and 77 (30, Ph^+); Found $M^{+\cdot}$ 557.1900. $C_{28}H_{31}O_{11}N$ requires M, 557.1867.

(b) When the reaction was performed with **1** (0.5 g, 1.43 mmol) and benzoyl chloride (0.6 g, 0.5 mL, 4.30 mmol) in pyridine (5 mL) at -15 °C as in (a), **2** (37%), **3** (2.0%), **4** (0.4%), and 1,3,6-tri-*O*-benzoyl-2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (**5**, 6 mg, 0.6%, R_F 0.71), were obtained.

Compound **5** had mp 194-195 °C (from ethanol), $[\alpha]_D^{19}$ +146.5° (*c* 0.4, dichloromethane); UV (CH_2Cl_2) 236.0 and 287.5 nm (ε_{mM} 27.1 and 16.6); IR 3435 OH), 3230 (NH), 1736, and 1723 (C=O free), 1657 (C=O bonded), 1603 (C=C and NH), and 1269 cm^{-1} (C-O-C); ^1H NMR ($CDCl_3$) Tables **2** and **3** , and 8.18-7.39 (m, 15H, 3Bz), 3.63 (bs, 1H, OH-4); ^{13}C NMR ($CDCl_3$) Table 4 and δ 168.9, 166.5, 165.8, 165.2, 164.3 (5C=O), 158.4 (=CH), 134.2-128.4 (18C, 3Ph), 92.6 (=C), 60.1, 59.8 ($2CH_2$), 14.3 and 14.1 ($2CH_3$). MS: *m/z* 253(3), 208(1), 207(1), 180 (8), 122 (52, $BzOH^+$), 105 (100, Bz^+), and 77 (66, Ph^+).

Anal. Calcd for $C_{35}H_{35}O_{12}N$: C, 63.53; H, 5.33; N, 2.11. Found: C, 63.24; H, 5.66; N, 2.06.

(c) When the reaction was carried out from **1** (0.5 g, 1.43 mmol) and benzoyl chloride (0.64 g, 0.53 mL, 4.58 mmol) at 0 °C as in (a), **3** (15%), **4** (5%), **5** (16%), and 1,3,4,6-tetra-*O*-benzoyl-2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (**6**, 0.143 g, 16%, R_F 0.79) were obtained.

Compound **6** had mp 181-182 °C (from ethanol), $[\alpha]_D^{22}$ + 219.2° (*c* 1.0, dichloromethane); UV (CH_2Cl_2) 239.5 and 276 nm (ε_{mM} 30.4 and 21.0); IR 3260 (NH), 1740 (C=O free), 1661 (C=O bonded), 1609 (C=C and NH) and 1260 cm^{-1} (C-O-C);

^{1}H NMR ($CDCl_3$) Tables 2 and 3, and δ 8.27-7.27 (m, 20H, 4Bz); ^{13}C NMR ($CDCl_3$) Table 4 and δ 167.9, 165.8, 165.6,165.0, 164.8, 164.2 (6C=O), 158.0 (=CH), 134.1-128.2 (24C, 4Ph), 92.8 (=C), 59.9, 59.5 ($2CH_2$), 14.1 and 14.0 ($2CH_3$). MS: *m/z* 244(2), 122 (85, $BzOH^+$), 105 (100, Bz^+), and 77 (32, Ph^+).

Anal. Calcd for $C_{42}H_{39}O_{13}N$: C, 65.88; H, 5.13; N, 1.83. Found: C, 65.93; H, 5.20; N, 1.89.

(d) To a stirred solution of **1** (2 g, 5.73 mmol), in pyridine (8 mL) at 0 °C was added gradually benzoyl chloride (3.62 g, 3.0 mL, 25.76 mmol). After 48 h at room temperature, the mixture was poured into ice-water (≈300 mL), and the crude product was treated as in (a) to give **5** (3.0%) and **6** (80%).

In each reaction (a)-(d) the absence of benzoyl derivatives **2-6** in the aqueous layer was confirmed by TLC of the residue of this layer after concentration to dryness.

(e) To a solution of **1** (0.5 g, 1.43 mmol) in pyridine (5 mL) was added benzoyl chloride (1.10 g, 0.91 mL, 7.86 mmol). After 24 h at 45 °C, the mixture was poured into ice-water (≈100 mL), and the crude product was crystallised from ethanol to give **6** (1.0 g, 92%).

1,4-Di-*O*-acetyl-3,6-di-*O*-benzoyl-2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose (**7**) and **1,3-Di-*O*-acetyl-4,6-di-*O*-benzoyl-2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranose** (**8**). Conventional treatments[19] of **3** and **4** (0.070 g, 0.125 mmol) with pyridine (3 mL) and acetic anhydride (0.025 g, 0.023 mL, 0.251 mmol) gave **7** (0.025 g, 31%) and **8** (0.073 g, 90%) respectively as pale and hygroscopic syrups. Compound **7** had $[\alpha]_D^{20}$+154.8° (c 0.7, dichloromethane); UV 233 and 278 nm (ε_{mM} 18.2 and 14.7); IR 3250 (NH), 1755, 1723 (C=O free), 1655 (C=O bonded), 1603 (C=C and NH), 1273 and 1237 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$) Tables 2 and 3, and δ 7.99-7.29 (m, 10H, 2Bz), 2.21 (s, 3H, 1-OAc) and 1.87 (s, 3H, AcO-4); ^{13}C NMR ($CDCl_3$) Table 4 and δ 169.2, 165.8, 165.4, 164.9, 164.3, 163.8 (6C=O), 158.1 (=CH), 133.5-128.2 (12C, 2Ph), 93.0

(=C), 60.0, 59.6 ($2CH_2$), 20.7, 20.4 ($2CH_3CO$), 14.3 and 14.1 ($2CH_3$). MS: *m/z* 641 (2, $M^{+\bullet}$), 581 (2, $M^{+\bullet}$-AcOH), 536 (1, $M^{+\bullet}$-Bz$^{\bullet}$), 508 (1, 581-CO_2Et), 459 (3, 581-BzOH), 430 (2), 249 (3), 270 (5), 122 (32, $BzOH^+$), 105 (100, Bz^+), 77 (27, Ph^+), 60 (12, $AcOH^+$), and 43 (30, Ac^+); Found $M^{+\bullet}$ 641.2080. $C_{32}H_{35}O_{13}N$ requires M, 641.2108. Compound **8** had $[\alpha]_D^{22}$ +54.7° (*c* 1.0, dichloromethane); UV 233 and 278 nm (ε_{mM} 17.6 and 15.8); IR 3260 (NH), 1753, 1726 (C=O free), 1660 (C=O bonded), 1609 (C=C and NH), 1256 and 1239 cm^{-1} (C-O-C); ^{1}H NMR ($CDCl_3$) Table 2 and 3, and δ 8.00-7.34 (m, 10H, 2Ph), 2.22 (s, 3H, AcO-1) and 1.85 (s, 3H, 3-OAc); ^{13}C NMR ($CDCl_3$) Table 4 and δ 169.8, 168.6, 168.4, 165.9, 165.3, 165.0 (6C=O), 158.6 (=CH), 133.6-128.2 (12C, 2Ph), 93.0 (=C), 60.7, 60.1 ($2CH_2$), 20.7, 20.3 ($2CH_3CO$), 14.26 and 14.10 ($2CH_3$); MS: *m/z* 641 (2, $M^{+\bullet}$), 596 (1, $M^{+\bullet}$-EtO$^{\bullet}$), 581 (2, $M^{+\bullet}$-AcOH), 508 (1, 581-CO_2Et), 399 (1, 581-BzOH-AcOH), 249 (2), 180 (5), 122 (45, $BzOH^+$), 105 (100, Bz^+), 77 (37, Ph^+), and 43 (18, Ac^+); Found $M^{+\bullet}$ 641.2098. $C_{32}H_{35}O_{13}N$ requires M, 641.2108.

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