Carbohydrate Research, 202 (1990) 151–164
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

The use of *N*-alkoxycarbonyl derivatives of 2-amino-2-deoxy-D-glucose as donors in glycosylation reactions

Paul Boullanger*, Martine Jouineau, Boufelja Bouammali, Dominique Lafont, and Gérard Descotes

Laboratoire de Chimie Organique II, C.N.R.S. U.A. 463, Université de Lyon I, E.S.C.I.L., 43 Bd. du 11 Novembre 1918, F-69622 Villeurbanne (France)

(Received August 8th, 1989; accepted for publication, October 4th, 1989)

ABSTRACT

1,3,4,6-Tetra-*O*-acetyl-2-alkoxycarbonylamino-2-deoxy-β-D-glucopyranoses and 3,4,6-tri-*O*-acetyl-2-alkoxycarbonylamino-2-deoxy-α-D-glucopyranosyl bromides have been used as donors in glycosylation reactions with model alcohols. β-Glycosides were obtained in good yields and with a high degree of 1,2-*trans* stereoselectivity. An oxazolidinone was formed as the main product from the reaction of some of the glucopyranosyl bromides with alcohols of low reactivity, but the formation of all products could be interpreted by a strong participation of the alkoxycarbonylamino group.

INTRODUCTION

Oligosaccharides of 2-amino-2-deoxy-D-glucose have great biological significance. The glycans of glycoproteins, such as human milk oligosaccharides, contain many β-D-GlcNAc-(1→n)-D-Man linkages together with β-D-GlcNAc-(1→4)-D-GlcNAc residues[1]. Blood-group substances possess β-D-GlcNAc-(1→3) and -(1→6)-D-Gal linkages[2]. In antigenic polysaccharides, the β-D-GlcNAc residue is often encountered in Gram-positive and Gram-negative bacteria[3]. Lipid A from lipopolysaccharides also comprises β-D-GlcNR-(1→6)-D-GlcNR derivatives[4] (R = fatty acid).

Due to this wide biological occurrence and the potential biomedical applications (diagnosis, vaccines) of synthetic oligosaccharides, there has been much research on new methods of synthesis in the past ten years.

The oxazoline procedure[5,6] and more recent developments[7,8] are restricted mostly to reactive aglycons, but their main advantage is the formation of pure *N*-acetylated β-glycosides.

The phthalimido procedure[9], in which bromide is the leaving group and silver triflate–collidine is the promoter, is of general use and β-glycosides are formed with a high degree of stereoselectivity and in high yields with most aglycons. A disadvantage of this method is the need for dephthaloylation and reacetylation after the glycosylation step[9]. This sequence cannot be applied to alkali-labile oligosaccharides.

* Author for correspondence.

0008-6215/90/$03.50

The last ten years have seen improvements in the above procedures. A new method for the preparation of oxazolines has been developed[10], but the glycosylation step has remained unchanged[11].

The phthalimido method has been improved in both the glycosylation and dephthaloylation steps. In the glycosylation step, better yields can be obtained using leaving groups and promoters different from those originally used[9]. Anomeric β-acetates can be used as the leaving group with various Lewis acids as promoters; for example, activation of the aglycon by tributylstannylation and stannic chloride[12] or trimethylsilyl trifluoromethanesulfonate[13] as promoter. Other groups have employed trimethylsilyl trifluoromethanesulfonate as promoter with a β-acetylated donor and without activation of the aglycon[14,15]. Boron trifluoride etherate has been used as a promoter for donors bearing a β-trichloroacetamidate leaving group[16] in the synthesis of oligosaccharides of glycoproteins[17], oligosaccharides with blood-group activity[18], glycosphingolipids[19], and a glycan-undecasaccharide[20]. The most recent improvement in the synthesis of 2-amino-2-deoxy-β-D-glucosides having an *N*-phthaloyl substituent was achieved by the use of methyl (or ethyl) β-thioglycosides with various promoters, *e.g.*, methyl triflate[21], dimethyl(methylthio)sulfonium triflate[22–24], alkylsulfenyl triflate[25], phenylselenenyl triflate[26], and nitrosyl tetrafluoroborate[27,28].

Although many improvements have been reported in the glycosylation step of the phthalimido procedure, few changes have been described[23] for the removal of the *N*-substituent.

New approaches have emerged which are based on the use of other participating *N*-substituents. The *N*-allyloxycarbonyl group gave satisfactory results with simple alcohols or monosaccharides[29,30], and selective deprotection can be achieved by reaction with Pd(0) complexes. This procedure has been extended to polyhydric alcohols[31] and bacterial oligosaccharides[32]. Recently, the acylvinyl group has been introduced[33] in reactions with simple alcohols. Similarly, cycloadducts of azodicarboxylates with glycals have been proposed[34] for β-glycosylation.

With a view to generalize the *N*-allyloxycarbonyl procedure, we have been interested in other *N*-alkoxycarbonyl substituents for β-glycosylation with 2-amino-2-deoxy-D-glucose.

Heyns *et al.*[35] reported that the reaction of 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranosyl bromide with benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside promoted by mercury(II) cyanide gave an oxazolidinone derivative with migration of the benzyl group to the aglycon. Condensations of several alcohols with 3,4,6-tri-*O*-acetyl-2-alkoxycarbonylamino-2-deoxy-α-D-glucopyranosyl chloride (ethyl, benzyl, and chloroethyl) promoted by silver salts gave β-glycosides in moderate yields (42–46%) despite the use of a large excess of alcohol[36]. Moderate yields were also obtained in the reaction of 3,4,6-tri-*O*-acetyl-2-deoxy-2-*o*-nitrobenzyloxycarbonylamino-α-D-glucopyranosyl chloride with methanol[37]. An encouraging result for such glycosylations was that of the reaction between 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl bromide and allyl 2-acetamido-3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-β-D-glucopyranoside, which gave a (1→6)-β-linked disaccharide derivative in good yield[38].

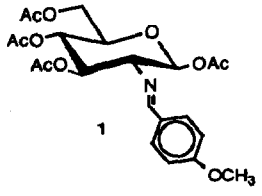
RESULTS AND DISCUSSION

In seeking to generalize the *N*-allyloxycarbonyl procedure, the glycosylation of simple alcohols was studied first. For model studies of the Koenigs–Knorr reaction, Garegg *et al.*[39] used only the primary alcohols mono-, di- and trichloroethanol. We have used 2-propanol and cyclohexanol (pK_a 16.0), *tert*-butyl alcohol (pK_a 18.0), and trichloroethanol (pK_a 12.5) to exemplify secondary alcohols, tertiary hindered alcohols, and low nucleophilicity.

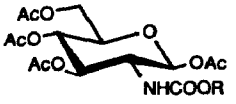
Of the carbamates of 2-amino-2-deoxy-D-glucose tested, the methyl and ethyl carbamates were used only as model compounds since *N*-deprotection requires drastic conditions. Allyl, benzyl, trichloroethyl, 4-nitrobenzyl, and *tert*-butyl carbamates were used because of their potential for selective removal variously by Pd(0) complexes[40], hydrogenolysis[41], metallic reduction[42], electrolysis[43], or acid[44].

The glycosyl donors 1,3,4,6-tetra-*O*-acetyl-2-alkoxycarbonylamino-2-deoxy-β-D-glucopyranoses (**2–8**) and 3,4,6-tri-*O*-acetyl-2-alkoxycarbonylamino-2-deoxy-α-D-glucopyranosyl bromides (**9–14**) were used.

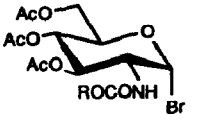
The common precursor of **2–14** was **1**[45] which, after treatment with acid and condensation with the appropriate chloroformate in the presence of sodium hydrogencarbonate, gave **2–8** in good yields (50–70%). Treatment of **2–8** conventionally with hydrobromic acid gave **9–14** almost quantitatively, except for **8** which underwent some hydrolysis.



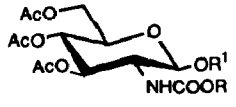
1

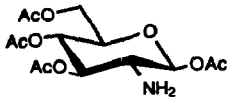


2 R = Me
3 R = Et
4 R = Allyl
5 R = Bn
6 R = CH_2CCl_3
7 R = 4-NO_2Bn
8 R = ^{t}Bu

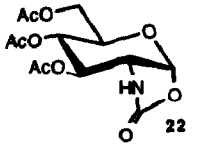


9 R = Me
10 R = Et
11 R = Allyl
12 R = Bn
13 R = CH_2CCl_3
14 R = 4-NO_2Bn





21



22

15 R = Me
16 R = Et
17 R = Allyl
18 R = Bn
19 R = CH_2CCl_3
20 R = 4-NO_2Bn

a R^1 = ^{i}Pr
b R^1 = Cyclohexyl
c R^1 = ^{t}Bu
d R^1 = CH_2CCl_3

TABLE I

Reactions of glucosyl donors **2–14** with alcohols[a]

Alcohol (R^1OH)		*Starting material* **2**	**3**	**4**	**5**	**6**	**7**	**8**
		Reaction product **15**	**16**	**17**	**18**	**19**	**20**	**21**
2-Propanol	**a**	76[b]	88	95	59	55	53	58 (35)[c]
Cyclohexanol	**b**	46	65	83	60	40	56	55 (34)
tert-Butyl alcohol	**c**	32	31	32	15	20	28	59 (36)
Trichloroethanol	**d**	57	44	69	34	34	56	
Alcohol (R^1OH)		*Starting material* **9**	**10**	**11**	**12**	**13**	**14**	
		Reaction product **15**	**16**	**17**	**18**	**19**	**20**	
2-Propanol	**a**	68	66	76 (5)	72 (28)	58	63 (2)	
Cyclohexanol	**b**	72	61	70 (10)	81 (10)	64	71 (2)	
tert-Butyl alcohol	**c**	74	64	55 (29)	45 (28)	53	47 (3)	
Trichloroethanol	**d**	13	14	9 (68)	2 (68)	2	1 (47)	

[a] Reactions involved 1 equiv. of the alcohols under the conditions noted in the text. [b] Yields (%) are given for products purified by column chromatography. [c] Values in parentheses represent the amount (%) of **22**.

The carbamates **2–8** were used in glycosylation reactions under the conditions reported[30] (dichloromethane, −35°, stoichiometric amounts of alcohol and trimethylsilyl trifluoromethanesulfonate as promoter). The expected β-glycosides **15a–20d** were obtained as major compounds (Table I), the only exception being **8**. The glycosyl bromides **9–14** were reacted with stoichiometric amounts of alcohols and mercury(II) cyanide as promoter in dichloromethane at room temperature. The β-glycosides **15a–20d** were obtained usually as major products together with the oxazolidinone **22** previously reported[35]. The ^{13}C-n.m.r. spectra of the donors **2–8** and of the products of glycosylation are reported in Table II.

The results in Table I accord with the conclusions drawn from studies of the *N*-allyloxycarbonyl glycosylation procedure[30]. The formation of **15–20** and **22** reflects participation of the *N*-alkoxycarbonyl group in the glycosylation step (Scheme 1).

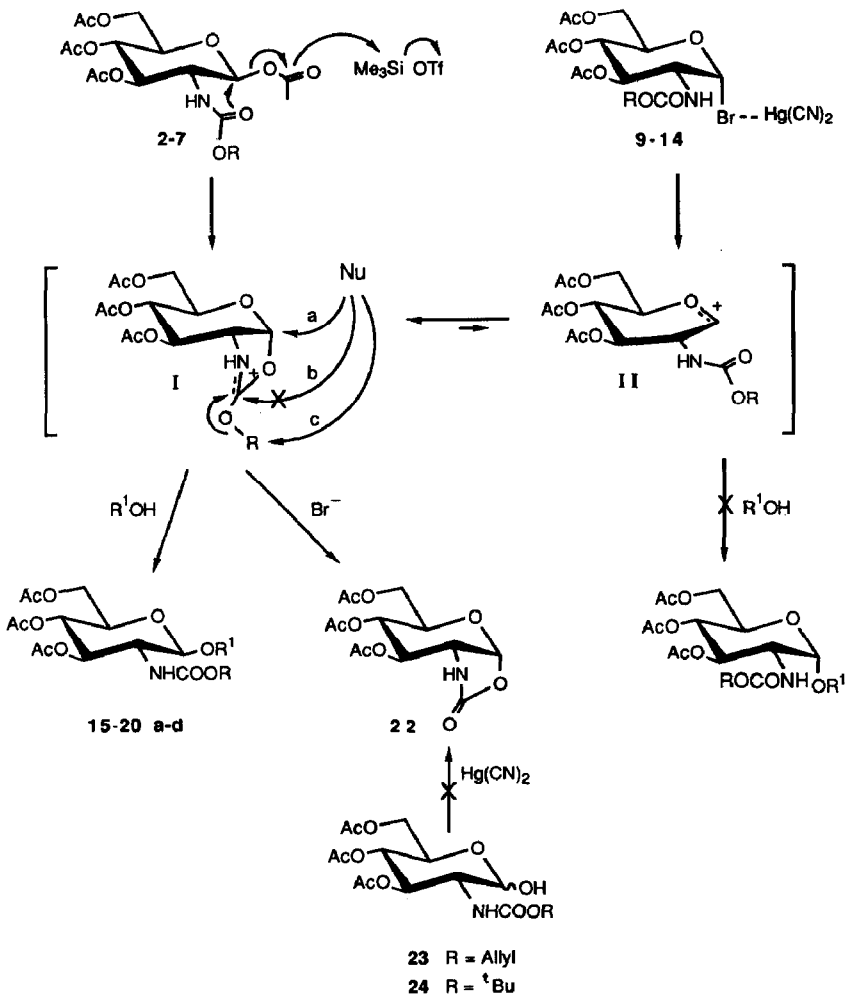
Starting from **2–7**, displacement of the anomeric group, promoted by the Lewis acid, is assisted by the *N*-alkoxycarbonyl group and yields the intermediate alkoxyoxazolinium ion **I**. Starting from **9–14**, the oxocarbenium ion **11**, obtained by the heavy-metal-salt-promoted cleavage of the carbon–halogen bond, can rearrange into **I** by participation of the *N*-substituent. Nucleophilic attack on the cyclic intermediate **I** can occur *via* pathways *a–c* (Scheme 1). As noted[30] for **4** and **11**, pathway *a* gives rise to β-glycosides by reaction with alcohols, products from pathway *b* are not observed, and

TABLE II

^{13}C-N.m.r. spectra of β-acetylated glycosyl donors and of β-glycosides (spectra recorded for solutions in CD_3COCD_3, unless otherwise stated)[a]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*R*	*R*[1]
2	93.07	55.71	73.28[b]	69.27	73.14[b]	62.51	52.29	
15a	100.61	57.12	73.68[b]	70.06	72.72[b]	63.04	52.01	72.24[b], 23.65, 22.17
15b	100.40	57.12	73.61[b]	70.11	72.22[b]	63.03	52.03	77.57, 5 CH_2
15c	96.56	57.37	73.51[b]	70.33	71.98[b]	63.27	52.02	76.37, 28.49
15d	102.34	56.61	73.08[b]	69.72	72.64[b]	62.64	52.08	97.37, 81.01
3	93.11	55.58	73.32[b]	69.24	73.15[b]	62.51	61.16, 14.86	
16a	100.61	56.97	73.67[b]	70.06	72.20[b]	63.03	60.83, 14.98	72.72[b], 23.68, 22.2
16b	100.37	56.98	73.61[b]	70.09	72.18[b]	63.01	60.8, 14.99	77.47, 5 CH_2
16c	96.54	57.23	73.50[b]	70.31	71.94[b]	63.25	60.77, 15.03	76.33, 28.77
16d	102.33	56.45	73.13[b]	69.69	72.62[b]	62.63	60.93, 14.95	97.37, 80.98
4	92.88	55.50	73.13[b]	69.08	72.98[b]	62.37	133.99, 116.83, 65.54	
17a	100.29	56.81	73.45[b]	69.84	71.96[b]	62.85	134.12, 116.66, 65.27	72.53[b], 23.59, 22.17
17b	100.24	56.96	73.59[b]	70.01	72.12[b]	62.96	134.42, 116.87, 65.42	77.52, 5 CH_2
17c	96.48	57.22	73.50[b]	70.24	71.92[b]	63.22	134.49, 116.90, 65.37	76.36, 28.78
17d	102.13	56.39	72.99[b]	69.60	72.50[b]	62.56	134.26, 117.06, 65.57	97.24, 80.89
5	93.11	55.71	73.31[b]	69.26	73.19[b]	62.50	5 Ph, 66.71	
18a[c]	98.52	55.34	71.68[b]	68.16	70.44[b]	61.42	5 Ph, 65.64	76.44, 19.71, 19.59
18b[c]	99.27	56.39	72.30[b]	69.22	71.47[b]	62.42	5 Ph, 66.67	77.77, 5 CH_2
18c[c]	95.49	56.59	72.32[b]	69.46	71.23[b]	62.70	5 Ph, 66.64	76.31, 28.32
18d	102.27	56.62	73.21[b]	69.71	72.70[b]	62.67	5 Ph, 66.64	97.37, 81.01
6	92.72	55.67	73.09[b]	69.13	72.92[b]	62.35	96.67, 74.61	
19a	100.26	57.07	73.36[b]	69.92	72.70[b]	62.90	96.88, 74.60	71.17[b], 23.61, 22.17
19b	99.98	57.05	73.29[b]	69.90	72.10[b]	62.84	96.83, 74.60	77.61, 5 CH_2
19c	96.55	57.42	73.48[b]	70.29	72.09[b]	63.27	96.55, 74.76	76.61, 28.86
19d	102.03	56.74	73.04[b]	69.63	72.70[b]	62.60	96.81, 74.86	96.81, 80.97
7	92.98	55.86	73.21	69.21	73.21	62.48	4 Ph, 65.49	
20a[c]	99.23	56.70	72.75[b]	69.00	71.68[b]	62.37	4 Ph, 65.29	71.68[b], 23.29, 21.87
20b[c]	98.99	56.69	72.04[b]	68.99	71.64[b]	62.33	4 Ph, 65.28	77.87, 5 CH_2
20c[c]	95.25	56.86	71.98[b]	69.27	71.40[b]	62.63	4 Ph, 65.22	76.51, 28.37
20d[c]	101.49	56.13	72.08[b]	68.60	71.60[b]	61.95	4 Ph, 65.43	96.29, 80.54
8	93.30	55.25	73.47[b]	69.35	73.24[b]	62.58	79.42, 28.40	

[a] The spectra contain additional signals corresponding to the acetyl (CH_3CO) group and a differentiated CO signal (δ 156.2 ± 1.2) for the carbamate function. [b] Attributions on the same line could be interchanged. [c] Spectra recorded for solutions in $CDCl_3$.



Scheme 1. Mechanism of the glycosylation reactions.

pathway *c* leads to the oxazolidinone **22** after elimination of the carbamate alkyl group R. The reactivity of **8** is different from that of **2**–**7**, because of instability of the *N*-substituent during glycosylation, and will be discussed separately.

Except for **8**, the formation of **22** was observed only when **9**–**14** were used as donors. Compound **22** could have resulted from the transcarbamoylation of the reducing sugar (*e.g.*, **23** or **24**, Scheme 1) formed by hydrolysis of the glycosyl bromide. However, **23** and **24**, prepared by selective hydrolysis[46] of **4** and **8**, did not react in the presence of mercury(II) cyanide. Therefore, **22** is formed by pathway *c* in Scheme 1. This reaction was observed mainly during glycosylation of alcohols of low nucleophilicity and with carbamates bearing alkyl groups which can accommodate a positive charge (allyl, benzyl, *p*-nitrobenzyl). Even with alcohols of higher molecular weight, the aglycon was never recovered in the etherified form as reported by Paulsen *et al.*[35],

showing that the cleavage of the alkyl group was not due to a nucleophilic attack by the acceptor alcohol. Furthermore, the nature of the by-products of the reaction and the acceleration of the rate of formation of the oxazolidinone by the addition of tetraethylammonium bromide demonstrated that bromide ion, formed by anomeric displacement, was the probable driving force.

Pathway *b* in Scheme 1 was not observed with **2–8** or **9–14**. This result differs from the observations made during glycosylations with 2-*O*-alkoxycarbonyl donors where the orthocarbonates could be isolated in good yields[47], and accords with the difference of reactivities between 2-*O*- and 2-*N*-acetylated donors.

The β-glycosides **15–20** were obtained generally in reasonable yields starting from both **9–14** or **2–7** but, as reported[30], were usually better from the latter (except with *tert*-butyl alcohol). The acidic conditions created by the use of trimethylsilyl triflate could explain the moderate yields [obtained from **2–7** with *tert*-butyl alcohol], since both the alcohol and the corresponding glycosides are acid labile. The appropriate choice of a donor allowed the glycosylation of all of the model alcohols as well as the mono- or oligo-saccharides which were studied in more detail with **4** and **11**[30–32,47]. Therefore, the glycosyl bromides **9–14** are suitable for the glycosylation of secondary and tertiary alcohols, but fail with acidic alcohols of low nucleophilicity, whereas the β-acetates **2–7** can glycosylate the latter alcohols but fail with acid-labile alcohols.

As noted above, the *N*-*tert*-butoxycarbonyl derivative of 2-amino-2-deoxy-D-glucose reacts in a way which is different from that of the other members of the series. Due to its acid lability, it was impossible to prepare the corresponding glycosyl bromide because of hydrolysis of the *N*-substituent. Reactions of less aggressive chlorinating agents (*e.g.* the Vilsmeier reagent[48]) on **24**, obtained by regioselective hydrolysis of **8**, led to mixtures of glycosyl chloride and oxazolidinone **22** which were difficult to purify. Attempts to use **8** as a donor in glycosylation reactions were also characterized by the cleavage of the *N*-substituent, and the main compounds recovered were the amine **21** and **22** (Table I). The unique formation of **22** from a β-acetylated derivative could be due to removal of one of the *tert*-butyl protons from the intermediate **I** (Scheme 1) to form isobutylene together with **22**.

The main advantage of all the above glycosylations is the high degree of stereoselectivity. The α-glycosides that could have resulted from an attack of the alcohol on the intermediate **II** were not detected. This finding indicates a strong participation of the *N*-substituent, leading to the exclusive attack on the ion **I**. The better delocalization of the positive charge in **I**, compared with the corresponding oxazolinium ions, is probably the main contribution to the lowering of the free energy of formation. The role of this delocalization can be quantified by comparison with results reported in the literature. Thus, the enthalpy of formation of trioxocarbenium ions from orthocarbonates was calculated to be 63 kcal.mol^{-1} lower than that of dioxocarbenium from orthoesters[49]. Therefore, the high reactivies and 1,2-*trans* stereoselectivities of the *N*-alkoxycarbonyl derivatives of 2-amino-2-deoxy-D-glucose probably can be explained in terms of participation of these *N*-substituents, which represent a compromise between the very largely delocalized phthaloyl, and the much less delocalized oxazolinium, intermediates.

The use of *N*-alkoxycarbonyl derivatives of 2-amino-2-deoxy-D-glucose for glycosylation complements the oxazoline and phthalimido procedures. The starting materials are easy to prepare and to handle; β-glycosides are obtained with a high stereoselectivity and in good yields, and the *N*-substituent can be removed selectively under various conditions depending on its nature.

Application of the method in the synthesis of oligosaccharides is being studied.

EXPERIMENTAL

Melting points were determined on a Büchi apparatus and are uncorrected. Optical rotations were measured at 21° with a Perkin–Elmer 241 polarimeter in a 1-dm cell. The ^{1}H- (300 MHz) and ^{13}C-n.m.r. (75.5 MHz) spectra (internal Me_4Si) were recorded with a Bruker AM 300 spectrometer. Elemental analyses were performed at the Laboratoire Central d'Analyses du CNRS (Solaize, France). Column chromatography was performed on Silica Gel 60 Merck (230–400 mesh).

*Synthesis of 1,3,4,6-tetra-*O*-acetyl-2-alkoxycarbonylamino-2-deoxy-β-*D*-glucopyranoses* (**2–7**). — Compound **1** (ref. 45) (56 g, 120 mmol) was dissolved in refluxing acetone (300 mL). After the addition of 5.5M hydrochloric acid (24.7 mL, 132 mmol), the amine hydrochloride precipitated immediately. The mixture was cooled to room temperature, and the product was filtered off, washed with ether, and dried. A solution of the hydrochloride (36.8 g, 94 mmol) in water (900 mL) was treated with sodium hydrogencarbonate (16.0 g, 188 mmol). After 10 min, the alkyl chloroformate (103 mmol) and chloroform (500 mL) were added and the mixture was stirred for 1 h at room temperature. The aqueous layer was extracted with chloroform twice, and the combined chloroform solutions were washed with water, dried ($CaCl_2$), and concentrated to dryness. The residue was triturated twice with ether before recrystallization from ether or ether–ethyl acetate. The following compounds were prepared in this manner. The ^{13}C-n.m.r. data are recorded in Table II.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-β-D-glucopyranose (**2**, 65%), m.p. 146–148°, $[\alpha]_D$ +16° (*c* 4.1, chloroform); lit.[50] m.p. 148–149°, $[\alpha]_D$ +21.4°. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.6 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-ethoxycarbonylamino-β-D-glucopyranose (**3**, 61%), m.p. 144–145°, $[\alpha]_D$ +16° (*c* 3.2, chloroform); lit.[50] m.p. 144–145°, $[\alpha]_D$ +16.1°. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.8 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1).

1,3,4,6-Tetra-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranose (**4**, 69%), m.p. 130–132°, $[\alpha]_D$ +16° (*c* 1.2, chloroform); lit.[30] m.p. 109–110°, $[\alpha]_D$ +25.9°.

1,3,4,6-Tetra-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranose (**5**, 55%), m.p. 150–151°, $[\alpha]_D$ +17° (*c* 2.8, chloroform); lit.[51] m.p. 150–151°, $[\alpha]_D$ +21.5°. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.8 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranose (**6**, 48%),122–123°, $[\alpha]_D$ +15° (*c* 3.2, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.9 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1).

Anal. Calc. for $C_{17}H_{22}Cl_3NO_{11}$: C, 39.06; H, 4.24; Cl, 20.35; N, 2.68. Found: C, 39.01; H, 4.00; Cl, 20.49; N, 2.52.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(4-nitrobenzyloxycarbonylamino)-β-D-glucopyranose (**7**, 48%), m.p. 139–140°, $[\alpha]_D$ +21° (*c* 2.9, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.8 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1).

Anal. Calc for $C_{22}H_{26}N_2O_{13}$: C, 50.19; H, 4.98; N, 5.32. Found: C, 50.39; H, 5.01; N, 5.52.

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-(1,1-dimethylethoxycarbonylamino)-β-D-glucopyranose (**8**). — The free amine **21** was extracted before treatment with di-*tert*-butyl dicarbonate (1.2 equiv.) in refluxing tetrahydrofuran for 6 h. The mixture was concentrated, and the residue was crystallised from ether to give **8** (72%), m.p. 185–187°, $[\alpha]_D$ +15° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.8 p.p.m. (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1).

Anal. Calc. for $C_{20}H_{29}NO_{11}$: C, 51.00; H, 6.53; N, 3.13. Found: C, 50.89; H, 6.49; N, 3.01.

Synthesis of 3,4,6-tri-O-acetyl-2-alkoxycarbonylamino-2-deoxy-α-D-glucopyranosyl bromides (**9**–**14**). — A solution of 1,3,4,6-tetra-*O*-acetyl-2-alkoxycarbonylamino-2-deoxy-β-D-glucopyranose (10 mmol) in acetic acid (20 mL) was treated at room temperature with 3 equiv. of hydrobromic acid (33% w/v in acetic acid) for 2–3 h. The mixture was then poured into ice–water and extracted with chloroform, and the extract was neutralized with cold, dilute aqueous sodium carbonate, washed with water, dried ($CaCl_2$), and concentrated to give the crude bromides **9**–**14** (72–91%) as chromatographically homogeneous products each of which had a characteristic resonance for H-1 at δ 6.7 ±0.5 ($J_{1,2}$ 3.5 ±0.1 Hz). Due to their low stability, **9**–**14** were used without further purification.

Glucosylation reactions. — (*a*) *From the β-acetates* **2**–**8**. A solution of the glycosyl donor (1 mmol) and the alcohol (1 mmol) in dichloromethane (10 mL) was flushed with dry nitrogen and cooled to −35°. Trimethylsilyl trifluoromethanesulfonate was then added through a syringe, and the mixture was stirred at −35° overnight, and then neutralized at −35° with triethylamine (2 mmol). When the temperature had reached 0°, the mixture was washed with dilute aqueous sodium hydrogencarbonate and then water, dried ($CaCl_2$), and concentrated. The residue was eluted from a column of silica gel with ethyl acetate–hexane (1:1). The yields are recorded in Table I.

(*b*) *From the glucopyranosyl bromides* **9**–**14**. — The glucosyl donor (1 mmol) and mercury(II) cyanide (1 mmol) were dried together overnight, then dissolved in dichloromethane (15 mL). The alcohol (1 mmol) was then introduced through a syringe, the mixture was stirred at room temperature, and the reaction was monitored by t.l.c. until the starting material had disappeared (5–20 h). The mixture was filtered through Celite, the filter pad was washed with chloroform, and the combined filtrate and washings were washed with dilute aqueous potassium iodide and water, dried ($CaCl_2$), and concentrated. The residue was eluted from a column of silica gel with ethyl acetate–hexane (1:1). The yields are recorded in Table I and the ^{13}C-n.m.r. data in Table II. The following compounds were prepared by these methods.

1-Methylethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-β-D-glucopyranoside (**15a**), m.p. 171–172°, $[\alpha]_D$ +0.3° (*c* 3.2, chloroform).

Anal. Calc. for $C_{17}H_{27}NO_{10}$: C, 50.37; H, 6.71; N, 3.46. Found: C, 49.96; H, 6.35; N, 3.42.

Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-β-D-glucopyranoside (**15b**), m.p. 169–170°, $[\alpha]_D$ −3.7° (*c* 3.9, chloroform).

Anal. Calc. for $C_{20}H_{31}NO_{10}$: C, 53.93; H, 7.01; N, 3.14. Found: C, 53.86; H, 6.96; N, 3.20.

1,1-Dimethylethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-β-D-glucopyranoside (**15c**), m.p. 163–164°, $[\alpha]_D$ +11° (*c* 2.5, chloroform).

Anal. Calc. for $C_{18}H_{29}NO_{10}$: C, 51.55; H, 6.97; N, 3.34. Found: C, 51.06; H, 6.78; N, 3.23.

2,2,2-Trichloroethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-β-D-glucopyranoside (**15d**), m.p. 184–185°, $[\alpha]_D$ −3.9° (*c* 2.5, chloroform).

Anal. Calc. for $C_{16}H_{22}Cl_3NO_{10}$: C, 38.85; H, 4.48; Cl, 21.50; N, 2.83. Found: C, 39.10; H, 4.61; Cl, 21.09; N, 2.99.

1-Methylethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-ethoxycarbonylamino-β-D-glucopyranoside (**16a**), m.p. 157–159°, $[\alpha]_D$ +2.1° (*c* 3.5, chloroform).

Anal. Calc. for $C_{18}H_{29}NO_{10}$: C, 51.55; H, 6.97; N, 3.34. Found: C, 51.18; H, 6.99; N, 3.26.

Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-ethoxycarbonylamino-β-D-glucopyranoside (**16b**), m.p. 144–145°, $[\alpha]_D$ −3.3° (*c* 2.8, chloroform).

Anal. Calc. for $C_{21}H_{33}NO_{10}$: C, 54.89; H, 7.24; N, 3.05. Found: C, 54.67; H, 7.27; N, 2.99.

1,1-Dimethylethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-ethoxycarbonylamino-β-D-glucopyranoside (**16c**), m.p. 169–170°, $[\alpha]_D$ +12° (*c* 3.2, chloroform).

Anal. Calc. for $C_{19}H_{31}NO_{10}$: C, 52.65; H, 7.21; N, 3.23. Found: C, 52.36; H, 7.27; N, 3.17.

2,2,2-Trichloroethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-ethoxycarbonylamino-β-D-glucopyranoside (**16d**), m.p. 142–143°, $[\alpha]_D$ −2.6° (*c* 2.5, chloroform).

Anal. Calc. for $C_{17}H_{24}Cl_3NO_{10}$: C, 40.14; H, 4.76; Cl, 20.91; N, 2.75. Found: C, 39.87; H, 4.66; Cl, 20.69; N, 2.52.

1-Methylethyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside[30] (**17a**), m.p. 148–149°, $[\alpha]_D$ +4.2° (*c* 1, chloroform).

Anal. Calc. for $C_{19}H_{29}NO_{10}$: C, 52.89; H, 6.78; N, 3.25. Found: C, 52.85; H, 6.75; N, 3.21.

Cyclohexyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**17b**), m.p. 138–139°, $[\alpha]_D$ −1.5° (*c* 3, chloroform).

Anal. Calc. for $C_{22}H_{33}NO_{10}$: C, 56.04; H, 7.05; N, 2.97. Found: C, 56.25; H, 7.22; N, 2.95.

1,1-Dimethylethyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**17c**), m.p. 164–165°, $[\alpha]_D$ +14° (*c* 3.9, chloroform).

Anal. Calc. for $C_{20}H_{31}NO_{10}$: C, 53.93; H, 7.01; N, 3.14. Found: C, 54.09; H, 6.91; N, 3.19.

2,2,2-Trichloroethyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**17d**), m.p. 157–158°, $[\alpha]_D$ −9.6° (*c* 3.4, chloroform).

Anal. Calc. for $C_{18}H_{24}Cl_3NO_{10}$: C, 41.52; H, 4.65; Cl, 20.42; N, 2.69. Found: C, 41.67; H, 4.62; Cl, 20.50; N, 2.73.

1-Methylethyl 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**18a**), m.p. 154–155°, $[\alpha]_D$ +3.0° (*c* 1.3, chloroform).

Anal. Calc. for $C_{23}H_{31}NO_{10}$: C, 57.37; H, 6.49; N, 2.91. Found: C, 57.38; H, 6.58; N, 3.04.

Cyclohexyl 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**18b**), m.p. 171–172°, $[\alpha]_D$ +6.2° (*c* 0.8, chloroform).

Anal. Calc. for $C_{26}H_{35}NO_{10}$: C, 59.88; H, 6.76; N, 2.69. Found: C, 59.93; H, 6.63; N, 2.60.

1,1-Dimethylethyl 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**18c**), m.p. 157–158°, $[\alpha]_D$ +15° (*c* 1.6, chloroform).

Anal. Calc. for $C_{24}H_{33}NO_{10}$: C, 58.17; H, 6.71; N, 2.83. Found: C, 57.88; H, 6.73; N, 2.85.

2,2,2-Trichloroethyl 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**18d**), m.p. 172–173°, $[\alpha]_D$ −3.0° (*c* 0.9, chloroform).

Anal. Calc. for $C_{18}H_{24}Cl_3NO_{10}$: C, 46.29; H, 4.59; Cl, 18.63; N, 2.45. Found: C, 46.23; H, 4.58; Cl, 18.21; N, 2.43.

1-Methylethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (**19a**), m.p. 134–135°, $[\alpha]_D$ +3.4° (*c* 1, chloroform).

Anal. Calc. for $C_{18}H_{26}Cl_3NO_{10}$: C, 46.29; H, 4.59; Cl, 18.63; N, 2.45. Found: C, 46.23; H, 4.58; Cl, 18.21; N, 2.43.

Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (**19b**), m.p. 136–137°, $[\alpha]_D$ ~0° (*c* 1.1, chloroform).

Anal. Calc. for $C_{21}H_{30}Cl_3NO_{10}$: C, 44.82; H, 5.37; Cl, 18.90; N, 2.49. Found: C, 45.10; H, 5.37; Cl, 18.82; N, 2.44.

1,1-Dimethylethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (**19c**), m.p. 173–174°, $[\alpha]_D$ +8.7° (*c* 1.2, chloroform).

Anal. Calc. for $C_{19}H_{28}Cl_3NO_{10}$: C, 42.51; H, 5.26; Cl, 19.81; N, 2.61. Found: C, 42.93; H, 5.32; Cl, 19.85; N, 2.98.

2,2,2-Trichloroethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (**19d**), m.p. 134–135°, $[\alpha]_D$ −9.0° (*c* 1.1, chloroform).

Anal. Calc. for $C_{17}H_{21}Cl_6NO_{10}$: C, 33.36; H, 3.46; Cl, 34.75; N, 2.29. Found: C, 33.75; H, 3.50; Cl, 34.35; N, 2.25.

1-Methylethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(4-nitrobenzyloxycarbonylamino)-β-D-glucopyranoside (**20a**), m.p. 187–188°, $[\alpha]_D$ +4.1° (*c* 0.7, chloroform).

Anal. Calc. for $C_{23}H_{30}N_2O_{12}$: C, 52.47; H, 5.74; N, 5.32. Found: C, 52.49; H, 5.77; N, 5.18.

Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(4-nitrobenzyloxycarbonylamino)-β-D-glucopyranoside (**20b**), m.p. 179–180°, $[\alpha]_D$ +2.0° (*c* 1.5, chloroform).

Anal. Calc. for $C_{26}H_{34}N_2O_{12}$: C, 55.12; H, 6.05; N, 4.94. Found: C, 55.20; H, 5.96; N, 4.85.

1,1-Dimethylethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(4-nitrobenzyloxycarbonylamino)-β-D-glucopyranoside (**20c**), m.p. 171–172°, $[\alpha]_D$ +15° (*c* 1.2, chloroform).

Anal. Calc. for $C_{24}H_{32}N_2O_{12}$: C, 53.33; H, 5.97; N, 5.18. Found: C, 53.29; H, 5.96; N, 5.06.

2,2,2-Trichloroethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(4-nitrobenzyloxycarbonylamino)-β-D-glucopyranoside (**20d**), m.p. 168–169°, $[\alpha]_D$ −8.2° (*c* 1.9, chloroform).

Anal. Calc. for $C_{22}H_{25}Cl_3N_2O_{12}$: C, 42.91; H, 4.09; Cl, 17.27; N, 4.55. Found: C, 43.19; H, 4.08; Cl, 16.97; N, 4.49.

*1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose* (**21**). — Compound **1** was treated as described above for the synthesis of **2–7** but the mixture was extracted with chloroform before addition of the chloroformate. After drying ($CaCl_2$) and concentration, the product was recrystallized from ethanol to give **21** (88%), m.p. 142–143°, $[\alpha]_D$ +28° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.45 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 5.20–4.95 (m, 2 H, H-3,4), 4.33 (dd, 1 H, $J_{5,6}$ 4.6, $J_{6,6'}$ 12.4 Hz, H-6), 4.07 (dd, 1 H, $J_{5,6'}$ 2.3 Hz, H-6'), 3.84 (m, 1 H, $J_{4,5}$ 9.6 Hz, H-5), 3.02 (m, 1 H, H-2).

Anal. Calc. for $C_{14}H_{21}NO_9$: C, 48.41; H, 6.09; N, 4.03. Found: C, 48.21; H, 6.17; N, 3.96.

*3,4,6-Tri-*O*-acetyl-2-amino-1,2-*N,O*-carbonyl-2-deoxy-α-D-glucopyranose* (**22**). — This material, recovered as a compound of lower R_F from the glycosylation mixtures of donors **17** or **18** with trichloroethanol (yields in Table I), had m.p. 174–175°, $[\alpha]_D$ +29° (*c* 1, chloroform); lit.[52] m.p. 170.5–171°, $[\alpha]_D$ +23.7°. N.m.r. data: ^{1}H ($CDCl_3$), δ 6.02 (d, 1 H, $J_{1,2}$ 6.9 Hz, H-1), 5.10 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 3.2 Hz, H-3), 4.95 (m, 1 H, $J_{4,5}$ 8.7, $J_{4,2}$ 1.1 Hz, H-4), 4.86 (dd, 1 H, $J_{5,6}$ 5.1, $J_{6,6'}$ 12.2 Hz, H-6), 4.21 (dd, 1 H, $J_{5,6'}$ 3.6 Hz, H-6'), 4.19 (m, 1 H, $J_{2,NH}$ 1.1 Hz, H-2), 4.06 (m, 1 H, H-5); ^{13}C ($(CD_3)COCD_3$), δ 157.24 (NHCOO), 96.15 (C-1), 70.80, 68.89, 68.19 (C-3,4,5), 63.96 (C-6), 52.92 (C-2).

*3,4,6-Tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-α-D-glucopyranose* (**23**). — To a solution of **4** (17.95 g, 41.6 mmol) in the minimum amount of *N*,*N*-dimethylformamide at 50° was added hydrazine acetate (4.59 g, 49.9 mmol), and the mixture was kept at 50° until dissolution was complete. After 10 min at room temperature, the mixture was diluted with ethyl acetate (150 mL), washed with brine, dried, and concentrated to dryness. Column chromatography (ethyl acetate–hexane, 2:1) of the residue and recrystallization from ether gave **23** (71%), m.p. 122–123°, $[\alpha]_D$ +37° (*c* 3.3, chloroform). ^{1}H-N.m.r. data ($(CD_3)COCD_3$): δ 5.30 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3), 5.21 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.89 (dd, 1 H, $J_{4,5}$ 9.4 Hz, H-4), 4.30–3.95 (m, 3 H, H-5,6,6'), 3.90 (m, 1 H, H-2).

Anal. Calc. for $C_{16}H_{23}NO_{10}$: C, 49.36; H, 5.95; N, 3.60. Found: C, 48.98; H, 5.95; N, 3.63.

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-(1,1-dimethylethoxycarbonylamino)-D-glucopyranose* (**24**). — Obtained from **8**, as an αβ-mixture, as described for **23**, **24** (82%, αβ-ratio 10:1) was a syrup. N.m.r. data ($(CD_3)COCD_3$): ^{1}H, δ 5.24 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3), 5.21 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1α), 5.01 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.25–4.00 (m, 3 H, H-5,6,6'), 3.86 (m, 1 H, H-2); ^{13}C, δ 157.92, 156.43 (NHCOO), 96.60 (C-1β), 92.49

(C-1*α*), 79.44, 79.12 [$C(CH_3)_3$], 74.10 (C-3*β*), 72.29, 72.07 (C-5), 69.97, 69.71 (C-4), 68.05 (C-3*α*), 63.16 (C-6), 57.76, 54.54 (C-2).

Anal. Calc. for $C_{18}H_{27}NO_{10}$: C, 51.79; H, 6.52; N, 3.35. Found: C, 51.51; H, 6.29; N, 3.14.

REFERENCES

1 J. Montreuil, *Adv. Carbohydr. Chem. Biochem.*, 37 (1980) 157–223.
2 C. Augé, S. David, and A. Veyrieres, *Nouv. J. Chim.*, 3 (1979) 491–497.
3 K. Jann and B. Jann, *Methods Enzymol.*, 50 (1978) 251–272.
4 E. T. Rietschel, H. -W. Wollenweber, R. Russa, H. Brade, and U. Zahringer, *Rev. Infect. Diseases*, 6 (1984) 432–438.
5 S. E. Zurabyan, T. S. Antonenko, and A. Ya. Khorlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 2043–2044.
6 S. E. Zurabyan, T. S. Antonenko, and A. Ya. Khorlin, *Carbohydr. Res.*, 15 (1970) 21–27.
7 M. Kiso and L. Anderson, *Carbohydr. Res.*, 72 (1979) c12–c14.
8 M. Kiso and L. Anderson, *Carbohydr. Res.*, 72 (1979) c15–c17.
9 R. U. Lemieux, M. T. Takeda, and B. Y. Chung, *ACS. Symp. Ser.*, 39 (1976) 90–115.
10 S. Nakabayashi, C. D. Warren, and R. W. Jeanloz, *Carbohydr. Res.*, 150 (1986) c7–c10.
11 M. Kiso and L. Anderson, *Carbohydr. Res.*, 136 (1985) 309–323.
12 T. Ogawa and S. Nakabayashi, *Carbohydr. Res.*, 97 (1981) 81–86.
13 T. Ogawa, K. Beppu, and S. Nakabayashi, *Carbohydr. Res.*, 93 (1981) c6–c9.
14 H. Paulsen and M. Paal, *Carbohydr. Res.*, 135 (1984) 53–69.
15 H. Paulsen and H. Tietz, *Angew. Chem. Int. Ed. Engl.*, 24 (1985) 128–129.
16 H. Ammann and G. Dupuis, *Can. J. Chem.*, 66 (1988) 1651–1655.
17 G. Grundler and R. R. Schmidt, *Carbohydr. Res.*, 135 (1985) 203–218.
18 A. Maranduba and A. Veyrieres, *Carbohydr. Res.*, 151 (1986) 105–119.
19 S. Sato, Y. Ito, T. Nukada, Y. Nakahara, and T. Ogawa, *Carbohydr. Res.*, 167 (1987) 197–210.
20 T. Ogawa, M. Sugimoto, T. Kitajama, K. Khan Sadozai, and T. Nukada, *Tetrahedron Lett.*, 27 (1986) 5739–5742.
21 H. Lönn, *Carbohydr. Res.*, 139 (1985) 105–113, 114–121.
22 P. Fügedi and P. J. Garegg, *Carbohydr. Res.*, 149 (1986) c9–c12.
23 F. Dasgupta and P. J. Garegg, *J. Carbohydr. Chem.*, 7 (1988) 701–707.
24 M. Nilsson and T. Norberg, *Carbohydr. Res.*, 183 (1988) 71–82.
25 F. Dasgupta and P. J. Garegg, *Carbohydr. Res.*, 177 (1988) c13–c17.
26 Y. Ito and T. Ogawa, *Tetrahedron Lett.*, 26 (1988) 1061–1064.
27 V. Pozsgay and H. J. Jennings, *J. Org. Chem.*, 52 (1987) 4635–4637.
28 V. Pozsgay and H. J. Jennings, *Carbohydr. Res.*, 179 (1988) 61–75.
29 P. Boullanger and G. Descotes, *Tetrahedron Lett.*, 27 (1986) 2599–2602.
30 P. Boullanger, J. Banoub, and G. Descotes, *Can. J. Chem.*, 65 (1987) 1343–1348.
31 P. Boullanger, D. Lafont, J. Banoub, and G. Descotes, *J. Carbohydr. Chem.*, 8 (1989) 343–356.
32 J. Banoub, P. Boullanger, D. Lafont, and G. Descotes, *Abstr. XIIIth Journées de la Chimie et Biochimie des Glucides*, Avignon Fr. (1990).
33 M. P. Borrachero and A. Gomez-Sanchez, *An. Quim., Ser. C*, 84 (1988) 55–59.
34 B. J. Fitzsimmons, Y. Leblanc, N. Chan, and J. Rokach, *J. Am. Chem. Soc.*, 110 (1988) 5229–5231.
35 K. Heyns, R. Harrison, and H. Paulsen, *Chem. Ber.*, 100 (1967) 271–279.
36 J. Lessard, H. Driguez, and J. P. Vermes, *Tetrahedron Lett.*, (1970) 4887–4890.
37 B. Amit, U. Zehavi, and A. Patchornic, *J. Org. Chem.*, 39 (1974) 192–196.
38 S. Kusumoto, H. Yoshimura, M. Imoto, T. Shimamoto, and T. Shiba, *Tetrahedron Lett.*, 26 (1985) 909–912.
39 P. J. Garegg, P. Konradsson, I. Kvarnström, T. Norberg, S. C. T. Svensson, and B. Wigilus, *Acta Chem. Scand., Ser. B*, 39 (1985) 569–577.
40 F. Guibe and Y. Saint M'Leux, *Tetrahedron Lett.*, 22 (1981) 3591–3594.
41 M. Bergmann and L. Zervas, *Ber.*, 65 (1932) 1192–1201.
42 G. Just and K. Grozinger, *Synthesis*, (1976) 457–458.

43 V. G. Mairanovsky, *Angew. Chem. Int. Ed. Engl.*, 15 (1976) 281–292.
44 G. L. Stahl, R. Walter, and C. W. Smith, *J. Org. Chem.*, 43 (1978) 2285–2286.
45 M. Bergmann and L. Zervas, *Ber.*, 64 (1931) 975–980.
46 G. Excoffier, D. Gagnaire, and J. P. Utille, *Carbohydr. Res.*, 39 (1975) 368–373.
47 E. Gentil, M. Potier, P. Boullanger, and G. Descotes, *Carbohydr. Res.*, 197 (1990) 79–91.
48 R. U. Lemieux, S. Z. Abbas, M. H. Burzynska, and R. M. Ratcliffe, *Can. J. Chem.*, 60 (1982) 63–67.
49 U. Pindur, J. Müller, C. Flo, and H. Witzel, *Chem. Soc. Rev.*, 16 (1987) 75–87.
50 W. H. Bromund and R. M. Herbst, *J. Org. Chem.*, 10 (1945) 267–276.
51 A. Neuberger and R. Pitt Rivers, *J. Chem. Soc.*, (1939) 122–126.
52 T. Suami, S. Ogawa, and S. Umezawa, *Bull. Chem. Soc. Jpn.*, 36 (1963) 459–462.