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SOLID-PHASE SYNTHESIS OF OLIGOSACCHARIDES

PART IV. METHANOLYSIS OF PHENYLCARBAMOYL AND *N*-METHYL-*N*-PHENYLCARBAMOYL DERIVATIVES OF α-D-GLUCOPYRANOSYL BROMIDE*

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ABSTRACT

The synthesis and methanolysis of 6-*O*-acetyl-2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranosyl bromide and 6-*O*-acetyl-2,3,4-tri-*O*-(*N*-methyl-*N*-phenylcarbamoyl)-α-D-glucopyranosyl bromide are described. The former compound reacted stereospecifically to give a β-D-glucoside *via* neighboring group participation whereas the latter gave a mixture of β- and α-D-glucosides (7:3). The solvolysis of α-D-glucopyranosyl bromides having three *N*-phenyl and *N*-methyl-*N*-phenylcarbamoyl groups as participating "persistent" blocking groups is not feasible for solid-phase synthesis of oligosaccharides because of their slow rates of reaction, but the former group acts as an effective participating group and may be useful in glycoside syntheses in solution.

INTRODUCTION

In the solid-phase synthesis of oligosaccharides, the steric outcome of the glycoside-forming reaction must be controlled. Fréchet and Schuerch[1] have investigated a number of 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl halides substituted at C-6 with various ester functions and have found that the proportion of anomers of the product of methanolysis can vary from over 90% of α to over 90% of β depending on the structure of the C-6 acyl group. However, when the just-mentioned technique was modified for solid-phase synthesis[2], it was found that steric control was lost and that the trimers and dimers formed had predominantly α-D linkages.

Participating groups at C-2 have been the most frequently used groups to control the formation of *trans*-1,2 glycosides from glycosyl halides. In general, the participating groups have been esters, namely acetates or benzoates. The acetates, however, are hydrolyzed under the reaction conditions of solvolysis[3], and the benzoates, though acid stable[4], are readily cleaved by base; consequently, they are con-

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venient temporary blocking groups at C-6. It is, therefore, of interest to look for a "persistent" blocking group which can also participate (from C-2) in the glycoside forming reaction.

The *N*-phenylcarbamate (carbanilate) group has been used as a blocking group because of its ease of preparation and its stability toward acid hydrolysis[5] and, as shown by Hearon *et al.*[6], it is also relatively stable toward mild base hydrolysis. Under alkaline conditions that completely removed acetyl groups, the *N*-phenylcarbamate groups were only partially hydrolyzed. If the *N*-phenylcarbamate group were to be used as a persistent blocking group, milder conditions of alkaline hydrolysis would be required than those used by Fréchet and Schuerch[2].

The polycondensation[7] of D-glucopyranose 2,3,6-tri-(*N*-phenylcarbamate) using phosphorus pentaoxide in dimethyl sulfoxide and chloroform gave a poly-(1→4)-linked D-glucan with most of the linkages being β-D-(1→4). Goldstein and Hullar[8] have explained the formation of the β-D links as a result of the formation of an intermediate acyloxonium species by participation of the *N*-phenylcarbamate group at C-2. The approach of the hydroxyl group at C-4 is thus from the β-side to give rise to the β-D linkages. The participation of an *N*-phenylcarbamate group in the solvolysis of a glycosyl halide has never been reported in the literature.

Christenson[9] has investigated the kinetics of the alkaline hydrolysis of several *N*,*N*-disubstituted urethanes and has reported that the *N*-methyl-*N*-phenylcarbamoyl group was seven times more resistant to hydrolysis than the corresponding *N*-phenylcarbamoyl group. The *N*-methyl-*N*-phenylcarbamate group has been mentioned only rarely in the literature as a blocking group for hydroxyl groups of carbohydrates. Bouveng[10] has reported that the *N*-methyl-*N*-phenylcarbamate group is not removed by mild alkaline hydrolysis and is partially removed by heating at reflux with sodium methoxide. The greater resistance of the *N*-methyl-*N*-phenylcarbamate group toward base should make it a better blocking group than the *N*-phenylcarbamate; however, the participating nature of the *N*-methyl-*N*-phenylcarbamate function has never been investigated.

We have undertaken an investigation of the methanolysis of α-D-glucopyranosyl bromides substituted in the 2,3, and 4 positions with *N*-phenyl- and *N*-methyl-*N*-phenylcarbamate groups to determine the effect each group has on the rate and stereochemistry of the glycoside-forming reaction.

RESULTS AND DISCUSSIONS

In an attempt to find a stable participating group to be used in the solid-phase synthesis of oligosaccharides, both the *N*-phenylcarbamate and *N*-methyl-*N*-phenylcarbamate groups were investigated.

N-Phenylcarbamate groups were introduced into the carbohydrate molecule by allowing the free hydroxyl groups to react with phenyl isocyanate in pyridine. The reaction was both rapid and complete. The *N*-methyl-*N*-phenylcarbamate group was prepared from the corresponding *N*-phenylcarbamate by *N*-methylation using the method reported by Dannley[11] for the *N*-methylation of amides. The solvent used for the methylation was 1,2-dimethoxyethane, since it is unreactive toward sodium hydride, and carbohydrates substituted with the *N*-phenylcarbamate group were extremely soluble in it.

Model compounds were prepared from methyl α- and β-D-glucopyranoside to develop a convenient method for preparing the *N*-phenyl- and *N*-methyl-*N*-phenylcarbamate derivatives and, second, to determine the methoxyl proton resonances for each of the glucopyranosides in the n.m.r. spectrum (see Table I).

Methanolyses of the three α-D-glucopyranosyl bromides were performed under the same conditions employed by Fréchet and Schuerch[1], so that comparisons could be made as to the rate of methanolysis and composition of the product. The stereospecificity of the methanolysis reaction was determined from the relative peak areas of the methoxyl protons, since the peaks of the anomeric protons (H-1) overlap other peaks in the n.m.r. spectrum and were not observed.

In the case of 6-*O*-acetyl-2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranosyl bromide, methanolysis gave 100% of the β-D-glucopyranoside with no trace of the α isomer. Direct comparison between the n.m.r. spectrum of the prepared methyl β-D-glucoside and the product of methanolysis showed them to be identical. In one instance, the product of methanolysis crystallized to give a 97% yield of methyl 2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-β-D-glucopyranoside.

The methanolysis of 6-*O*-acetyl-2,3,4-tri-*O*-(*N*-methyl-*N*-phenylcarbamoyl)-α-D-glucopyranosyl bromide gave a mixture of anomers: 70% of β and 30% of α. This result indicates that the *N*-methyl-*N*-phenylcarbamate group does not participate fully in the methanolysis reaction. The reason for the nonparticipation of the group may be due to a steric effect of the *N*-methyl group in preventing the carbonyl group from adopting a conformation in which the intermediate acyloxonium species can be formed. Without participation, the attack of the nucleophile (methanol) can occur from either direction and thus give a mixture of methyl D-glucosides. The proportion of anomers formed is almost identical to that of the mixture formed from the methanolysis of 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl bromide reported by Fréchet and Schuerch[1]. Since the benzyl groups are known to be nonparticipating, it may be assumed that the *N*-methyl-*N*-phenylcarbamate is also nonparticipating.

The methanolysis of both D-glucopyranosyl bromides was performed with 2,6-dimethylpyridine (0.02 ml) as an acid acceptor. In these cases, the 6-*O*-acetyl group was not cleaved off and the ratio of the methyl D-glucosides formed was found to be identical to the ratio of methyl D-glucosides formed when the methanolyses were performed without an acid-acceptor.

In an attempt to increase the degree of steric control of the *N*-methyl-*N*-phenylcarbamate, an electron-releasing group was substituted on the phenyl group. It was postulated that the methoxyl group substituted on the phenyl group would increase the electron density on the carbonyl oxygen atom making participation more probable. However, the methanolysis of 6-*O*-acetyl-2,3,4-tri-*O*-[*N*-methyl-*N*-(*p*-methoxyphenyl)-carbamoyl]-α-D-glucopyranosyl bromide gave the same ratio of anomers as the

N-methyl-*N*-phenylcarbamate derivative. The indication is that the methoxyl group does not increase the electron density of the carbonyl oxygen or, more probably, that the steric influence of the *N*-methyl group is the controlling factor for the nonparticipation of the group.

All methanolyses were followed polarimetrically and from a plot of rotation *versus* time. The first order rate constants were determined using the expression:

$$k = 1/t \ln (\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty)$$

For the *N*-phenylcarbamate derivative, the rate constant was 3.24×10^{-5} sec^{-1} and the time at half-life was 4.3 h. The corresponding *N*-methyl-*N*-phenylcarbamate derivative had a rate constant of 2.60×10^{-5} sec^{-1} and a time at half-life of 5.5 h.

The methanolyses of the 6-*O*-acyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl bromide have been shown to have times at half-life of under 30 min[1] and the time required to achieve 85–90% coupling to the solid support was 4 days for these D-glucosyl bromides[2]. The 6-*O*-acetyl-2,3,4-tri-*O*-(*N*-phenyl and *N*-methyl-*N*-phenylcarbamoyl)-α-D-glucopyranosyl bromides have times at half-life on the order of 4 to 5.5 h. These times are 8 to 10 times longer than those for the benzyl derivatives, and the time that would be required to achieve the same degree of coupling to the solid support would make the reaction impractical. The rates were not changed or increased when an acid-acceptor was used.

The participating nature of the *N*-phenylcarbamoyl group apparently allows it to be used effectively in glycoside synthesis. However, problems remain in its use for the synthesis of β-D-linked oligosaccharides by solid-phase synthesis. These include the slow rate of glucoside formation and the possibility of acyl migration in basic medium[10]. The cleavage of a temporary blocking group under neutral conditions or a very weak base would have to be accomplished before the *N*-phenylcarbamoyl group could be used as a participating "persistent" blocking group in stepwise synthesis.

EXPERIMENTAL

General procedures. — N.m.r. spectra were measured on a Varian A-60A spectrometer in chloroform-*d*, acetone-d_6, or dimethyl-d_6 sulfoxide with tetramethylsilane as internal reference. Optical rotations were determined with a Perkin–Elmer Model 141 polarimeter using jacketed 1-dm cells kept at a constant temperature with a circulation of water from a constant-temperature bath. Microanalyses were performed by Galbraith Laboratories. All melting points are uncorrected.

Starting materials. — Methyl 2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-6-*O*-trityl-α- and β-D-glucopyranoside, and methyl 2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-α- and β-D-glucopyranoside were synthesized with the method reported by Hearon *et al.*[12] and the physical constants of these compounds are given in Table I.

*Methyl 2,3,4-tri-*O*-(*N*-methyl-*N*-phenylcarbamoyl)-6-*O*-trityl-α- and β-D-glucopyranosides.* — Methyl 2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-6-*O*-trityl-α-, respectively β-D-glucopyranoside, (10.0 g) was dissolved in anhyd. 1,2-dimethoxyethane (50 ml).

TABLE I

PREPARATION OF METHYL D-GLUCOPYRANOSIDE DERIVATIVES

Compound	*Anomeric form*	*Yield* (%)	*M.p.* (*degrees*)[a]	$[\alpha]_D^{23}$ (*degrees*)[a]	*Analysis*[b]			*Methoxyl resonance*[c]
					C	*H*	*N*	
2,3,4-Tri-*O*-(*N*-phenylcarbamoyl)-6-*O*-trityl	α	90	228–231	+51.5[d]				
			229–231	+52				
	β	89	231–234	−5.2[d]				
			232–234	−5.0				
2,3,4-Tri-*O*-(*N*-methyl-*N*-phenylcarbamoyl)-6-*O*-trityl	α	70		+39.7[d]	72.07	5.82	4.82	
					71.87	5.86	5.03	
	β	80		+7.0[d]	71.82	6.00		
					71.87	5.86		
2,3,4-Tri-*O*-(*N*-phenylcarbamoyl)-	α	63	190–192	+84[d]				3.43 (acetone-d_6)
			192–193	+84				
	β	68	217–219	−2.9[e]				3.52 (acetone-d_6)
			218–219	−3.0				
2,3,4-Tri-*O*-(*N*-methyl-*N*-phenylcarbamoyl)	α	65	167–169	+34.8[d]	62.92	5.89	7.05	3.35–3.31 (chloroform-*d*)[f]
					62.72	5.94	7.08	
	β	86		−8.8[g]				3.43 (chloroform-*d*)

[a] Upper line, observed value; lower line, reported by Hearon *et al.*[12]. [b] In percent; upper line, experimental value; lower line, calculated value. [c] δ values are ±0.03 p.p.m.; the methoxyl resonances of methyl 6-*O*-acetyl-2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-α-D- and methyl 6-*O*-acetyl-2,3,4,-tri-*O*-(*N*-methyl-*N*-phenylcarbamoyl)-β-D-glucopyranosides are 3.47 (dimethyl-d_6 sulfoxide) and 3.43 (chloroform-*d*), respectively. [d] Measured in chloroform, *c* 1. [e] Measured in pyridine, *c* 1. [f] Within the *N*-Me region. [g] Measured in acetone, *c* 1.

Sodium hydride (0.94 g) was added slowly and the mixture stirred until the evolution of hydrogen ceased. Methyl iodide (2.8 ml) was added dropwise and the solution stirred for 3 h. The excess sodium hydride was destroyed with methanol and a mixture of carbon tetrachloride (50 ml) and water (30 ml) was added. The organic layer was washed with dilute acid, a 10% sodium hydrogen carbonate solution, and water, and then dried with magnesium sulfate, decolorized with activated charcoal, and evaporated to a syrup that formed a glass upon being cooled. The glass was powdered and extracted with petroleum ether in a Soxhlet extractor for 24 h. The petroleum ether solution was concentrated to a small volume with a stream of dry air, and the white precipitate that formed was filtered off and dried. The yields and physical constants of the two compounds are given in Table I.

*Methyl 2,3,4-tri-*O-(N-*methyl-*N-*phenylcarbamoyl)-α-* and *β-D-glucopyranosides.* — Methyl 2,3,4-tri-*O*-(*N*-methyl-*N*-phenylcarbamoyl)-6-*O*-trityl-α-, respectively *β*-D-glucopyranoside, (5.0 g) was dissolved in a minimum volume of hot glacial acetic acid. The solution was cooled in ice and 32% HBr in acetic acid (1.6 ml) was added. The flask was swirled for 30 sec and the precipitated bromotriphenylmethane was filtered off. The filtrate was poured into an ice–water mixture and an oil precipitated which was dissolved in chloroform. The solution was washed with a 10% sodium hydrogen carbonate solution and water. The organic phase was dried over magnesium sulfate, decolorized with activated charcoal, and evaporated to a syrup. The α-D isomer crystallized from carbon tetrachloride while the *β*-isomer did not crystallize. The yields and physical constants of the two isomers are given in Table I.

*1,6-Anhydro-2,3,4-*O-(N-*monosubstituted carbamoyl)-β-D-glucopyranose.* — The compounds were prepared by a modified method of Wolff and Rist[13]. 1,6-Anhydro-*β*-D-glucopyranose (levoglucosan, 3.4 g) was dissolved in dry pyridine (60 ml) and phenyl isocyanate (4.0 g) or *p*-methoxyphenyl isocyanate (10 ml) was added dropwise while the pyridine solution was cooled in an ice bath. After the addition of the isocyanate, the solution was allowed to reach room temperature, and then it was stirred for 3 days. Methanol (5 ml) was added and the mixture was heated for 10 min on a steam bath, and then poured into hot water. The white precipitate was filtered off, washed with water, and dried. The product was crystallized from ethanol–acetone. The yields and physical constants are given in Table II.

*1,6-Anhydro-2,3,4-tri-*O-(N-*methyl-*N-*monosubstituted carbamoyl)-β-D-glucopyranose.* — 1,6-Anhydro-2,3,4-tri-*O*-(*N*-substituted carbamoyl)-*β*-D-glucopyranose (5.2 g) was dissolved in anhyd. 1,2-dimethoxyethane (50 ml) and sodium hydride (1.44 g, 52% in mineral oil) was added slowly. After the evolution of hydrogen ceased, methyl iodide (2.0 ml) was added dropwise and the mixture was stirred for 2 h at room temperature. The excess sodium hydride was destroyed with methanol, and a mixture of carbon tetrachloride and water was added. The organic phase was washed with water, 10% sodium hydrogen carbonate, and water, and then dried over magnesium sulfate. After the solution was decolorized with activated charcoal, the solvent was evaporated. The residue was dissolved in a minimum volume of ether and the solution poured into petroleum ether. The liquid was decanted, and the precipitate

TABLE II

PREPARATION OF D-GLUCOPYRANOSE DERIVATIVES

Compound	*Anomeric form*	*Yield (%)*	*M.p. (degrees)*[a]	$[\alpha]_D^{23}$ *(degrees)*[a]	*Analysis*[b]		
					C	*H*	*N*
1,6-Anhydro-2,3,4-tri-*O*-(*N*-phenylcarbamoyl)	β	83	235–336	−43.9[c]	62.30	4.92	8.23
			234–235	−44.9	62.42	4.82	8.09
(*N*-Methyl-*N*-phenylcarbamoyl)	β	88		−14.7[d]	64.34	5.48	7.67
					64.13	5.56	7.48
[*N*-(*p*-Methoxyphenyl)carbamoyl]	β	65	235–239	−36.0[c]	59.31	5.19	6.78
					59.11	5.13	6.89
[*N*-Methyl-*N*-(*p*-methoxyphenyl)carbamoyl]	β	94		−13.1[d]	60.59	5.86	6.27
					60.82	5.72	6.45
1,6-Di-*O*-acetyl-2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-	α	85	250–251	+58.7[d]	60.01	5.18	6.97
					59.90	5.03	6.76
(*N*-Methyl-*N*-phenylcarbamoyl)	β	74	168–171	+17.5[d]	61.60	5.74	6.30
					61.53	5.62	6.33
[*N*-Methyl-*N*-(*p*-methoxyphenyl)carbamoyl]	α,β	83	—	+22.8[d]	58.66	5.80	5.55
					58.96	5.75	5.58

[a] Upper line, observed value; lower line, reported by Wolff and Rist[13]. [b] In percent; upper line, experimental value; lower line, calculated value. [c] Measured in pyridine, *c* 1. [d] Measured in acetone, *c* 1.

TABLE III

PREPARATION AND METHANOLYSIS OF 6-*O*-ACETYL-2,3,4-TRI-*O*-CARBAMOYL-α-D-GLUCOPYRANOSYL BROMIDES

Compound	*Physical constants of the bromides*				*Methanolysis*		
	M.p. (degrees)	$[\alpha]_D^{23}$ *(degrees)*[a]	*N.m.r. spectrum*		k[d] *(sec*$^{-1}$*)*	t½ *(h)*	*Glucoside β:α ratio*[e]
			p.p.m.	$J_{1,2}$ *(Hz)*			
(*N*-Phenylcarbamoyl)	188–190	+104	6.35[b]	3.2	3.24×10^{-5}	4.3	1:0
(*N*-Methyl-*N*-phenylcarbamoyl)		+60.2	6.64[c]	4.2	2.60×10^{-5}	5.5	7:3
[*N*-Methyl-*N*-(*p*-methoxyphenyl)carbamoyl]		+67.4	6.60[c]	4.0			7:3

[a] Measured in acetone, *c* 1. [b] Measured in acetone-d_6. [c] Measured in chloroform-*d*. [d] Reaction temperature 23°. [e] Ratios determined from the peak areas of the methoxyl protons (chemical shifts are identical to those given in Table I for the compounds without acetyl groups, even when acid acceptor is used and acetyl groups are retained).

was washed with a small amount of petroleum ether and then dried in a vacuum oven at 50°. The yields and physical constants of the compounds formed are given in Table II.

*1,6-Di-*O*-acetyl-2,3,4-tri-*O*-(*N*-substituted carbamoyl)-*D*-glucopyranose.* — 1,6-Anhydro-2,3,4-tri-*O*-(*N*-substituted carbamoyl)-β-D-glucopyranose derivative (3.0 g) was dissolved in acetic anhydride (50 ml) and a solution of acetic anhydride (5 ml) and conc. sulfuric acid (0.2 ml) prepared at 0° was added. The mixture was stirred at room temperature for 30 min and then poured into ice–water. The white precipitate was filtered off, washed with water until free of acid, and dried. The product was crystallized from abs. ethanol. The yields and physical constants of the compounds are given in Table II.

*6-*O*-Acetyl-2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-α-*D*-glucopyranosyl bromide.* — 1,6-Di-*O*-acetyl-2,3,4-tri-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranose (3.5 g) was dissolved in glacial acetic acid (15 ml), and 32% HBr in acetic acid (5 ml) was added. The solution was stirred for 3 h at room temperature. The reaction mixture was evaporated to a red powder by azeotropic distillation with dry toluene at 50° under reduced pressure. The powder was stirred with abs. methanol for 24 h at 0° to remove the red color. The white solid was filtered off and dried at 50° under vacuum (2.0 g, 55%), m.p. 188–190° (dec.), $[\alpha]_D^{23}$ +104° (*c* 1, acetone). Titration for bromine gave 98% of the theoretical amount. The n.m.r. spectrum shows a doublet ($J_{1,2}$ 3.2 Hz) centered at δ 6.35 which indicates the α-D anomer and the spectrum did not show the presence of any methoxyl protons.

*6-*O*-Acetyl-2,3,4-tri-*O*-(*N*-methyl-*N*-monosubstituted carbamoyl)-α-*D*-glucopyranosyl bromide.* — 1,6-Di-*O*-acetyl-2,3,4-tri-*O*-(*N*-methyl-*N*-monosubstituted carbamoyl)-D-glucopyranose (0.5 g) was dissolved in dry dichloromethane (10 ml) and dry hydrogen bromide gas was bubbled in for 45 min. The resulting yellow solution was evaporated to a syrup at room temperature under vacuum. Dichloromethane and dry benzene was added to the syrup and evaporated several times to remove most of the hydrogen bromide and acetic acid. The yields and physical constants of the D-glucosyl bromides are given in Table III.

*Methanolysis of the substituted *D*-glucopyranosyl bromides.* — A sample of the D-glucopyranosyl bromide (150 mg or 0.047 mmole) was placed in a volumetric flask (5 ml) and dissolved in dry acetone (1.0 ml). Methanol (3.75 ml) was added and the volume completed to 5.0 ml by the addition of dry acetone. An aliquot (1.0 ml) was placed in a 1-dm polarimeter tube kept at 23° and the reaction was followed by the change in optical rotation. When the rotation became constant (48–120 h), the solution was evaporated under reduced pressure at room temperature. The residue was dried by several additions and evaporations of dichloromethane and dry benzene. After being dried in a vacuum oven at 50°, the samples were dissolved in an appropriately deuterated solvent and the n.m.r. spectrum recorded. In all cases, the C-6 acetyl group was cleaved during the methanolysis. The ratio of β to α anomers was determined by the ratio of the peak areas in the n.m.r. spectrum of the methoxy protons.

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