Anal. Calcd for $C_{30}H_{35}NO_6$ (505.62): C, 71.26; H, 6.98; N, 2.77. Found: C, 71.07; H, 7.15; N, 2.53.

Methanolysis of 2-Acetamido-1-*O*-acetyl-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranose (X).—The ester X (0.17 g) was dissolved in methanol (5 ml) and the solution boiled under reflux for 10 hr. The crystalline product which separated on cooling the solution was recrystallized from methanol to give essentially pure 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranose (IX): 0.08 g (51%), mp 189–190° alone or in admixture with authentic material.

Methanolysis of 2-Acetamido-1-*O*-benzoyl-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranose (XI).—A solution of XI (0.08 g) in methanol (5 ml) was boiled under reflux for 48 hr. Thin layer chromatography, using ether–benzene (2:1), then showed the presence of three components: methyl benzoate, starting material, and 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranose (IX). The solution was concentrated, the residue was dissolved in chloroform and the solution was poured on a column of silica gel (2 × 15 cm). Elution with ether–benzene (2:1) gave, first, methyl benzoate and then 2-acetamido-1-*O*-benzoyl-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranose (0.022 g). Elution with ether–methanol (1:1) afforded 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranose (IX): 0.035 g (73%, corrected for starting material recovered), mp 185–188° alone or in admixture with authentic IX.

Methanolysis of 2-Acetamido-1-*O*-benzoyl-2-deoxy-β-D-galactopyranose (XVI).—A solution of XVI[4] (100 mg) in methanol (10 ml) was boiled under reflux for 30 hr and then concentrated to a volume of *ca.* 2 ml to give a crystalline product (0.03 g) which was acetylated with acetic anhydride and pyridine in the usual manner to yield, from methanol, **methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranoside**: 20 mg (28%), mp 217–218°, $[\alpha]^{20}D$ −16.4° (*c* 0.75, $CHCl_3$). Tarasiejska and Jeanloz[17] reported mp 216–217° and $[\alpha]^{20}D$ −17° ($CHCl_3$) for this substance.

Hydrolysis of 2-Acetamido-1-*O*-acyl-3,4,6-tri-*O*-benzyl-D-hexopyranoses.—Each substance (10^{-5} mole) was dissolved in purified dioxane (30 ml), previously heated to 50°, and water (20 ml), also preheated to 50°, was added. The reaction mixture was held at 49.5 ± 0.5° while, at intervals, 5-ml aliquots were removed, diluted with 20 ml of cold water, and titrated with 0.01 *N* sodium hydroxide, using phenolphthalein as an indicator. The titer of sodium hydroxide as a function of time is plotted in Figure 1; it will be noted that 1.00 ml of 0.01 *N* sodium hydroxide is equivalent to 1 molar equiv of benzoic acid liberated.

Acknowledgment.—We are indebted to Mr. Harry W. Diehl for assistance in the preparation of starting materials and to the staff of the Section on Microanalytical Services and Instrumentation for elementary analyses and nmr spectra.

(17) Z. Tarasiejska and R. W. Jeanloz, *J. Am. Chem. Soc.*, **80**, 6325 (1958).

N-Acyl Derivatives of 2-Acylamino-2-deoxy-D-glucopyranose[1]

THOMAS D. INCH[2] AND HEWITT G. FLETCHER, JR.

National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Public Health Service, U. S. Department of Health, Education, and Welfare, Bethesda, Maryland 20014

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N-Acetylbenzamidocyclohexane, (±)-*trans*-2-(*N*-acetylbenzamido)cyclohexyl benzoate, and (±)-*trans*-2-(*N*-acetylacetamido)cyclohexyl acetate have been prepared and the behavior of the first two has been studied with a variety of reagents. Such diacylamines are readily attacked by nucleophilic agents, losing a single acyl group; where two dissimilar acyl groups are attached to nitrogen a mixture of products often (if not always) results. Replacement of the nitrogen-attached proton in 2-acylamino-2-deoxy-D-glucopyranose derivatives by a second acyl group is comparatively easily accomplished and a variety of *N*-acylacylamino-2-deoxy-D-glucopyranose derivatives have been prepared. Like the cyclohexane derivatives mentioned above, these readily lose one of the nitrogen-attached acyl groups. Isopropenyl acetate in the presence of a trace of *p*-toluenesulfonic acid is shown to be an effective reagent both for *O*-acetylation and for the acetylation of monoacylamines.

In the course of a recent study[3] of the benzoylation of 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose and -D-galactopyranose, we have observed that, in addition to normal *O*-acylation, *N*-acylation may take place and we have described the preparation of 2-(*N*-acetylbenzamido)-1-*O*-benzoyl-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranose. Whereas some cyclic *N*-acylacylamino derivatives of the aminosugars such as the phthalimido[4] and succinimido[5] sugars have been investigated, comparatively little attention has been directed toward the acyclic analogs of these substances. Thus, Ohle and Lichtenstein[6] found that benzoylation of 6-amino-6-deoxy-D-glucose afforded a hexabenzoyl derivative while Druey and Huber[7] were able to obtain a hexaacetyl derivative of 1-amino-1-deoxy-D-fructose. More recently, Coxon and Fletcher[8,9] have reported several *N*-acylacylamino derivatives of 1-amino-2,6-anhydro-1-deoxyheptitols. It should be noted that the nitrogen atom in all these examples is attached to an exocyclic carbon atom while the attachment in the hexosamines is to a ring carbon atom. The investigation which we will report here was primarily designed to study the preparation and some of the properties of 2-(*N*-acylacylamino)-2-deoxy-D-glucopyranose derivatives.

Since the pioneering work of Titherley,[10] the problem of the acylation of amides has received only sporadic attention although Rothman and his

(1) Compounds of the type R-N(COR')$_2$ have been variously called diacylamines, acyclic imides, diacylimides, diacylamides, etc.; of these terms, we believe that diacylamine is least confusing. We have chosen to use the prefix *N*-acylacylamino when describing individual compounds since this is in accord with accepted practice although, from the viewpoint of clarity, prefixes such as *N*-acetyl-*N*-benzoylamino might be preferable since nomenclature of this type, although more cumbersome, emphasizes the fact that such compounds are indeed *N*-diacyl derivatives of primary amines. These compounds, incidentally, should not be confused with the *N,N'*-diacyl derivatives produced in the Wohl degradation of acylated nitriles. These substances, containing the -CH(NHCOCH$_3$)$_2$ group, have been widely termed diacetamides.

(2) Fellow in the Visiting Program of the National Institutes of Health, 1964–1965.

(3) T. D. Inch and H. G. Fletcher, Jr., *J. Org. Chem.*, **31**, 1810 (1966).

(4) B. R. Baker, J. P. Joseph, R. E. Schaub, and J. H. Williams, *ibid.*, **19**, 1786 (1954).

(5) S. Akiya and T. Osawa, *Chem. Pharm. Bull.* (Tokyo), **8**, 588 (1960).

(6) H. Ohle and R. Lichtenstein, *Ber.*, **63**, 2905 (1930).

(7) J. Druey and G. Huber, *Helv. Chim. Acta*, **40**, 342 (1957).

(8) B. Coxon and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **85**, 2637 (1963).

(9) B. Coxon and H. G. Fletcher, Jr., *ibid.*, **86**, 922 (1964).

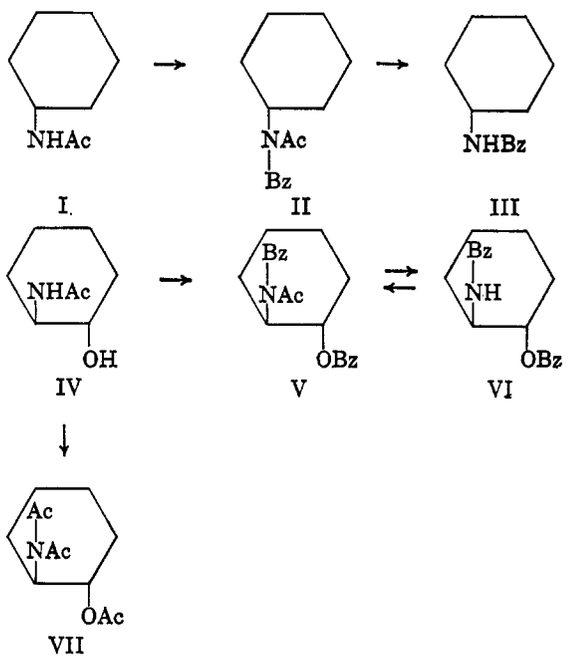
(10) A. W. Titherley, *J. Chem. Soc.*, **85**, 1673 (1904).

co-workers[11] have recently supported Titherley's conclusion that there is no satisfactory general method for the synthesis of *N*,*N*-diacyl derivatives.

A few methods for the preparation of individual diacylamines have been developed in recent years. Cramer and Baer[12] have formed mixed diacylamines from imino chlorides by a Mumm rearrangement while Heyns and Pyrus[13] have utilized a Grignard type of reaction. Ketene[14] has been used to acetylate amides. However, none of these methods appears to be suited for application to hexosamine derivatives.

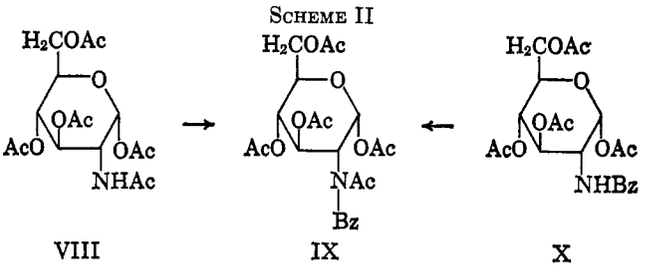
As shown by Titherley[10] and, more recently, by Thompson,[15] benzoyl chloride in pyridine solution is a fairly effective reagent for the preparation of *N*-acetylbenzamido derivatives under comparatively mild conditions although no detailed reaction mechanism has been proposed. Preliminary to the application of this reagent to glucosamine derivatives, we have studied its behavior with certain members of the cyclohexane series. Acetamidocyclohexane (I) (Scheme I), for instance, was found to be converted to *N*-

SCHEME I

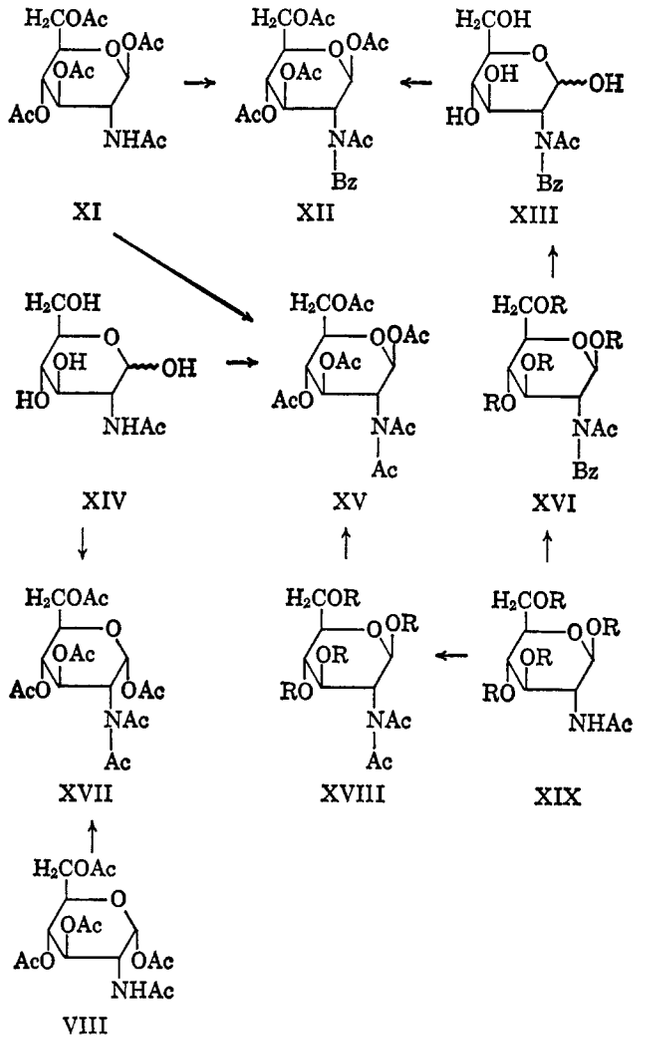


acetylbenzamidocyclohexane (II) in good yield. Likewise, (±)-*trans*-2-acetamidocyclohexanol (IV) was both *O*- and *N*-benzoylated to give (±)-*trans*-2-(*N*-acetylbenzamido)cyclohexyl benzoate (V). With 2-acetamido-2-deoxy-D-glucopyranose derivatives, *N*-benzoylation proved equally practicable. Thus 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (VIII) (Scheme II) and its anomer XI (III) gave *N*-acetylbenzamido derivatives (IX and XII, respectively). One, XII, was prepared by an independent synthesis. Benzyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside[16] (XIX) was *N*-benzoylated to give XVI and the four benzyl groups

SCHEME II



SCHEME III



were removed by hydrogenolysis. Acetylation of the product, XIII, then gave XII, identical with the product prepared through the *N*-benzoylation of XI. *N*-Benzoylation of 2-acetamido-2-deoxy-D-glucose derivatives takes place with such ease that it is probably always a concomitant of *O*-benzoylation. As shown by us in a previous paper[3] the extent of *N*-benzoylation, when only *O*-benzoylation is desired, may be minimized but not entirely eliminated by the avoidance of an excess of benzoyl chloride over that needed for *O*-benzoylation.

Moore and Marascia[17] have shown that certain aminopyridine derivatives may be di-*N*-benzoylated with benzoyl chloride in pyridine and there appears to be no reason *a priori* why *N*,*N*-dibenzoyl derivatives of 2-amino-2-deoxyaldoses, analogous to the previously cited 6-amino-6-deoxy-D-glucose derivative

(11) E. S. Rothman, S. Serota, and D. Swern, *J. Org. Chem.*, **29**, 646 (1964).
(12) F. Cramer and K. Baer, *Ber.*, **93**, 1231 (1960).
(13) K. Heyns and W. Pyrus, *ibid.*, **88**, 678 (1955).
(14) R. E. Dunbar and G. C. White, *J. Org. Chem.*, **23**, 915 (1958).
(15) Q. E. Thompson, *J. Am. Chem. Soc.*, **73**, 5841 (1951).
(16) R. Harrison and H. G. Fletcher, Jr., *J. Org. Chem.*, **30**, 2317 (1965).
(17) J. A. Moore and F. J. Marascia, *J. Am. Chem. Soc.*, **81**, 6049 (1959).

of Ohle and Lichtenstein,[6] should not be preparable; attempts to benzoylate the anomeric 2-benzamido-1,3,4,6-tetra-*O*-benzoyl-2-deoxy-D-glucopyranoses met, however, with no success.

Since Baker and his co-workers[4] successfuly prepared a phthalimido derivative of 2-amino-2-deoxy-D-glucopyranose *via* a mixed carbonic–carboxylic anhydride and Kopple and Renick[18] claim to have prepared an *N*-acylamide through the condensation of glycine ethyl ester with a similar mixed anhydride derived from *N*-carbobenzoxyglycine, we attempted to benzoylate acetamidocyclohexane (I) using C_2H_5OCOO-COC_6H_5, prepared as described by Tarbell and Leister.[19] A variety of reaction conditions were investigated but no *N*-acetylbenzamidocyclohexane (II) could be detected chromatographically.

Attention was now turned to *N*-acetylacetamido derivatives. Coxon and Fletcher[8,9] made representatives of this class of substance through the use of boiling acetic anhydride and sodium acetate while Druey and Huber[7] di-*N*-acetylated 1-amino-1-deoxy-D-fructose with acetic anhydride and pyridine at room temperature and Anet, Bannard, and Hall[20] made two *N*-acetylacetamidocyclohexane derivatives with boiling acetic anhydride alone. We have found that boiling acetic anhydride with sodium acetate effectively converts (±)-*trans*-2-acetamidocyclohexanol (IV) to (±)-*trans*-2-(*N*-acetylacetamido)cyclohexyl acetate (VII) but is not suitable for the preparation of di-*N*-acetylhexosamines although traces of these substances were detected chromatographically. Acetic anhydride with other acid catalysts such as sulfuric acid, perchloric acid, and zinc chloride gave similar results. Recourse was, therefore, had to a procedure devised by Hagemeyer[21] for the acylation of amides through acid-catalyzed reaction with alkenyl esters. In the presence of a trace of *p*-toluenesulfonic acid, hot isopropenyl acetate was found to be a most effective agent for both *O*- and *N*-acetylation. Methyl α-D-glucopyranoside was smoothly converted to its tetraacetate while D-mannitol gave its hexaacetate, no evidence for the formation of isopropylidine derivatives being observed. Isopropenyl acetate–*p*-toluenesulfonic acid similarly converted (±)-*trans*-2-acetamidocyclohexanol (IV) to (±)-*trans*-2-(*N*-acetylacetamido)cyclohexyl acetate (VII) and (±)-*trans*-2-benzamidocyclohexyl benzoate (VI) to (±)-*trans*-2-(*N*-acetylbenzamido)-cyclohexyl benzoate (V), both in excellent yield. With aminosugar derivatives it proved equally satisfactory. 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (XI) (Scheme III) was smoothly converted to 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-β-D-glucopyranose (XV); the same substance was also made by replacing the amide proton of XIX with an acetyl group, removing the benzyl groups from the product, XVIII, and acetylating with acetic anhydride in pyridine. Treatment of 2-acetamido-2-deoxy-D-glucose (XIV) with isopropenyl acetate and *p*-toluenesulfonic acid gave both anomeric 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-D-glucopyranoses, XV and XVII. Under these acetylating conditions sugar esters may anomerize. Thus 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (VIII) afforded 9% of the β anomer XV although the unanomerized product XVII predominated. Acetylation of a benzamido group in the sugar series was demonstrated through the conversion of X to IX.

The properties of the diacylamines have received even less attention than their methods of preparation. When two acyl groups are attached directly to a central atom they render each other mutually more susceptible to attack by nucleophilic agents. In the only quantitative study of the hydrolysis of diacylamines Lamberton and Standage[22] have shown that *N*-benzoylbenzanilide is hydrolyzed by potassium hydroxide 1000 times more rapidly than benzanilide; Satchell[23] has suggested that substances of this class may behave as acylating agents although, at the moment, there appears to be little evidence to support this.

In order to investigate some of the properties of the diacylamines, we turned initially to those of the cyclohexane series. *N*-Acetylbenzamidocyclohexane (II) proved to be stable in boiling methanol but, in the presence of a little hydrochloric acid, cleavage of the acetyl group predominated, III being isolated in 68% yield. When sodium methoxide was used, loss of the benzoyl group appeared to predominate, acetamidocyclohexane (I) being isolated in 43% yield and benzamidocyclohexane (III) in 16% yield. Aqueous methylamine at room temperature caused rapid cleavage of the acetyl group, III being isolated in 70% yield. Chromatographic evidence indicated the concomitant formation of *N*-methylacetamide. Aniline caused the formation of III in 72% yield, gas–liquid partition chromatography demonstrating the formation of acetanilide. With either methylamine or aniline V lost an *N*-acetyl group to give VI in good yield. When 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-α-D-glucopyranose (IX) was treated with sodium methoxide and the product was then reacetylated with acetic anhydride in pyridine, 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (VIII) was the major product although a minor product having the chromatographic mobility of 1,3,4,6-tetra-*O*-acetyl-2-benzamido-2-deoxy-D-glucopyranose was isolated. That removal of the *N*-benzoyl group here takes place to a much greater extent than removal of the *N*-acetyl group was shown by an alternative method. The immediate product from the treatment of IX with sodium methoxide was converted into its trimethylsilyl derivative and subjected to gas–liquid partition chromatography. By comparison with the products obtained through the trimethylsilylation of 2-acetamido-2-deoxy-D-glucose (XIV) and of 2-benzamido-2-deoxy-D-glucose, the mixture was shown to contain these two substances in the ratio of 6:1. That anomeric configuration has little bearing on the nature of the *N*-deacylation with sodium methoxide was demonstrated through a parallel experiment with 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-β-D-glucopyranose (XII); here the ratio of 2-acetamido-2-deoxy-D-glucose to 2-benzamido-2-deoxy-D-glucose was 5:1.

Treatment of XII with aniline at 95 ± 5° gave a crystalline product (38% yield) with a composition

(18) K. D. Kopple and R. J. Renick, *J. Org. Chem.*, **28**, 1565 (1958).
(19) D. S. Tarbell and N. A. Leister, *ibid.*, **23**, 1149 (1958).
(20) F. A. L. Anet, R. A. B. Bannard, and L. D. Hall, *Can. J. Chem.*, **41**, 2331 (1963).
(21) H. J. Hagemeyer, Jr., U. S. Patent 2,656,360 (Oct 20, 1953).
(22) A. H. Lamberton and A. E. Standage, *J. Chem. Soc.*, 2957 (1960).
(23) D. P. N. Satchell, *Quart. Rev.* (London), **17**, 160 (1963).

and nmr spectrum which was consistent with what would be expected of an *N*-phenyl-3,4,6-tri-*O*-acetyl-2-benzamido-2-deoxy-D-glucopyranosylamine, a product arising from loss of the *N*-acetyl (as well as the C-1 *O*-acetyl) group. The yield was too low to indicate whether loss of *N*-acetyl or *N*-benzoyl had predominated.

In summary, sodium methoxide preferentially removed *N*-benzoyl groups from II, IX, and XII while methylamine attacked the *N*-acetyl groups of II and V. It is probable that, in all cases, the *N*-acetyl and *N*-benzoyl groups compete in reaction with the reagent. That the rate of attack by a nucleophile may vary widely with the nature of the attacking species is well known but an understanding of the factors which govern the behavior of a nucleophile when confronted with two closely related substrates of the type described here must await further research.

One feature of the behavior of 2-(*N*-acylacylamido)-2-deoxy-D-glucopyranoses deserves special comment. The acylation of 2-acylamino-2-deoxy-D-glucopyranoses such as XIV with acetic anhydride in pyridine at room temperature normally leads to a product in which the α anomer predominates[24] while Schiff bases derived from 2-amino-2-deoxy-D-glucose give, predominantly, β esters.[25] In the light of these facts it is interesting to note that the acetylation of 2-(*N*-acetylbenzamido)-2-deoxy-D-glucose (XIII) and of the product from the debenzylation of XVIII [2-(*N*-acetylacetamido)-2-deoxy-D-glucose] gave, in both cases, the β anomers XII and XV, respectively.

In the paper immediately following this one we describe a further reaction of a diacylamine, the intramolecular rearrangements of 2-(*N*-acetylbenzamido)-2-deoxy-D-glucose.[26]

Experimental Section[27]

***N*-Acetylbenzamidocyclohexane (II).**—A solution of acetamidocyclohexane[28] (4.8 g) and benzoyl chloride (5 ml) in pyridine (30 ml) was stored at room temperature overnight and then poured into cold water. The product was extracted with dichloromethane and the extract was washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate solution, and water. Moisture was removed with magnesium sulfate and the solution was concentrated to a dark yellow syrup which was dissolved in benzene and adsorbed on a column of silica gel. Benzene was used for elution, 50-ml portions being collected. Fractions 3–7 were combined and concentrated to yield a chromatographically homogeneous (tlc, benzene) pale yellow syrup which was distilled at 180° (bath temperature) and 0.1 mm to give 5.2 g (62%) of a pale yellow liquid: nmr data, τ 8.08 (N–$COCH_3$); infrared spectrum, ν_{max}^{Nujol} (cm^{-1}) 1710, 1668.

Anal. Calcd for $C_{15}H_{19}NO_2$ (245.33): C, 73.44; H, 7.81; N, 5.71. Found: C, 73.39; H, 7.68; N, 5.69.

Behavior of *N*-Acetylbenzamidocyclohexane (II) with Various Reagents. A. Methanol.—A solution of II in methanol was boiled under reflux and periodically examined by thin layer chromatography (benzene). After 10 hr the material was essentially unchanged. To ascertain the effect of U.S.P. chloroform on the system, a solution of II (0.3 g) in a mixture of methanol (2 ml) and U.S.P. chloroform (5 ml) was also boiled under reflux for 10 hr. The infrared spectrum and chromatographic behavior of the residue remaining after removal of the solvent showed it to be essentially unchanged II.

B. Sodium Methoxide in Methanol.—A solution of II (1 g) in a mixture of 0.2 *N* sodium methoxide (2 ml) and methanol (10 ml) was held at room temperature for 1 hr, neutralized with carbon dioxide, and concentrated *in vacuo*. The residue was dissolved in dichloromethane and the solution was washed with water. Moisture was removed with magnesium sulfate, the solution was concentrated *in vacuo*, and the mixture was chromatographed on a column (2.2 × 30 cm) of silica gel. Elution with ether gave benzamidocyclohexane (III),[28] mp (from methanol) 148–149° (0.13 g, 16%), and acetamidocyclohexane (I), mp (from hexane) 106° (0.25 g, 43%). Both products were identified through comparison of their infrared spectra, melting points, and thin layer chromatographic properties with those of authentic specimens.

C. Methanol with Trace of Concentrated Hydrochloric Acid.—A solution of II (0.8 g) in methanol (10 ml) containing a few drops of concentrated hydrochloric acid was boiled under reflux for 30 min and then poured into aqueous sodium bicarbonate solution. The precipitate which formed was filtered off and recrystallized from aqueous methanol: mp 146–147°, 0.45 g, 68%. The infrared spectrum of the product was indistinguishable from that of benzamidocyclohexane (III).

D. Aqueous Methylamine.—An excess (*ca.* 3 ml) of a 40% aqueous solution of methylamine was added to II (1.2 g), sufficient alcohol being added to effect complete solution. A white precipitate began to form almost immediately; after 10 min it was removed by filtration: mp 147–148°. Recrystallized from aqueous methanol, the product (0.7 g, 70%) had mp 148–149° either alone or in admixture with authentic benzamidocyclohexane (III).

Examination of the original filtrate by thin layer chromatography (benzene–ether 1:1) showed it to contain a major component migrating at the same rate as *N*-methylacetamide and a trace of *N*-acetylcyclohexylamine.

E. Aniline.—A solution of II (1 g) in freshly purified aniline (5 ml) was heated at 95 ± 5° for 6 hr. The reaction mixture was diluted with dichloromethane, washed successively with dilute hydrochloric acid (three times), aqueous sodium bicarbonate solution, and water, dried with magnesium sulfate, and concentrated. Crystallization of the residue from methanol gave III: mp 136–140°, 0.6 g, 72%. The product did not depress the melting point of authentic material; its infrared spectrum and behavior on thin layer chromatography were indistinguishable from those of authentic material.

Vapor phase chromatography of the original reaction mixture showed the presence of acetanilide and of a trace of I.

(±)-*trans*-2-(*N*-Acetylbenzamido)cyclohexyl Benzoate (V). A. From (±)-*trans*-2-Acetamidocyclohexanol (IV).—A solution of IV[29] in a mixture of benzoyl chloride (0.35 ml, 2.4 moles) and pyridine (2 ml) was stored at room temperature for 40 hr and then poured into water. The product was extracted with dichloromethane, the extract being washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate solution, and water. Moisture was removed with magnesium sulfate and the solution then concentrated *in vacuo* to afford a syrup which was crystallized from isopropyl ether. After three recrystallizations, the pure product (0.3 g, 65%) had mp 116–117°; nmr data, τ 8.2 (N–$COCH_3$); infrared spectrum, ν_{max}^{Nujol} (cm^{-1}) 1712, 1700, 1680.

Anal. Calcd for $C_{22}H_{23}NO_4$ (365.43): C, 72.31; H, 6.34; N, 3.83. Found: C, 72.59; H, 6.22; N, 3.82.

B. From (±)-*trans*-2-Benzamidocyclohexyl Benzoate (VI).—A solution of VI[29] (0.11 g) in isopropenyl acetate[30] (30 ml) containing *p*-toluenesulfonic acid monohydrate (5 mg) was boiled under reflux for 5 hr and the solvent was then removed *in vacuo*. Chromatography on a column of silica gel using benzene–ether (9:1) as eluent gave V which was recrystallized from isopropyl ether (0.10 g, 80%), mp 114–115° either alone or in admixture with the product prepared from IV.

Behavior of (±)-*trans*-2-(*N*-Acetylbenzamido)cyclohexyl Benzoate A. With Aqueous Methylamine.—Compound V (0.3 g) was shaken with an aqueous ethanolic solution of methylamine for 15 min and the precipitate which formed was removed by filtra-

(24) D. Horton, *Advan. Carbohydrate Chem.*, **15**, 159 (1960), ref 1–10.

(25) M. Bergmann and L. Zervas, *Ber.*, **64**, 975 (1931).

(26) T. D. Inch and H. G. Fletcher, Jr., *J. Org. Chem.*, **31**, 1821 (1966).

(27) Melting points are corrected. Thin layer chromatography was conducted on silica gel G (E. Merck A.-G., Darmstadt) using the solvent systems specified; development was made with iodine vapor, followed in some cases with a spray of 10% sulfuric acid. Column chromatography was carried out using silica gel (0.05–0.20 mm) of E. Merck A.-G. The nmr spectra were measured in $CDCl_3$ solution using a Varian A-60 spectrometer. Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrometer. Pyridine was dried by three successive distillations from P_2O_5.

(28) A. Baeyer, *Ann.*, **278**, 88 (1894).

(29) G. E. McCasland, R. K. Clark, Jr., and H. E. Carter, *J. Am. Chem. Soc.*, **71**, 637 (1949).

(30) Eastman Organic Chemicals, No. 6324.

tion and dried: 0.21 g, 79%. Either alone or in admixture with an authentic sample of VI it melted at 208–210°.

B. With Aniline.—A solution of V (0.2 g) in freshly distilled aniline (5 ml) was stored at 95 ± 5° for 4 hr. After cooling, the solution was diluted with dichloromethane and washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate solution, and water. Moisture was removed with magnesium sulfate and the solution was concentrated *in vacuo* to a residue in which (±)-*trans*-2-acetamidocyclohexyl benzoate[29] could not be detected by thin layer chromatography. The residue was chromatographed on a silica gel column, using benzene–ether (4:1) as eluent, and a crystalline product (0.1 g, 56%) obtained; alone or in admixture with authentic (±)-*trans*-2-benzamidocyclohexyl benzoate (VI), it melted at 210°.

(±)-*trans*-2-(*N*-acetylacetamido)cyclohexyl Acetate (VII). A. Acetylation with Acetic Anhydride.—A solution of IV (1.0 g) and anhydrous sodium acetate (1.5 g) in acetic anhydride (10 ml) was boiled under reflux for 4 hr, cooled, and poured into ice-cold aqueous sodium bicarbonate. The mixture was stirred for 1 hr and then was extracted with dichloromethane, the combined extracts then being washed with water, dried with magnesium sulfate, and concentrated *in vacuo*. After solution in benzene–ether (1:1), the amorphous residue was chromatographed on a column of silica gel (2.28 × 15 cm). Elution with the same mixture of solvents afforded 0.7 g of chromatographically homogeneous material which was distilled at 150° (bath temperature) and 0.1 mm. On standing overnight, the product crystallized; it was then sublimed twice *in vacuo* to give pure VII: 0.7 g (46%); mp 38–39°; infrared spectrum, ν_{max}^{Nujol} (cm^{-1}) 1708, 1748.

Anal. Calcd for $C_{12}H_{19}NO_4$ (241.29): C, 59.73; H, 7.94; N, 5.81. Found: C, 60.04; H, 7.97; N, 5.94.

Further elution of the column of silica gel with methanol gave (±)-*trans*-2-acetamidocyclohexyl acetate,[29] mp 118–120° (from benzene–ether).

B. Using Isopropenyl Acetate.—A solution of (±)-*trans*-2-acetamidocyclohexyl acetate[29] (0.90 g) in isopropenyl acetate (40 ml) containing *p*-toluenesulfonic acid monohydrate (5 mg) was boiled under reflux overnight, cooled, and concentrated *in vacuo*. The product was isolated in pure form by chromatography on a column of silica gel using benzene–ether (10:1): 1.01 g (93%). It was indistinguishable from that prepared by the use of sodium acetate and acetic anhydride.

***O*-Acetylations with Isopropenyl Acetate.**—A solution of methyl α-D-glucopyranoside (2.0 g) in isopropenyl acetate (20 ml) containing 1 drop of 10% *p*-toluenesulfonic acid in methanol was boiled under reflux for 1 hr after the methyl α-D-glucopyranoside had dissolved completely. The solution was cooled and concentrated *in vacuo*, the residue then being crystallized from benzene: 2.2 g (59%), mp 101–102°. A mixture melting point with authetic **methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside** was undepressed.

A solution of D-mannitol (2.5 g) in isopropenyl acetate containing a few drops of a 10% solution of *p*-toluenesulfonic acid in methanol was boiled under reflux for 1 hr after all of the D-mannitol had dissolved (*ca.* 8 hr in all). The solution was concentrated *in vacuo* and the **D-mannitol hexaacetate** crystallized from ethanol: 4.4 g (74%), mp 118–120°. A mixture melting point with authentic material was undepressed.

1,3,4,6-Tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-α-D-glucopyranose (IX). A. From 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (VIII).—A solution of VIII (1.0 g) in a mixture of benzoyl chloride (0.3 ml) and pyridine (3 ml) was stored ovenight at room temperature and then poured into ice–water. The pale yellow, amorphous precipitate which formed was removed by filtration, washed thoroughly with cold water, and dissolved in dichloromethane. The solution was dried with magnesium sulfate and concentrated *in vacuo* to a residue which was crystallized four times from ether to give pure 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-α-D-glucopyranose: 0.6 g (47%), mp 115–117°, $[\alpha]^{20}D$ +88° (*c* 0.88, $CHCl_3$).

Anal. Calcd for $C_{23}H_{27}NO_{11}$ (493.47); C, 55.98; H, 5.52; N, 2.84. Found: C, 56.10; H, 5.89; N, 2.78.

The nmr spectrum of the substance showed signals at τ 8.22 ($N-COCH_3$), 8.16, 8.12, 7.96, 7.88 (OAc) and a doublet with a spacing of 3 cps centered at 3.6 (H_1); infrared spectrum, ν_{max}^{Nujol} (cm^{-1}) 1760, 1750, 1720, 1660 (CO).

B. From 1,3,4,6-Tetra-*O*-acetyl-2-benzamido-2-deoxy-α-D-glucopyranose (X).—A solution of X[31] (0.34 g) in isopropenyl acetate (50 ml) containing *p*-toluenesulfonic acid monohydrate (5 mg) was boiled under reflux for 4 hr. Thin layer chromatography (benzene–ether–methanol, 14:14:1) showed that conversion of X to IX was essentially complete. The solution was concentrated *in vacuo* and the material purified by column chromatography using benzene–ether (9:1). Crystallized from ether, the product (0.18 g, 48%) had mp 112–115° and, when mixed with IX prepared as described in A above, mp 114–115°. The nmr spectra of IX from the two sources were indistinguishable.

Behavior of 1,3,4,6-Tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-α-D-glucopyranose (IX) with Sodium Methoxide.—Sodium methoxide in methanol (0.2 *M*, 2 ml) was added to a solution of IX (1 g) in methanol (50 ml). The reaction mixture was kept at room temperature for 2 hr, neutralized with carbon dioxide, and concentrated *in vacuo* to a residue which was extracted twice with warm ethanol. The combined ethanolic extracts were filtered and concentrated to a residue which was dissolved in 5 ml of pyridine. The solution was cooled to 0° and treated with a solution of 2 ml of acetic anhydride in 2 ml of pyridine. After storage overnight at room temperature, the mixture was poured into ice–water and the aqueous solution was extracted with dichloromethane. The extract was washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate solution, and water, dried with magnesium sulfate, and concentrated *in vacuo* to a pale yellow syrup. The syrup was dissolved in benzene–ether (1:1) and the solution was stored overnight at room temperature to yield 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (VIII) (0.1 g, mp 138–139°). The filtrate was concentrated and chromatographed on a column of silica gel using ether–methanol (20:1) as eluent. Early fractions contained a substance (0.02 g, 2%) of mp 230° with the chromatographic mobility of 1,3,4,6-tetra-*O*-acetyl-2-benzamido-2-deoxy-D-glucopyranose.[32] The β anomer of this structure has been reported to have mp 240°.[25,33] Later fractions contained further quantities of VIII, raising the total yield of this substance to 0.30 g (38%).

In another experiment, a few drops of methanolic sodium methoxide (0.2 *M*) were added to a solution of 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-α-D-glucopyranose (0.05 g) in methanol (3 ml) and the solution was stored at room temperature for 2 hr. The solution was neutralized with solid carbon dioxide, concentrated *in vacuo*, and the residue was trimethylsilylated according to the procedure of Sweeley, *et al.*[34] The mixture was analyzed by gas–liquid partition chromatography at 200° on a column (0.25 in. × 6 ft) of 3% SE 52 on Gaschrom A,[35] using an F & M Model 500 instrument with a flame ionization detector. Comparisons were made using silylated specimens of authentic 2-acetamido-2-deoxy-D-glucose, 2-benzamido-2-deoxy-D-glucose, and a 1:1 mixture of the two. From the relative magnitudes of the peak areas, the product from IX was found to contain 2-acetamido-2-deoxy-D-glucose and 2-benzamido-2-deoxy-D-glucose in the ratio of 6:1.

1,3,4,6-Tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-β-D-glucopyranose (XII) from 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (XI).—A solution of XI[36] (1.0 g) in a mixture of benzoyl chloride (0.3 ml) and pyridine (10 ml) was stored overnight at room temperature and then poured into ice water, the product being salted out with ammonium chloride. The amorphous white solid was filtered off and dissolved in dichloromethane. Moisture was removed from the solution with magnesium sulfate and the solution was concentrated *in vacuo* to a pale yellow oil which was purified by chromatography on a column of silica gel using ether–benzene (1:1) as eluent. The resulting, chromatographically pure product was dissolved in ether–heptane and the solution was stirred vigorously at room temperature in an open flask while crystallization progressed. The pure 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-β-D-glucopyranose (XII) thus obtained (0.5 g, 39%) had mp 118–119° and $[\alpha]^{20}D$ −22° (*c* 0.85, $CHCl_3$).

Anal. Calcd for $C_{23}H_{27}NO_{11}$ (493.47): C, 55.98; H, 5.52; N, 2.84. Found: C, 56.23; H, 5.76; N, 2.71.

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(31) F. Micheel, F.-P. van de Kamp, and H. Petersen, *Ber.*, **90**, 521 (1957). The material was slightly contaminated with the β anomer; *cf.* ref 26.

(32) The anomeric forms of this structure were not separable in the solvent system employed (benzene–ether–methanol, 14:14:1); *cf.* ref 26.

(33) F. Micheel and H. Köchling, *Ber.*, **91**, 673 (1958).

(34) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, **85**, 2497 (1963).

(35) Applied Science Laboratories, Inc., State College, Pa.

(36) J. K. N. Jones, M. B. Perry, B. Shelton, and D. J. Walton, *Can. J. Chem.*, **39**, 1005 (1961).

The nmr spectrum of the compound in deuteriochloroform showed signals at τ 8.08 (N–$COCH_3$), 7.94 (X2), 7.99 (X2) (OAc), and a doublet with a spacing of 8.5 cps centered at 3.4 (H_1). The addition of benzene to the deuteriochloroform solution caused the spectrum in the τ 8 region to be resolved into only two peaks; infrared spectrum, ν_{max}^{Nujol} (cm^{-1}), 1750, 1740, and 1705.

Behavior of 1,3,4,6-Tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-β-D-glucopyranose (XII). A. With Sodium Methoxide.—A sample of XII was treated with sodium methoxide in methanol and the ratio of products determined by gas–liquid partition chromatography as described for IX. The ratio of 2-acetamido-2-deoxy-D-glucose to 2-benzamido-2-deoxy-D-glucose thus found was 5:1.

B. With Aniline.—A solution of XII (0.4 g) in aniline (5 ml) was stored at 95 ± 5° for 6 hr. It was then cooled, diluted with dichloromethane, and washed successively with dilute hydrochloric acid (three times), aqueous sodium bicarbonate, and water. Moisture was removed with magnesium sulfate and the solution was concentrated to a black syrup which crystallized spontaneously upon the addition of methanol. Recrystallization from methanol gave a chromatographically homogeneous product: 0.15 g (38%), mp 230–231°, $[\alpha]^{20}D$ −11° (*c* 0.9, chloroform).

Anal. Calcd for $C_{25}H_{28}N_2O_8$ (484.52): C, 61.97; H, 5.82; N, 5.78. Found: C, 62.36; H, 5.73; N, 5.50.

Integration of the nmr spectrum of the substance showed the presence of 10 aromatic protons and 9 acetoxy protons [τ 7.92 (6H) and 7.94 (3H)]. The substance is probably an *N*-phenyl-3,4,6-tri-*O*-acetyl-2-benzamido-2-deoxy-D-glucopyranosylamine.

Benzyl 2-(*N*-Acetylbenzamido)-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (XVI).—A solution of benzyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (XIX)[16] (4.1 g) in a mixture of pyridine (10 ml) and benzoyl chloride (1.2 ml) was stored at room temperature overnight and then poured into ice water. The product was extracted with dichloromethane, the extract being washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and water. After being dried with magnesium sulfate, the solution was concentrated *in vacuo* and the residual syrup was chromatographed on silica gel using benzene–ether (20:3). Thus obtained, the benzyl 2-(*N*-acetylbenzamido)-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (4.3 g, 89%) was amorphous but essentially pure: $[\alpha]^{20}D$ −14.3° (*c* 4.13, $CHCl_3$); nmr, τ 7.88 (N–$COCH_3$); infrared spectrum, ν_{max}^{Nujol} (cm^{-1}), 1695 and 1665.

Anal. Calcd for $C_{43}H_{43}NO_7$ (685.82): C, 75.31; H, 6.32; N, 2.04. Found: C, 75.61; H, 6.01; N, 2.16.

2-(*N*-Acetylbenzamido)-2-deoxy-D-glucopyranose (XIII).—Palladium chloride (*ca.* 0.1 g) was suspended in methanol and reduced with hydrogen, the precipitated palladium black being washed repeatedly by decantation with methanol until free of acid. To the catalyst thus prepared was added a solution of benzyl 2-(*N*-acetylbenzamido)-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (1.3 g) in ethanol (100 ml) and the suspension was then stirred with hydrogen until the theoretical volume of the gas (170 ml) had been absorbed. After filtration, the solution was concentrated *in vacuo* to a colorless syrup (0.6 g, 97%).

The infrared absorption spectrum of the substance, ν_{max}^{neat} (cm^{-1}), showed bands at 1667 and 1616, characteristic of many diacylamine derivatives; a very small band at 1520 (NH) was also observed.

1,3,4,6-Tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-β-D-glucopyranose (XII) from 2-(*N*-Acetylbenzamido)-2-deoxy-D-glucopyranose (XIII).—A portion (0.60 g) of the syrupy XIII, prepared as described above, was dissolved in pyridine (10 ml) and the solution was cooled to 0°. Acetic anhydride (1.5 ml) was added, the solution was stored at room temperature for 44 hr and then poured into ice–water. The product was extracted with dichloromethane, the extract being washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate solution, and water. After drying, the solution was concentrated *in vacuo* and the residual syrup was chromatographed on silica gel using ether–benzene (3:2). A fraction of essentially pure 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylbenzamido)-2-deoxy-β-D-glucopyranose (XII) was obtained and crystallized from heptane–ether: 0.45 g (49%), mp 118–119°, $[\alpha]^{20}D$ −21° (*c* 1.16, chloroform). A mixture melting point with XII, obtained as described earlier through the benzoylation of XI, was undepressed.

Benzyl 2-(*N*-Acetylacetamido)-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (XVIII).—A solution of benzyl 2-acetamido-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (XIX, 2.0 g) in isopropenyl acetate (50 ml) containing *p*-toluenesulfonic acid monohydrate (10 mg) was boiled under reflux for 15 hr. The solution was concentrated and the syrup thus obtained was chromatographed on a column of silica gel using benzene–ether (20:3) as eluent. The early fractions contained essentially pure XVIII, a syrup: 1.6 g (75%); $[\alpha]^{20}D$ +0.5° (*c* 2.35, $CHCl_3$); nmr data, τ 7.79, 7.63 (NAc_2), and 4.77 (H_1, $J_{1,2}$ = 8 cps); infrared spectrum, ν_{max}^{neat} (cm^{-1}) 1710.

Anal. Calcd for $C_{38}H_{41}NO_7$ (623.76): C, 73.17; H, 6.63; N, 2.25. Found: C, 73.45; H, 6.42; N, 2.10.

1,3,4,6-Tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-β-D-glucopyranose (XV). A. From Benzyl 2-(*N*-Acetylacetamido)-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (XVIII).—A solution of XVIII (1.0 g) in ethanol was shaken with hydrogen and palladium black prepared through the reduction of 0.1 g of palladium chloride. After absorption of the hydrogen had ceased (*ca.* 0.5 hr) the solution was filtered and concentrated *in vacuo* at 40° (bath temperature). The infrared spectrum of the resulting syrup (ν_{max}^{neat}) showed only a slight band at 1520 cm^{-1} (NH), indicating that loss of the *N*-acetyl group had been slight. The syrup was immediately treated with acetic anhydride (2 ml) and pyridine (20 ml) and the resulting solution was stored at room temperature for 6 hr. It was then concentrated *in vacuo* and the residual pyridine was removed by codistillation with toluene. Thin layer chromatography of the resulting syrup, using benzene–methanol–ether (14:14:1), revealed the presence of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-glucopyranose as a contaminant of a major, faster moving component. This latter component was isolated by chromatography on a column of silica gel, using benzene–ether (1:1): 0.4 g (58%), $[\alpha]^{20}D$ +9° (*c* 1.03, $CHCl_3$). On standing, the material crystallized; recrystallized from ether–heptane, it had mp 84–85°; infrared data, ν_{max}^{Nujol} (cm^{-1}) 1770, 1755, and 1720; nmr data, τ 7.63 (NAc_2), 7.90 (2H), 7.97, 7.98 (OAc), and 3.45 (H_1, $J_{1,2}$ = 8 cps).

Anal. Calcd for $C_{18}H_{25}NO_{11}$ (431.41): C, 50.11; H, 5.84; N, 3.25. Found: C, 50.06; H, 5.43; N, 3.31.

B. From 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (XI).—A solution of XI (1.3 g) and *p*-toluenesulfonic acid monohydrate (5 mg) in isopropenyl acetate (50 ml) was boiled under reflux for 15 hr. It was then concentrated *in vacuo* and the residue was chromatographed on silica gel using benzene–ether (1:1). The pure product thus obtained (0.8 g, 56%) rotated $[\alpha]^{20}D$ +3.2° (*c* 1.9, $CHCl_3$); its chromatographic properties, infrared absorption spectrum, and nmr spectrum were indistinguishable from those of XV prepared from XVIII. On crystallization from ether–heptane the product had mp 83–84°.

1,3,4,6-Tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-α-D-glucopyranose (XVII).—A solution of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose[36] (VIII, 1.0 g) and *p*-toluenesulfonic acid monohydrate (5 mg) in isopropenyl acetate (50 ml) was boiled under reflux for 20 hr and then concentrated *in vacuo* to a syrup which was chromatographed on a column of silica gel using ether as a solvent. The first component (0.10 g, 9%) showed the chromatographic behavior and infrared absorption spectrum of XV. The second component was crystallized from ether: 0.25 g (23%), mp 111–112°, $[\alpha]^{20}D$ +96° (*c* 0.89, $CHCl_3$). Further washing of the column gave unchanged VIII: 0.5 g, mp 132–133°; infrared spectrum, ν_{max}^{Nujol} (cm^{-1}), 1750, 1740, and 1675; nmr data, τ 7.67 (NAc_2), 7.87, 7.90, 7.97, 8.04 (OAc), and 3.75 (H_1, $J_{1,2}$ = 3.5 cps).

Anal. Calcd for $C_{18}H_{25}NO_{11}$ (431.41): C, 50.11; H, 5.84; N, 3.25. Found: C, 50.40; H, 5.55; N, 3.31.

Acetylation of 2-Acetamido-2-deoxy-D-glucopyranose (XIV) with Isopropenyl Acetate.—A solution of XIV (1.0 g) and *p*-toluenesulfonic acid (5 mg) in isopropenyl acetate (50 ml) was boiled under reflux for 20 hr. Solvent was removed *in vacuo* and the residue was chromatographed on a column of silica gel using ether as the eluent. XV was eluted first: 0.6 g, 31%, mp 83–84° (from ether–pentane). XVII then emerged: 0.1 g, 5%, mp 108–109° (from ether). A third component was eluted from the column with methanol and crystallized from ether; it proved to be VIII (0.6 g).

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