The Behavior of 2-Acetamido-2-deoxy-D-mannose with Isopropenyl Acetate in the Presence of *p*-Toluenesulfonic Acid. II. Evidence Bearing on the Mechanism of the Formation of 3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose and of 2-(D-*glycero*-1,2-Diacetoxyethyl)-4-(*N*-acetylacetamido)furan

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Evidence which is described suggests that the conversion of 2-acetamido-2-deoxy-D-mannose (**1**) into the 2-amino-D-glucal derivative, 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (**2**), by the action of isopropenyl acetate and *p*-toluenesulfonic acid goes through the following series of steps: **1** → 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-mannopyranose (**5**) → 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-α-D-mannopyranose (**9**) → **2**. A mechanism for the conversion of **9** to **2** is proposed; that 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-β-D-glucopyranose does not undergo an analogous elimination to give **2** under the reaction conditions employed emphasizes the fact that a *trans* diaxial arrangement of the groups at C-1 and C-2 is probably a prerequisite of the reaction. It is suggested that 2-(D-*glycero*-1,2-diacetoxyethyl)-4-(*N*-acetylacetamido)furan (**3**) is probably formed from **1** by an analogous mechanism involving 1,3,5,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-α-D-mannofuranose (**15**).

In the preceding paper[2] we have shown that the acetylation of 2-acetamido-2-deoxy-D-mannose (**1**) with isopropenyl acetate in the presence of a trace of *p*-toluenesulfonic acid gives at least five products; among these are two of particular interest: 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (**2**), a derivative of the unknown D-glucosamine-related glycal, and 2-(D-*glycero*-1,2-diacetoxyethyl)-4-(*N*-acetylacetamido)furan (**3**). The behavior of 2-acetamido-2-deoxy-D-mannose (**1**) in this respect contrasts sharply with that of its epimer 2-acetamido-2-deoxy-D-glucose which, with this reagent, affords only the two anomeric 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-D-glucopyranoses.[3] The present investigation was undertaken in order to provide a mechanistic basis for rationalizing this diverse behavior of these two closely related 2-acetamido-2-deoxy-D-hexoses.

The conversion of 2-acetamido-2-deoxy-D-mannose (**1**) into the glycal derivative **2** is certainly a multistep reaction since acetylation as well as elimination takes place. In order to throw some light on the sequence of these two steps, the behavior of the two anomeric 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-mannopyranoses (**4** and **5**) with isopropenyl acetate was examined. Of these two derivatives, only the β anomer (**4**) is known in pure crystalline form.[4] With boiling isopropenyl acetate in the presence of *p*-toluenesulfonic acid for 5 days, **4** gave **2** in 7% yield, the major part (67%) of **4** being recovered unchanged. None of its α anomer (**5**) was detected nor was any evidence for the formation of the furan derivative **3** or of a di-*N*-acetyl derivative (other than **2**) found. In order to obtain a sample of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-mannopyranose (**5**), the mixture of products from the pyridine–acetic anhydride acetylation of **1** was largely freed of the β anomer (**4**) by crystallization. Treatment of the material remaining in the mother liquor, which was rich in the α anomer (**5**), with isopropenyl acetate for 24 hr led to the isolation of **4** in 18% yield, **2** in 46% yield, and **3** in 1% yield.

Since the direct treatment of 2-acetamido-2-deoxy-D-mannose (**1**) with isopropenyl acetate affords **2** in 14% yield and **3** in 13% yield,[2] we may conclude that the elimination is preceded by *O*-acetylation. None of **5** was detected after the acetylation of **4** and the **4** which was recovered subsequent to the acetylation of crude **5** may well have been present in the mixture from the outset; it is evident, therefore, that the anomeric integrity of **4** and **5** is largely (if not wholly) retained under the conditions of the reaction. In any case, the fact that the yield of **2** is much higher from the α anomer (**5**) than from the β anomer (**4**) or from 2-acetamido-2-deoxy-D-mannose (**1**) suggests that **5** is a precursor of **2**. Before pursuing this point further, however, we will discuss the question of the introduction of the second *N*-acetyl group since both **2** and **3** have two *N*-acetyl groups.

No di-*N*-acetyl derivatives related to **4** and **5** have ever been detected in the course of our studies. If isopropenyl acetate can *N*-acetylate these substances, the products either undergo further reactions or lose one *N*-acetyl group in the course of silica gel chromatography; the latter possibility appears remote in view of the fact that the two anomeric 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-D-glucopyranoses may be isolated by chromatography on silica gel.[3] In the preceding paper[2] we described the preparation of ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-α-D-mannopyranoside (**6**); this thioglycoside derivative has now been subjected to the action of isopropenyl acetate. While 48% of the material was recovered unchanged, the glycal derivative **2** was isolated in 5% yield and, more significantly, the di-*N*-acetyl derivative (**7**) of the thioglycoside (4%). This latter substance proved to be unstable; in solution in deuteriochloroform (which had been used to measure its nmr spectrum) it decomposed at room temperature over the course of 3 weeks, giving the glycal derivative **2**. In addition, **6** and **8** were detected; these may be regarded as the normal products to be expected from the spontaneous de-*N*-acetylation of **7** and **2**, respectively. (See Chart I.) The formation of **2** from the di-*N*-acetylthioglyco-

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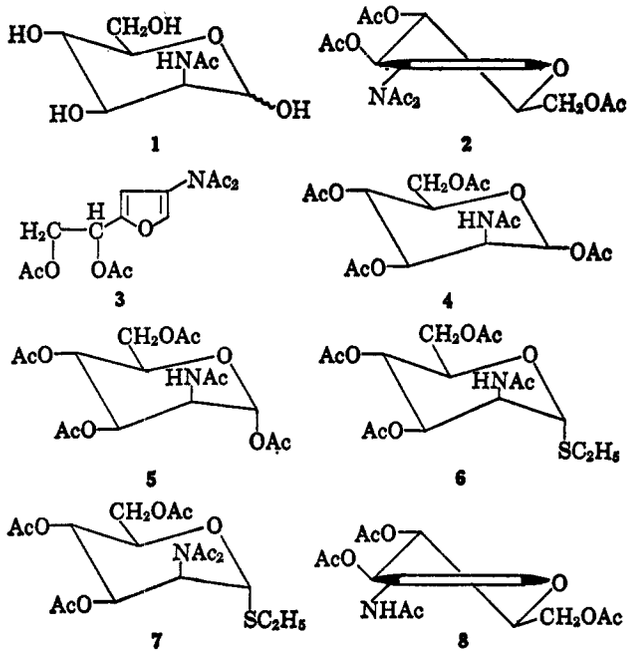
(2) N. Pravdić and H. G. Fletcher, Jr., *J. Org. Chem.*, **32**, 1806 (1967).

(3) T. D. Inch and H. G. Fletcher, Jr., *ibid.*, **30**, 1815 (1965).

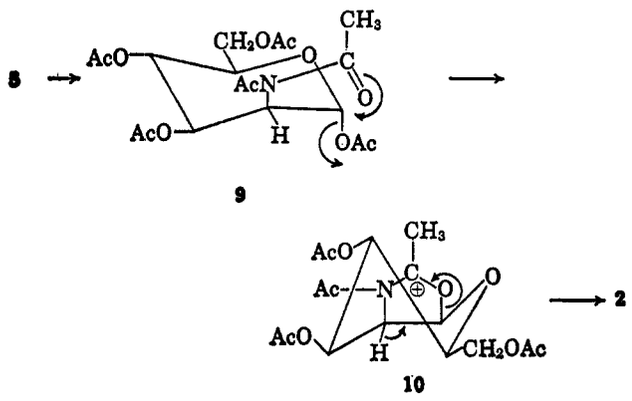
(4) A. N. O'Neill, *Can. J. Chem.*, **37**, 1747 (1959).

CHART I



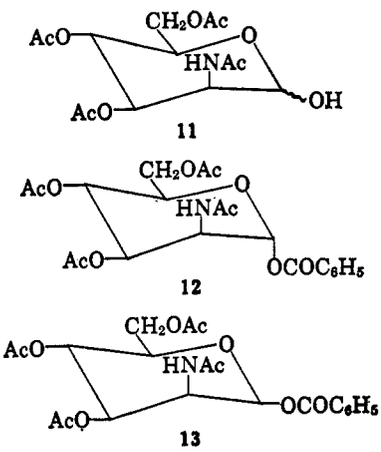
side **7** shows that the elimination step may follow *N*-acetylation. Evidence to support this contention was obtained by tlc monitoring of the reaction of **6** with isopropenyl acetate; the presence of the di-*N*-acetyl derivative **7** was clearly evident before **2** could be detected. It seems reasonable, therefore, to assume that a second *N*-acetyl group is introduced into **5** prior to its conversion into **2**.

In view of the above facts, the following mechanism for the conversion of **5** to the glycal derivative **2** is proposed.



One of the *N*-acetyl groups of the di-*N*-acetyl derivative **9** initially attacks C-1. The acetoxy group at C-1 might be protonated to give acetic acid or react with either an acetylium ion or a protonated form of isopropenyl acetate to give acetic anhydride. If such a loss is postulated, one can envisage the cyclic intermediate **10** as forming and then ejecting the proton at C-2 to give **2**. Actually, there is no necessity of invoking **10** as a discrete intermediate; **2** may be formed directly from **9** through a series of electron shifts in which the C-2 proton is donated directly to the C-1 acetoxy group. Indeed, a mechanism analogous to this appears attractive for the conversion of **7** into **2** where the elimination takes place in the absence of both *p*-toluenesulfonic acid and of isopropenyl acetate.[5] However, regardless of the fine details of the mechanism, its essential feature involves a *trans* diaxial arrangement of the *N*-acetylacetamido group at C-2 with respect to the substituent at C-1; on thermodynamic grounds it is not surprising that 1,3,4,6-tetra-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-β-D-glucopyranose does not give **2** under the reaction conditions which we have employed.

The mechanism proposed suggests that the initial presence at C-1 of a leaving group better than acetoxy should facilitate the reaction. To investigate this point and, in part, to confirm our previous observations with regard to the stereochemical requirements of the reaction, we have synthesized the two anomeric forms of 2-acetamido-3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy-D-mannopyranose (**12** and **13**) from the known 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-mannopyranose (**11**).[6] While neither **12** or **13** could be made from **11** in



anomerically pure form, condensation of **11** with benzoic acid in the presence of *N*,*N*′-dicyclohexylcarbodiimide afforded a mixture of **12** and **13** in which the β anomer (**13**) predominated in a ratio of *ca.* 3:2 as shown by its nmr spectrum. Treatment of this mixture with isopropenyl acetate led to the isolation of **2** in 41% yield. Not only is this almost exactly the yield to be expected had only the α anomer (**12**) reacted, but the β anomer, unchanged and in apparently pure anomeric form, was recovered. When **11** was benzoylated with benzoyl chloride in pyridine solution, a mixture of **12** and **13** was again obtained but, with these reagents, the α anomer (**12**) predominated in a ratio of *ca.* 3:1. With isopropenyl acetate this mixture afforded **2** in 76% yield.

It thus seems that the formation of **2** is facilitated by the initial presence of an effective leaving group at C-1 and that the stereochemical requirements of the reaction are as evident when a benzoyl group is at C-1 as when an acetyl group is at this position.

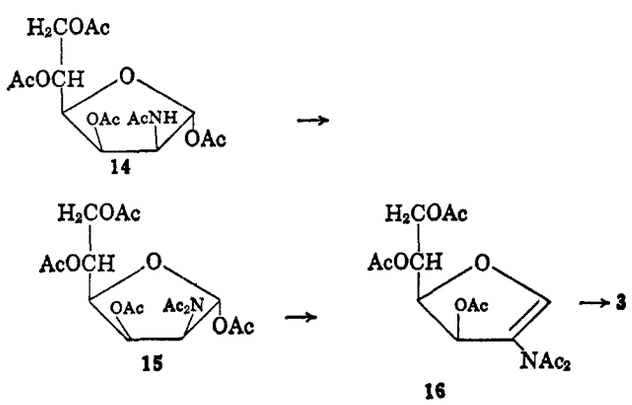
The failure to isolate or detect **9** (or the 1-*O*-benzoyl analog of it from **12**) may be explained on the assump-

(5) However, since *N*-deacetylation also took place, both water and acetic acid must have been present. The tetramethylsilane which was present is assumed to have been inert.

(6) N. Pravdić, T. D. Inch, and H. G. Fletcher, Jr., *J. Org. Chem.*, **32**, 1815 (1967). These authors prepared **11** through the action of anhydrous zinc chloride and acetic anhydride on 2-acetamido-2-deoxy-D-mannose (**1**). In the course of unsuccessful attempts to prepare 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-mannopyranosyl chloride by a method which D. Horton and M. L. Wolfrom [*ibid.*, **27**, 1794 (1962)] used for its D-glucopyranose analog, we have found an improved method for the preparation of **11**; see the Experimental Section.

tion that the elimination step is significantly faster than *N*-acetylation. Only steric effects can be invoked to rationalize the failure of the corresponding β derivatives (**4** and **13**) to form di-*N*-acetyl compounds. That **7** proved to be isolable is probably due to the fact that the ethylthio group is a poorer leaving group than the acetoxy and the benzoyloxy groups and thus the rate of elimination of ethanethiol from **7** is less than the rate of elimination of acetic acid from **9** or of benzoic acid from the *N*-acetyl derivative of **12**.

Attention is now turned to the problem of the mechanism of the formation of 2-(D-*glycero*-1,2-diacetoxyethyl)-4-(*N*-acetylacetamido)furan (**3**) from 2-acetamido-2-deoxy-D-mannose (**1**). As has been noted, this substance was not detected when pure 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-mannopyranose (**4**) was treated with isopropenyl acetate but was isolated when the crude anomer (**5**) of this substance was employed. In this crude product were all of the by-products from the acetic anhydride–pyridine acetylation of **1**. It is, therefore, suggested that the furan derivative **3** arises from 2-acetamido-1,3,5,6-tetra-*O*-acetyl-2-deoxy-α-D-mannofuranose (**14**) and that the first two steps in the reaction (to give **15** and **16**) are mechanistically analogous to those postulated for the conversion of **5** into **2**. The final step, conversion of



16 into **3**, may be viewed as a simple *trans* elimination to give a conjugated system—a transformation which should be extremely facile.

Experimental Section[7]

Reaction of 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-mannopyranose (4) with Isopropenyl Acetate.—2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-mannopyranose[4] (**4**, 3.0 g) was dissolved in isopropenyl acetate (50 ml) containing *p*-toluenesulfonic acid monohydrate (*ca.* 25 mg) and the solution was boiled under reflux for 5 days. The solvent was removed *in vacuo* and the dark residue dissolved in ether (10 ml); on standing at room temperature the solution deposited 2.0 g (67%) of unreacted **4**, identified by its infrared spectrum, melting point and mixture melting point with authentic **4**. The combined ethereal mother liquor and washings were passed through a column of silica gel (30 ml), ether being used for elution. A chromatographically pure product was obtained and crystallized from ether (200 mg, 7%), mp 94–96°; its infrared spectrum and chromatographic behavior were idential with those of a specimen of **3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (2)** prepared earlier.[2]

Reaction of Crude 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-mannopyranose (5) with Isopropenyl Acetate.—2-Acetamido-2-deoxy-D-mannose monohydrate[8] (**1**) was acetylated with acetic anhydride and pyridine in conventional fashion and the main product (**4**) was crystallized from ethanol–pentane. Concentraon of the mother liquor afforded a syrup in which 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-mannopyranose (**5**) predominated as shown by nmr.[9] A sample of this syrup [2.0 g, $[\alpha]^{22}D$ +29° (*c* 1.43, $CHCl_3$)] was dissolved in isopropenyl acetate (50 ml) containing *p*-toluenesulfonic acid monohydrate (*ca.* 15 mg) and the solution was boiled under reflux for 24 hr. The solvent was removed *in vacuo* and the residue treated with ether (10 ml) to give 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-mannopyranose (**4**): 350 mg (18%); $[\alpha]^{21}D$ −16.1° (*c* 1.12, $CHCl_3$). The material remaining in the solution was chromatographed on a column of silica gel (250 ml) using ether for elution. Fractions 26–29 contained **2-(D-*glycero*-1,2-diacetoxyethyl)-4-(*N*-acetylacetamido)furan (3**, 20 mg, 1%), identified by comparison (tlc) with a specimen prepared earlier.[2] Fractions 31–39 contained **3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (2**, 870 mg, 46%), mp 95–96°.

Reaction of Ethyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-α-D-mannopyranoside (6) with Isopropenyl Acetate.—Ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-α-D-mannopyranoside[2] (**6**, 1.16 g) was dissolved in isopropenyl acetate (30 ml) containing *p*-toluenesulfonic acid monohydrate (*ca.* 10 mg) and the solution was boiled under reflux for 22 hr. Examination of the reaction mixture (tlc, ether and ether–methanol, 9:1, v/v) showed already after 5 min the presence of a fast-moving product which gave a yellow spot when sprayed with dilute sulfuric acid and heated; after 4 hr another component, giving a grey spot and migrating at very nearly the same rate as the first, was detected. The reaction mixture was concentrated *in vacuo* and the residue was chromatographed on a column of silica gel (130 ml) using ether as eluent. Fraction 13 contained **ethyl 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-1-thio-α-D-mannopyranoside (7**, 55 mg, 4%) which was obtained as a syrup: $[\alpha]^{24}D$ +24° (*c* 0.4, $CHCl_3$); nmr peaks at τ 7.40 (quartet, J = 7.5 cps, SCH_2), 7.64 (NAc), 7.90 and 7.97 (OAc), and 8.75 (triplet, J = 7.5 cps, CH_3). On tlc this compound gave a yellow spot when sprayed with dilute sulfuric acid and heated.

Anal. Calcd for $C_{18}H_{27}NO_9S$ (433.49): C, 49.87; H, 6.28; S, 7.40. Found: C, 50.07; H, 6.37; S, 7.59.

Fractions 14–16 contained a mixture of the two components (230 mg). Fractions 17–19 yielded the second component (55 mg, 5%); its chromatographic behavior and infrared absorption spectrum identified it as **2**. On tlc it gave a grey spot when sprayed with dilute sulfuric acid and heated.

The eluent was changed to ether–methanol (9:1, v/v). Fractions 36–40 were found to contain unreacted **6**: 560 mg (48%); $[\alpha]^{21}D$ +84.0° (*c* 1.0, $CHCl_3$).

Behavior of Ethyl 3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-2-deoxy-1-thio-α-D-mannopyranoside (7) on Storage in Deuteriochloroform Solution.—The solution of **7** in $CDCl_3$ which had been used to determine the nmr spectrum was stored at room temperature for 3 weeks and then examined by tlc using ether, ether–methanol (9:1, v/v), and ether–acetone (5:1, v/v). Cochromatography with authentic materials showed that the major product of the decomposition of **7** was **6**; in addition **2** and its *N*-deacetylated derivative (**8**)[2] were detected.

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-mannopyranose (11).—A mixture of powdered 2-acetamido-2-deoxy-D-mannose mohohydrate[8] (7.0 g) and acetyl chloride (15 ml) was stirred at 0° for 1 hr and then at room temperature for 45 min. The thick, colorless liquid was poured into ice–water and the suspension was neutralized with sodium bicarbonate. The crude product was extracted with dichloromethane and the combined extracts, dried with sodium sulfate, were concentrated *in vacuo* to give a crude product as a colorless foam (9.0 g). Tlc showed this to be heterogeneous, several close-moving components being detected. The syrup was chromatographed on a column of silica gel (750 ml) using ether–methanol (19:1, v/v) as an eluent.

(7) Melting points are corrected. Thin layer chromatography was conduced on silica gel G (E. Merck A.G., Darmstadt) using the solvent systems specified, components being detected by spraying with 10% sulfuric acid and heating at 100°. Column chromatography was carried out with silica gel (0.05–0.20 mm) of E. Merck A.G., 15-ml fractions being collected. Nmr spectra were obtained in $CDCl_3$ solution using a Varian A-60 spectrometer and tetramethylsilane as an internal standard. Infrared spectra were recorded for Nujol mulls (or neat in the case of amorphous materials) using Perkin-Elmer Model 137 and 221 spectrometers.

(8) Pfanstiehl Laboratories, Inc., Waukegan, Ill.

(9) T. D. Inch, J. R. Plimmer, and H. G. Fletcher, Jr., *J. Org. Chem.*, **31**, 1825 (1966).

Fractions 87–103 contained the desired product which was obtained in crystalline form on concentration (2.5 g, 25%). The material was recrystallized from ethanol–hexane: mp 142–148°, $[\alpha]^{20}D$ +33.6° (*c* 0.8, $CHCl_3$). Its infrared spectrum and chromatographic behavior in several solvent systems were indistinguishable from those of a sample of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-mannopyranose (**11**) prepared as described earlier.[6] A mixture melting point was undepressed.

Fractions prior to 87 and subsequent to 103 contained further quantities of **11** but were not homogeneous; they were combined and rechromatographed on silica gel using ether–acetone (5:1, v/v). In this fashion the total yield of pure **11** was increased to 35%.

2-Acetamido-3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy-D-mannopyranoses (12 and 13) from 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-mannopyranose (11). A. Using *N,N'*-Dicyclohexylcarbodiimide.—A procedure modeled after one developed for the synthesis of various methyl 2,3,4-tri-*O*-acetyl-1-*O*-acyl-D-glucopyranuronates[10] was employed. To a solution of benzoic acid (490 mg) in dichloromethane (10 ml), containing dry pyridine (2 drops), *N,N'*-dicyclohexylcarbodiimide (410 mg) was added; the mixture was left, with occasional shaking, at room temperature for 4 hr. Precipitated *N,N'*-dicyclohexylurea (83%) was removed by filtration and to the filtrate was added a second portion of *N,N'*-dicyclohexylcarbodiimide (410 mg) and then 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-mannopyranose (**11**, 600 mg). After standing at room temperature overnight, the reaction mixture was freed of a second crop of *N,N'*-dicyclohexylurea and then concentrated *in vacuo* to a syrup which, upon treatment with ether (10–15 ml), gave *N*-benzoyl-*N,N'*-dicyclohexylurea (300 mg, mp 165–167°[10]). The filtrate was concentrated *in vacuo* to give a syrup which was chromatographed on a column of silica gel (100 ml) using ether–acetone (5:1, v/v) as eluent. The product (600 mg, 77%) was obtained in the form of a fine powder: mp 75–78°; $[\alpha]^{20}D$ +14.3° (*c* 1.26, $CHCl_3$); infrared absorption (Nujol) at 3400 (NH), 1740 (OAc), 1670 (NAc), 1600 (aromatic), and 1550 cm^{-1} (amide II); nmr peaks at τ 3.68 (doublet, J = 2.0 cps, H_1, α anomer) and 3.82 (doublet, J = 1.8 cps, H_1, β anomer). The relative intensities of the two doublets suggested that the ratio of **12** to **13** was 2:3.

Anal. Calcd for $C_{21}H_{25}NO_{10}$ (451.44): C, 55.87; H, 5.58; N, 3.10. Found: C, 55.65; H, 5.73; N, 3.20.

B. Using Benzoyl Chloride.—2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-mannopyranose (**11**, 0.9 g) was dissolved in dry pyridine (2 ml) and the solution, cooled in ice, was treated with benzoyl chloride (0.3 ml, 1 mole equiv). After standing at room temperature for 2 hr, the reaction mixture was poured into ice–water and the product was extracted with dichloromethane. The extract was washed successively with 1 *N* sulfuric acid, aqueous sodium bicarbonate, and water. Moisture was removed with sodium sulfate and the solution was concentrated to give a syrup (820 mg) which was chromatographed on a column of silica gel (120 ml) using ether–acetone (5:1, v/v). The product (700 mg, 60%) was obtained in the form of a fine powder: mp 76–80°, $[\alpha]^{20}D$ +55.0° (*c* 1.35, $CHCl_3$). The chromatographic behavior and infrared spectrum of the product were identical with those of the product from A. The nmr spectrum of the material showed the predominance of the α anomer (**12**), the ratio of **12** to **13** being at least 3:1.

Reaction of 2-Acetamido-3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy-D-mannopyranose (12 and 13) with Isopropenyl Acetate. A. The Mixture Richer in 13.—A solution of 2-acetamido-3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy-D-mannopyranose (**12** and **13**, 1.0 g, $[\alpha]^{20}D$ +14.3°) in isopropenyl acetate (30 ml) containing *p*-toluenesulfonic acid monohydrate (*ca.* 15 mg) was boiled under reflux for 24 hr. The reaction mixture was concentrated *in vacuo* and the residue was chromatographed on a column of silica gel (120 ml) using ether as eluent.

Fractions 14–17 contained **3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose** (**2**) (340 mg, 41%): mp 94–96°; the infrared absorption spectrum was identical with that of an authentic sample of **2**.

The eluent was changed to ether–acetone (5:1, v/v). Fractions 37–44 were concentrated to give **2-acetamido-3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy-β-D-mannopyranose** (**13**, 450 mg, 45%) as a fine powder: mp 85–90°; $[\alpha]^{22}D$ −42.3° (*c* 1.05, $CHCl_3$); nmr peak at τ 3.82 (doublet, J = 1.8, H_1, β anomer), no signal at 3.68. Since the H_1 signal for the α anomer was absent, the compound may be regarded as essentially pure **13**.

Anal. Calcd for $C_{21}H_{25}NO_{10}$ (451.44): C, 55.87; H, 5.58; N, 3.10. Found: C, 55.59; H, 5.61; N, 3.22.

B. The Mixture Richer in 12.—The procedure described in A was repeated using a sample of **12** + **13** (370 mg, $[\alpha]^{20}D$ +55.0°) which had been made through the benzoylation of **11** with benzoyl chloride in pyridine. **3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose** (**2**) was isolated (230 mg 76%), mp 91–94°.

Registry No.—**1**, 6730-06-9; isopropenyl acetate, 108-22-5; *p*-toluenesulfonic acid, 104-15-4; **2**, 10293-54-6; **3**, 10293-53-5; **4**, 6730-10-5; **5**, 4539-83-7; **6**, 10277-32-4; **7**, 10294-11-8; **11**, 10294-12-9; **12**, 10277-39-1; **13**, 10294-13-0.

Acknowledgment.—We are indebted to Dr. Louis A. Cohen of this laboratory for stimulating discussions of mechanistic problems and to the staff of the Section on Microanalytical Services and Instrumentation of this institute for spectra and elementary analyses.

(10) N. Pravdić and D. Keglević, *J. Chem. Soc.*, 4633 (1964).