Dioxolanylium Ions Derived from Carbohydrates. XI. Aminosugar Formation by *trans* Opening with the Trichloroacetimidoyl Neighbouring Group

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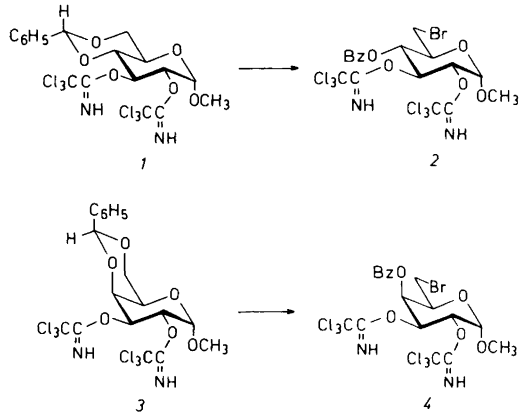
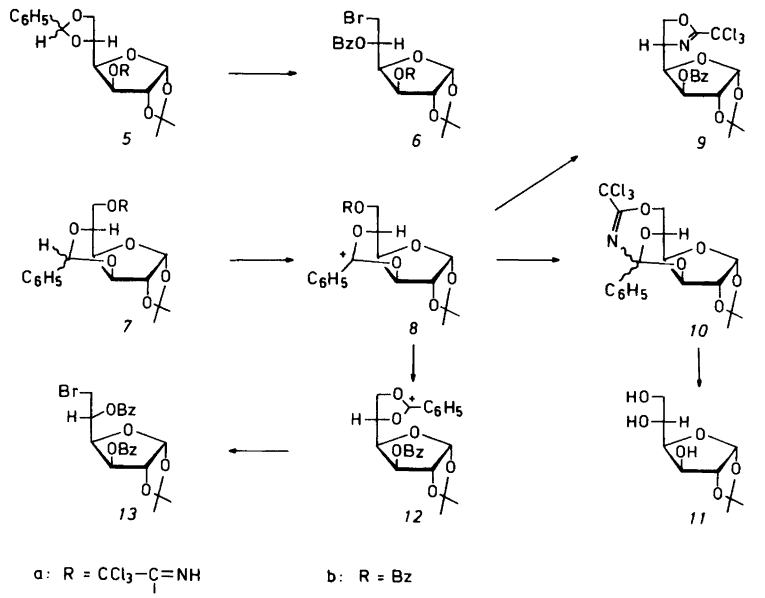
A variety of benzylidene sugars containing vicinal trichloroacetimidoyl groups have been oxidized by *N*-bromosuccinimide, to ascertain which structural features are necessary for neighbouring group participation from the iminoester in the opening of the transitory benzoxonium ion. The results indicate that the trichloroacetimidoyl group closely resembles the acyl group in its ability to participate, and that the resulting iminoester is strongly favoured compared to the benzoxonium ion. The outcome of the reaction in these cases is therefore a clean, regiospecific introduction of an amino group into the carbohydrate molecule.

In the preceding paper,[1] it was shown that a benzoxonium ion having a trichloroacetimidoyl neighbouring group could rearrange to a derivative of an amino-deoxy sugar. In the present paper, further examples of this reaction are described, and the behaviour of various types of benzylidene compounds containing iminoester neighbouring groups towards *N*-bromosuccinimide (NBS) has been investigated.

A preliminary search to establish which types of benzylidene compounds would undergo rearrangement to oxazolines when oxidized with NBS was carried out by treating a benzylidene sugar containing a free hydroxy group with sodium hydride and trichloroacetonitrile to form the iminoester. The crude iminoester was directly oxidized with NBS and the product examined by ^{1}H and ^{13}C NMR spectroscopy. The emergence of new absorptions below 40 ppm in the ^{13}C NMR spectrum was taken as an indication of the formation of bromo-deoxy derivatives, i.e., of failure to undergo rearrangement to an oxazoline, the outcome of the reaction instead being substitution by the bromide ion present, the Hanessian-Hullar reaction (Ref. 2). Using this method, it was found that methyl 4,6-*O*-benzylidene-2,3-di-*O*-trichloroacetimidoyl-α-D-gluco- and galactopyranosides (*1* and *3*) gave 6-bromo-deoxy-4-benzoates (*2* and *4*) on reaction with NBS, in agreement with the behaviour previously found for 4,6-dioxanylium ions with a neighbouring benzoyloxy group at C-3.[3] In these compounds, no rearrangement took place when the neighbouring group was in a *cis* or *trans* equatorial position.

Reaction between 5,6-*O*-benzylidene-1,2-*O*-isopropylidene-3-*O*-trichloroacetimidoyl-α-D-glucofuranose (*5a*) and NBS proceeded to give a





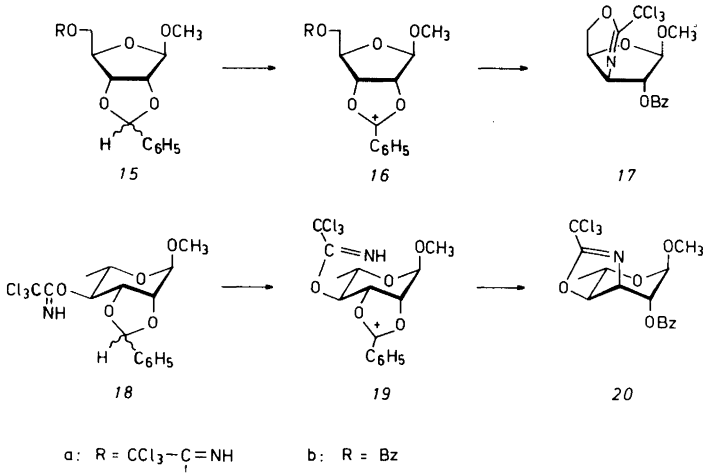
6-bromo-6-deoxy compound (*6a*). In this case also, the analogy to the 3-*O*-benzoate *5b* was obvious, since the derived 5,6-benzoxonium ion underwent substitution at C-6 on reaction with bromide ion to give *6b* and no products resulting from rearrangement to the 3,5-benzoxonium ion.[4] The "complementary" system was encountered in 3,5-*O*-benzylidene-1,2-*O*-isopropylidene-6-*O*-trichloroacetimidoyl-α-D-glucofuranose (*7a*), which oxidized smoothly with NBS, to give a compound assigned the structure *10* on the basis of the following observations. Elementary analysis, IR and NMR spectra excluded the possibility that the product was a result of either simple hydrolysis or bromide ion substitution of the benzoxonium ion *8a,* and, since the NH absorptions from the free trichloroacetimidoyl group had disappeared in both the IR and the NMR spectrum, a reaction involving the imidate had clearly taken place. This left two possibilities, *9* and *10,* for the structure of the product, both compatible with the ^1H and ^{13}C NMR spectra. Of these possibilities, *10* was preferred on the basis of the IR spectrum, since *9* would be expected to show two absorptions at 1650–1660 and 1715 cm^{-1} from the cyclic iminoester and benzoate respectively; whereas the product (*10*) showed only a single absorption at 1700 cm^{-1}. Since no model compounds with a seven-membered cyclic iminoester of trichloroacetic acid were available to support this assignment, *10* was hydrolyzed with trifluoroacetic acid/water and deacylated to give 1,2-*O*-isopropylidene-α-D-glucofuranose, proving that the reaction product did indeed have the structure *10.* That the failure of the intended rearrangement to *9* was not due to a hindrance to the rearrangement between a 3,5- and 5,6-benzoxonium ion, was deduced from the behaviour of 6-benzoyl-3,5-*O*-benzylidene-1,2-*O*-isopropylidene-α-D-glucofuranose (*7b*) towards NBS. This reaction proceeded to give a 4:1 mixture of two compounds which could not be separated chromatographically. The major compound was identified as a 6-bromo-6-deoxy compound due to the presence in the ^{13}C NMR spectrum of a high field absorption at 30.6 ppm and the absence of absorption at 65 ppm normally resulting from a primary benzoyloxy-substituted carbon atom. The ^1H NMR spectrum also exhibited a high field absorption for H-6 (3.6–3.7 ppm) which could only be a result of bromine substitution at C-6. This outcome of the reaction must have been a result of formation of the 3,5-benzoxonium ion *8b* followed by rearrangement to the 5,6-benzoxonium ion *12* of the *ido* configuration, which was subsequently opened by bromide ion at the primary carbon atom to give 3,5-di-*O*-benzoyl-6-bromo-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (*13*).

The minor product exhibited a ^{1}H NMR spectrum differing from that of *13* mainly with respect to the chemical shifts of H-5 and H-6, *ca.* 1 ppm upfield and downfield, respectively, corresponding to a 5-bromo-5-deoxy structure. Since a 3,5-benzoxonium ion attached to a 1,2-*O*-isopropylidene-α-D-glucofuranose is known[2] to give a 5-bromo-5-deoxy-β-L-idofuranose derivative, while a 5,6-benzoxonium ion is known[4] to react with bromide ion exclusively at C-6, the most probable structure for the minor product is 3,6-di-*O*-benzoyl-5-bromo-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (*14*). From the behaviour of the benzoate *8b*, it was concluded, that the failure of the rearrangement of the imidate *8a* was not due to hindrance to the neighbouring group participation from the substituent at O–6, but rather to a trapping of the 3,5-benzoxonium ion as an orthoamide by the imidate nitrogen atom prior to rearrangement.

When methyl 2,3-*O*-benzylidene-5-*O*-trichloroacetimidoyl-β-D-ribofuranoside (*15a*) was treated with NBS a reaction took place presumably with initial formation of the benzoxonium ion *16a*, which subsequently rearranged to the oxazoline *17*. The same type of rearrangement of the corresponding 5-*O*-benzoyl-substituted benzoxonium ion *16b* was inferred from the outcome of the nucleophilic opening with *p*-toluenesulfonate ion, which led to methyl 2,3-di-*O*-benzoyl-5-*O*-tosyl-β-D-zylofuranoside, a result of rearrangement to a 3,5-benzoxonium ion prior to attack by the nucleophile.[5] When the equilibrium between the 2,3- and 3,5-benzoxonium ions was investigated, it was found to favour the 2,3-benzoxonium ion strongly, while the trichloroacetimidate *16a* behaved quite differently, rearranging completely to the 3,5-fused cyclic iminoester *17*.

Rearrangement between a trichloroacetimidate and a 1,3-dioxolanylium ion situated *trans* on a pyranose ring proceeded smoothly. When methyl 2,3-*O*-benzylidene-4-*O*-trichloroacetimidoyl-α-L-rhamnopyranoside (*18*) was treated with NBS, the initially formed 2,3-benzoxonium ion *19* rearranged to methyl 3-amino-2-*O*-benzoyl-3,6-dideoxy-α-L-altropyranoside 3-*N*,4-*O*-trichloroacetimidate (*20*), which could be crystallized directly or hydrolyzed and rebenzoylated to methyl 2,4-di-*O*-benzoyl-3,6-dideoxy-3-trichloroacetamido-α-L-altropyranoside (*21*). In this case, Paulsen *et al.*[6] have investigated the equilibrium between the corresponding acetoxonium ions, derived from α-D-rhamnopyranoside and 6-deoxy-α-D-altropyranoside and found these ions to be of comparable stability; in the present case, the formation of an iminoester instead of an acyloxonium ion on rearrangement shifted the equilibrium strongly in favour of the iminoester derivative with the *altro* configuration.

In summary, the results obtained here allow the conclusions that neighbouring group participation from a trichloroacetimidoyl group follows the same pattern (mostly from *trans* vicinal groups) as that found previously for neighbour-



ing acyloxy groups in carbohydrate compounds. On the other hand, the trichloroacetomidoyl group differs from the acyl groups in that, when rearrangement does take place, the equilibrium is shifted completely in favour of the resulting oxazoline, presumably due to the stabilization gained on deprotonation of the primary product, an oxazolinium salt. The same stabilization may be responsible for the trapping of the acyloxonium ion taking place prior to rearrangement in the rare cases where the steric arrangement allows an intramolecular approach by the iminoester group. The result of a successful rearrangement is equivalent to a clean regiospecific *trans* opening of the ambident acyloxonium ion with a nitrogen nucleophile. The advantage of the present procedure is that the amino sugar resulting from hydrolysis of the oxazoline will not be carrying a substituent on the nitrogen atom, as was the case in the previously published procedure using an *N*-alkylbenzimidate neighbouring group.[7]

Experimental

For general experimental details, see the preceding paper.[1] 500 MHz ^{1}H and 125.73 MHz ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer.

Preliminary experiments. The benzylidene compound (5 mmol), trichloroacetonitrile (1.25 mmol/free hydroxy group) and imidazole (1 mmol) were dissolved in THF, cooled to 0 °C and a 50 % suspension of sodium hydride in mineral oil (0.25 mmol/free hydroxy group) was added. The suspension was stirred for 5 min at 0 °C and 15 min at room temperature and poured into ice-water/chloroform, extracted with chloroform, washed with water, dried over magnesium sulfate, treated with activated carbon and crystallized from ether/pentane to give a crude product which was usually of >90 % purity (NMR). This crude product (1 mmol) was refluxed for 1 h with NBS (1.5 mmol) and pyridine (1.5 mmol) in carbon tetrachloride (50 ml), evaporated to dryness, and redissolved in ether and dilute aqueous sodium hydrogen carbonate. Extraction with ether, drying over magnesium sulfate and treatment with charcoal gave a crude product, which was directly examined by ^{13}C NMR spectroscopy. Appearance of an absorption in the range 25–35 ppm was taken as an indication of formation of bromo-deoxy sugars rather than the desired amino-deoxy sugars.

3,5-O-benzylidene-1,2-O-isopropylidene-6-O-trichloroacetimidoyl-α-D-glucofuranose (7a). 3,5-*O*-benzylidene-1,2-*O*-isoprophylidene-α-D-glucofuranose[8] (1.54 g) was dissolved in THF containing trichloroacetonitrile (0.90 g, 0.63 ml) and imidazole (17 mg), the solution cooled to 0 °C and sodium hydride (60 mg) added as a 50 % suspension in mineral oil. The suspension was stirred for 5 min at 0 °C and 5 min at room temperature then poured into a stirred mixture of chloroform and ice water containing a small amount of sodium hydrogen carbonate. The chloroform phase was separated, washed with water, dried over magnesium sulfate, treated with charcoal, evaporated to dryness, and crystallized from ether/pentane to give a product with m.p. 91–94 °C containing 1–2 % of the starting material. This material was used for the reactions described below, and could be purified by preparative TLC (ethyl acetate/hexane 1:2) followed by several recrystallizations from ether/pentane to give an analytical specimen of *7a,* m.p. 93–94 °C, $[\alpha]_D^{25}$ 0° (c 1.2, $CHCl_3$), anal $C_{18}H_{20}Cl_3NO_6$: C,H,Cl,N. ^{1}H NMR (500 MHz): δ 6.05 (H1), 4.68 (H2), 4.65 (H3), 4.25 (H4), 4.63 (H5), 4.68 (H6); $J_{12} = 3.8$ Hz, $J_{23} \sim 0$, $J_{34} = 2.0$, $J_{45} \sim 0$, $J_{56} \sim 4$. ^{13}C NMR: δ 95.1 (C1), 83.9, 78.0, 72.7, 71.4, 70.4 (C2–C6), 104.8 (Ar*CH*), 26.6, 26.1 (CH_3), 162.1 (C = NH). IR (KBr): 1660 cm^{-1} (C = NH), 3344 (NH).

(*1*R-, *2*R-, *4*R-, *8*R-, *9*S-, *11*R- or S-) *6,6-Dimethyl-11-phenyl-13-trichloromethyl-3,5,7,10,14,16-hexaoxa-12-aza-tetracyclo[9,4,1,0^{2,9},0^{4,8}]-hexadex-12-ene* (10). To *7a* (500 mg) and pyridine (131 mg) in dry tetrachloromethane (50 ml) was added NBS (295 mg). The suspension was refluxed 1¼ h, evaporated to dryness, and redissolved in ether and dilute aqueous sodium hydrogen carbonate. Extraction with ether, drying over magnesium sulfate, treatment with charcoal, evaporation to dryness and crystallization from ethyl acetate/hexane gave 316 mg of *10,* m.p. 194–196 °C. Flash chromatography[9] of the mother liquors (ethyl acetate/hexane 1:4) gave an additional 68 mg of *10,* m.p. 185–190 °C. Recrystallization of the combined products gave 235 mg (47 %) of *10,* m.p. 193–194 °C, $[\alpha]_D^{20}$ +35° (c 2.7, $CHCl_3$), anal. $C_{18}H_{18}Cl_3NO_6$:C,H,Cl,N. ^{1}H NMR

(500 MHz): δ 6.03 (H1), 4.62 (H2), 4.3 (H3, H4), 4.70 (H5), 4.66 (H6), 4.43 (H6'), 1.54 and 1.32 (CH_3); $J_{12} = 3.6$ Hz, $J_{23} = J_{45} \sim 0$, $J_{56} = 2.2$, $J_{56'} = 1.8$, $J_{66'} = 12.5$. ^{13}C NMR: δ 104.3 (C1), 84.3, 74.3, 74.3, 71.3, 71.3 (C2–C6), 26.6 and 25.9 (CH_3). IR (KBr): 1700 cm^{-1} (C = O, C = N). 220 Mg of *10* were dissolved in chloroform, stirred for 1 min with 1 ml trifluoroacetic acid/water (1:1), neutralized with aqueous sodium hydrogen carbonate, extracted with chloroform, dried, evaporated to dryness and deacylated with sodium methoxide in methanol. Neutralization with mixed bed ion exchange resin and concentration gave 64 mg (60 %) of 1,2-*O*-isopropylidene-α-D-glucofuranose, m.p. 148–149 °C (litt.[10] 160–161 °C), ^{13}C NMR: δ 113.4 ($(CH_3)_2C$), 105.4 (C1), 85.2, 80.5, 74.4, 69.2 (C2–C5), 64.3 (C6), 26.3, 25.9 (CH_3), identical to that of an authentic sample.[10]

Reaction between 6-O-benzoyl-3,5-O-benzylidene-1,2-O-isopropylidene-α-D-glucofuranose (7b) *and NBS.* A mixture of *7b*[11] (500 mg), pyridine (135 μl) and NBS (298 mg) was refluxed in dry tetrachloromethane (50 ml) for 15 min, evaporated to dryness, dissolved in ether and water containing a small amount of sodium hydrogen carbonate and sodium sulfite. The organic phase was separated, washed with water, dried over magnesium sulfate and evaporated to dryness. Flash chromatography[9] (ethyl acetate/hexane 1:1) gave 483 mg of a 4:1 mixture of 3,5-*O*-benzoyl-6-bromo-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (*13*) and 3,6-di-*O*-benzoyl-5-bromo-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (*14*). For *13,* ^1H NMR (500 MHz): δ 6.05 (H1), 4.68 (H2), 4.60 (H3), 4.87 (H4), 5.68 (H5), 3.73 (H6), 3.56 (H6'); $J_{12} = 3.7$ Hz, $J_{23} \sim 0$, $J_{34} = 3.5$, $J_{45} = 7.4$, $J_{56} = J_{56'} = 4.5$, $J_{66'} = 11.6$. ^{13}C NMR (125.73 MHz): δ 104.8 (C1), 83.8, 78.6, 76.7, 70.5 (C2–C5), 30.6 (C6). For *14,* ^1H NMR (500 MHz): δ 6.02 (H1), 4.72 (H2), 5.51 (H3), 4.62 (H4), 4.71 (H5), 4.63–4.57 (H6); $J_{12} = 3.7$ Hz, $J_{23} \sim 0$, $J_{34} = 3.2$. ^{13}C NMR (125.73 MHz): δ 104.2 (C1), 80.2, 45.7 (C5), 65.5 (C6).

Methyl 2,3-O-benzylidene-5-O-trichloroacetimidoyl-β-D-ribofuranoside (15a). Methyl β-D-ribofuranoside[12] (3.28 g), benzaldehyde dimethylacetal (3.34 g) and *p*-toluenesulfonic acid (100 mg) in DMF (25 ml) were refluxed under water aspirator vacuum for 1 h, evaporated to dryness and dissolved in ether and saturated aqueous sodium hydrogen carbonate. The organic phase was separated, washed with water, dried over sodium sulfate, concentrated on a rotary evaporator (70 °C, 0.1 mmHg) to give 4.50 g of crude methyl 2,3-*O*-benazylidene-β-D-ribofuranoside, which was dissolved in THF (25 ml) containing trichloroacetonitrile (3.23 g, 2.24 ml) and imidazole (68 mg). The mixture was cooled to 0 °C, a 50 % suspension of sodium hydride (214 mg) added, the suspension stirred for 5 min at 0 °C and 5 min at 20 °C and poured into a stirred mixture of chloroform (50 ml) and ice water (200 ml) containing a small amount of sodium hydrogen carbonate. The chloroform phase was separated, washed with water, dried over sodium sulfate, evaporated to dryness and crystallized from toluene (10 ml) and hexane (50 ml) to give 4.61 g of *15a,* m.p. 82–85 °C as an epimeric mixture (*endo/exo* ~ 1:15). Recrystallization from toluene/hexane gave 2.80 g (35 %) of *15a,* m.p. 85–87 °C, anal. $C_{15}H_{16}Cl_3NO_5$: C,H,Cl,N. For the exo-H *15a,* ^1H NMR: δ 5.17 (H1), 4.9–4.6 (H2, H3, H4), 4.37 (H5), 3.39 (OCH_3), 5.79 (ArC*H*). ^{13}C NMR: δ 106.2 (C1), 85.7 (C4), 83.2, 82.4 (C2, C3), 68.9 (C5), 54.8 (OCH_3), 109.0 (Ar*C*H). For the endo-H *15a,* ^1H NMR: δ 5.98 (ArC*H*).

Methyl 3-amino-2-O-benzoyl-3-deoxy-β-D-xylofuranoside 2O, *3*N-*trichloroacetimidate* (17). To *15* (2.41 g) and pyridine (0.72 g) in dry tetrachloromethane (125 ml) was added NBS (1.63 g). The suspension was refluxed for 1.5 h, evaporated to dryness and redissolved in ether and dilute aqueous sodium hydrogen carbonate solution. Extraction with ether, drying over magnesium sulfate and treatment with charcoal gave 2.22 g of crude *17,* which was crystallized from ether/pentane to give 1.33 g (55 %) of *17,* m.p. 118–119 °C. Recrystallization from ether/pentane gave an analytical specimen with m.p. 119–120 °C, $[\alpha]_D^{25}$ −51° (c 1.3, $CHCl_3$), anal. $C_{15}H_{14}Cl_3NO_5$: C,H,Cl,N. ^1H NMR (500 MHz): δ 5.08 (H1), 5.42 (H2), 4.39 (H3), 4.73 (H4), 4.66 (H5), 4.24 (H5'), 3.38 (OCH_3); $J_{12} = J_{23} \sim 0$ Hz, $J_{34} = 5.5$, $J_{45} = J_{45'} \sim 1.5$ Hz, $J_{55'} = 12.1$. ^{13}C NMR: 107.0 (C1), 80.9 (C2), 57.9 (C3), 73.9 (C4), 66.9 (C5), 55.0 (OCH_3), 164.8 (C = O), 154.7 (C = N), 91.9 (CCl_3). IR (KBr): 1715 cm^{-1} (C = O), 1680 (C = N).

Methyl 2,3-O-benzylidene-4-O-trichloroacetimidoyl-α-L-rhamnopyranoside (18). Methyl α-L-

rhamnopyranoside[13] (3.56 g), benzaldehyde dimethylacetal (3.65 g) and *p*-toluenesulfonic acid (100 mg) in DMF (20 ml) were refluxed under water aspirator vacuum for 1 h, evaporated to dryness and dissolved in ether and saturated sodium hydrogen carbonate, washed with water, dried over sodium sulfate and concentrated on the rotary evaporator (70°, 1 mmHg) to give 5.36 g of the crude epimeric methyl 2,3-*O*-benzylidene-α-L-rhamnopyranosides, which were dissolved in THF (25 ml) containing trichloroacetonitrile (3.61 g, 2.51 ml) and imidazole (68 mg). The mixture was cooled to 0 °C and a 50 % suspension of sodium hydride in mineral oil (240 mg) was added. The suspension was stirred for 5 min at 0 °C and 5 min at 20 °C then poured into a stirred mixture of chloroform (50 ml) and ice water (200 ml) containing a small amount of sodium hydrogen carbonate. The chloroform phase was separated, washed with water, dried over magnesium sulfate, treated with charcoal, evaporated to dryness and crystallized from ether/pentane to give 3.37 g of crude *18*, m.p. 110–125 °C. Recrystallization from ethyl acetate/hexane gave 2.60 g (32 %) of endo-H *18*, m.p. 125–126 °C, $[\alpha]_D^{25}$ −21° (c 1.9, $CHCl_3$), anal. $C_{16}H_{18}Cl_3NO_5$: C,H,Cl,N. ^{1}H NMR: δ 4.98 (H1), 4.18 (H2), 4.64 (H3), 5.19 (H4), 3.96 (H5), 1.36 (H6), 6.23 (ArC*H*), 3.41 (OCH_3), 9.62 (NH); $J_{12} \sim 0$ Hz, $J_{23} = 5.5$, $J_{34} = 7.7$, $J_{45} = 9.9$, $J_{56} = 6.2$. ^{13}C NMR: δ 97.9 (C1), 75.6 (C2), 77.3 (C3), 76.1 (C4), 63.5 (C5), 17.0 (C6), 54.9 (OCH_3), 103.1 (ArCH), 162.3 (C = NH), 91.2 (CCl_3). IR (KBr): 1655 cm^{-1} (C = N), 3330 (NH).

Methyl 3-amino-2-O-benzoyl-3,6-dideoxy-α-L-altropyranoside 3N,4O-trichloroacetimidate (20). To *18* (500 mg) and pyridine (150 µl) in 50 ml of dry tetrachloromethane was added NBS (325 mg). The suspension was refluxed for 1 h, evaporated to dryness and redissolved in ether and dilute aqueous sodium hydrogen carbonate solution. Extraction with ether, drying over magnesium sulfate and treatment with charcoal gave 502 mg of crude *20* on evaporation to dryness. Flash chromatography[9] in ethyl acetate/hexane (1:3) gave 244 mg (49 %) of *20*, m.p. 142–147 °C. Recrystallization from ethyl acetate/hexane gave 167 mg of an analytical sample, m.p. 149–150 °C, $[\alpha]_D^{25}$ −37° (c 1.6, $CHCl_3$), anal. $C_{16}H_{16}Cl_3NO_5$: C,H,Cl,N. ^{1}H NMR: δ 4.80 (H1), 5.52 (H2), 4.51 (H3), 4.74 (H4), 3.96 (H5), 1.43 (H6), 3.41 (OCH_3); $J_{12} = 3.0$ Hz, $J_{34} = 9.0$, $J_{45} = 8.2$, $J_{56} = 6.2$. ^{13}C NMR: δ 99.1 (Cl), 69.6 (C2), 66.7 (C3), 82.6 (C4), 62.4 (C5), 18.9 (C6), 55.2 (OCH_3), 164.7 (C = O), 163.1 (C = N), 86.2 (CCl_3). IR (KBr): 1718 cm^{-1} (C = O), 1655 (C = N).

Methyl 2,4-di-O-benzoyl-3,6-dideoxy-3-trichloroacetamido-α-L-altropyranoside (21). The crude trichloroimidate *20* prepared from 500 mg of *18* as described above was dissolved in chloroform (10 ml) and stirred at room temperature for 5 min with 1 ml of trifluoroacetic acid/water (1:1), neutralized with aqueous sodium hydrogen carbonate, extracted with chloroform, dried over magnesium sulfate, evaporated to dryness and benzoylated with benzoyl chloride (0.5 ml) in pyridine. Work-up in the usual manner, followed by flash chromatography[9] (ethyl acetate/hexane 1:4) gave 110 mg (41 %) of pure *21* followed by 265 mg (41 %) of pure *21* as a syrup, $[\alpha]_D^{25}$ +62° (c 1.1, $CHCl_3$), anal. $C_{23}H_{23}Cl_3NO_7$: C,H,Cl,N. ^{1}H NMR: δ 4.93 (H1), 5.23 (H2), 4.85 (H3), 5.38 (H4), 4.21 (H5), 1.38 (H6), 3.57 (OCH_3), 8.42 (NH); $J_{12} = 1.6$ Hz, $J_{23} = 3.7$, $J_{34} = 4.0$, $J_{45} = 10.3$, $J_{3NH} = 9.0$. ^{13}C NMR: δ 98.0 (C1), 70.3, 69.6 (C2, C4), 49.0 (C3), 62.3 (C5), 17.5 (C6), 55.7 (OCH_3), 165.3, 164.9 (C = O), 161.5 (C = N), 92.5 (CCl_3).

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