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THE REDUCTION OF AZIDES WITH SODIUM BOROHYDRIDE: A CONVENIENT SYNTHESIS OF METHYL 2-ACETAMIDO-4,6-*O*-BENZYLIDENE-2-DEOXY-α-D-ALLOPYRANOSIDE

Y. ALI AND A. C. RICHARDSON
Department of Chemistry, The University, Reading (Great Britain)
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INTRODUCTION

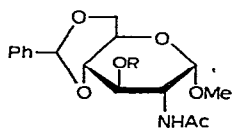
Carbohydrate azides, prepared by replacement of sulphonyloxy groups by azide, are valuable intermediates in the synthesis of amino sugars. The azide group is usually reduced to the amino function by catalytic reduction (using Raney nickel, palladium, etc) or by treatment with lithium aluminium hydride. We have found that the yields of the amine obtained by catalytic hydrogenation are, in some cases, low or variable, and the products are difficult to purify[1]. Moreover, the use of lithium aluminium hydride is often precluded because of the presence of other groups sensitive to this reagent. The results of Boyer and Ellzey[2] suggested that sodium borohydride was not a satisfactory reductant for azides, whereas Stevens *et al.*[3] used this reagent in 2-propanol, without comment, for the reduction of ethyl 4-azido-2,3,4,6-tetradeoxy-α-D-*threo*-hexopyranoside and obtained the corresponding amine in 85% yield. In the course of our studies on the synthesis of amino sugars, we have found sodium borohydride to be an excellent reagent for the reduction of azido derivatives, and our results are described below.

RESULTS AND DISCUSSION

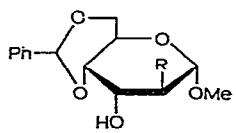
In pursuit of a synthesis of methyl 2,3,4,6-tetra-acetamido-2,3,4,6-tetradeoxy-α-D-galactopyranoside[4], methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside (**10**) was required as starting material. We found that the method[5] involving solvolysis of methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-mesyl-α-D-glucopyranoside (**3**) was inconvenient for large-scale work. We considered that the method of Baker and Buss[6], in which the configuration at C-3 of methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**1**) was inverted by sequential oxidation with the Pfitzner–Moffatt reagent and reduction of the resulting ketone with sodium borohydride, was more promising, particularly if methyl sulphoxide–acetic anhydride[7] could be used. However, it was subsequently found that oxidation of compound **1** with the latter reagent gave a mixture of two products, suspected of being the required ketone and the corresponding 3-acetate (**2**) formed by acetylation.

We considered that competing acetylation, which effectively blocks oxidation, would be less likely for an axial hydroxyl group. Baker and Buss[6] have shown that,

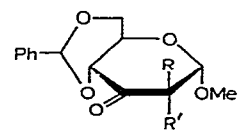
during the oxidation of a hydroxyl group with the Pfitzner–Moffatt reagent, epimerisation of the axial substituent on an adjacent position may occur. Thus, methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (**4**) afforded methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hex-3-ulopyranoside (**6**), identical with that obtained from the *gluco*-isomer **1**. We have therefore studied the oxidation of methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (**5**) with methyl sulphoxide–acetic anhydride. The 2-azide (**5**) was readily prepared in 85% yield by ring-opening of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside by azide[8]. This epoxide is normally prepared from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside *via* the ditoluene-*p*-sulphonate[9], but we have found it more convenient, and less time-consuming, to go by way of the dimethanesulphonate (readily obtained in near quantitative yield), which yields the epoxide in 70% yield when heated with ethanolic sodium ethoxide. The formation of the epoxide by this route was first described by Honeyman and Morgan[10], but little emphasis was placed on it, and its usefulness has not been widely appreciated.



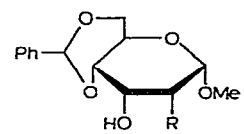
1 R=H
2 R=Ac
3 R=MS



4 R=NHAc
5 R=N_3



6 R=H, R'=NHAc
7 R=H, R'=N_3
8 R=D, R'=N_3

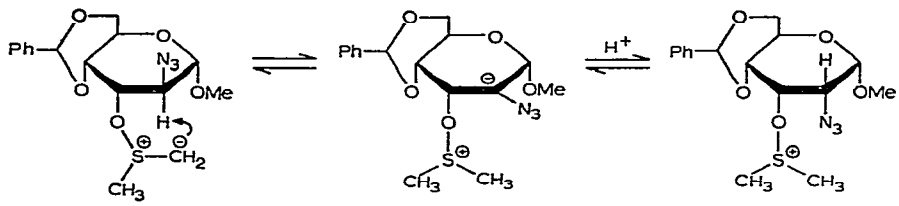


9 R=N_3
10 R=NHAc

Oxidation of the 2-azide (**5**) with methyl sulphoxide–acetic anhydride gave a ketone in 65% yield. Reduction of this ketone with a large excess of borohydride gave a basic product, the infrared spectrum of which indicated the absence of an azide group. The product was best isolated, in an overall yield of 86%, as its *N*-acetyl derivative (formed by treatment with acetic anhydride in ethanol), which was shown to be methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside (**10**) by comparison with a sample prepared by the method of Jeanloz[5]. Hence, not only had borohydride reduced the ketone stereospecifically by equatorial attack, but reduction of the azide substituent and inversion of configuration at C-2 had also occurred. It was found that the ketone could be specifically reduced, to give a mono-azide (**9**), if a smaller proportion of borohydride was used. Since further reduction of this azide, followed by *N*-acetylation, afforded the 2-acetamido-alloside (**10**), and oxidation with methyl sulphoxide–acetic anhydride gave the same ketone (**7**) from which it was derived, all three products must have the same configuration at C-2. Hence, epimerisation must have occurred during the oxidation step and not under the mildly basic conditions of the borohydride reduction.

The exact mechanism by which this epimerisation takes place is worthy of discussion. Epimerisation at asymmetric centres adjacent to a carbonyl function are more generally observed under basic conditions, than under the mildly acidic con-

ditions used for the oxidation. We therefore considered initially that epimerisation may occur during the transition-state phase of the oxidation reaction. It is probable that the sulphonium "ylid" **11** is a key intermediate in the oxidation[11,12], and we



11 **12** **13**

speculated initially that this could function as a sufficiently powerful base to remove H-2 to give carbanion **12**, which would re-combine with a proton from the solvent to give the thermodynamically more-favoured, equatorial epimer **13**. If epimerisation took place by such a mechanism, since the reaction is irreversible, no further exchange of H-2 would occur subsequent to the collapse of "ylid" **11** to the ketone. However, if epimerisation is caused by an acid-catalysed enolisation, exchange of H-2 in the resulting ketone (**7**) should be observed. To test these two possible mechanisms, we allowed the azido-ketone **7** to stand in a mixture of methyl sulphoxide, acetic anhydride, and deuterium oxide, in order to simulate the post-oxidation conditions experienced by the ketone in the oxidation reaction mixture. We then re-isolated the ketone and found that, in agreement with the acid-catalysed enolisation mechanism, complete exchange of H-2 for deuterium had taken place to give the 2-deutero derivative **8**. The completeness of the exchange was convincingly demonstrated by n.m.r. spectroscopy. Before exchange, the H-1 doublet of **7** was the only ring-proton readily recognised (τ 4.84, $J_{1,2} \sim 4$ Hz), but, after exchange, this resonance collapsed to a singlet, and a doublet previously observed at τ 6.22 disappeared completely, and was consequently assigned to H-2 (Fig. 1). No other changes in the spectrum were observed, indicating that no exchange took place at C-4, which is a bridgehead carbon atom. The ketone **7** should be a valuable intermediate for the synthesis of amino sugars specifically tritiated or deuterated at C-2, and, if tritiated or deuterated borohydride is used, at C-2 and C-3. The 2-acetamido-alloside **10** should be readily converted into the *gluco*-isomer **1** by treatment of its 3-methanesulphonate with sodium benzoate in *N*,*N*-dimethylformamide (*cf.* ref. 4), hence providing a convenient route to specifically tritiated and deuterated derivatives of 2-amino-2-deoxy-D-glucose. Horton and Jewell[13] have previously utilised hexulopyranose derivatives for the preparation of specifically deuterated carbohydrates by base-catalysed exchange.

Application of this oxidation–reduction procedure to methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside (**14**) was only partially successful. The oxidation product was obtained as an oil that contained at least three components. Reduction of the crude product, followed by *N*-acetylation, gave methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-glucopyranoside (**16**; 19%). The formation of the

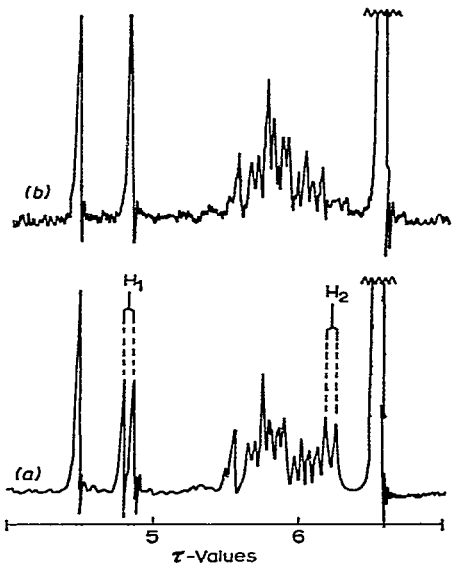
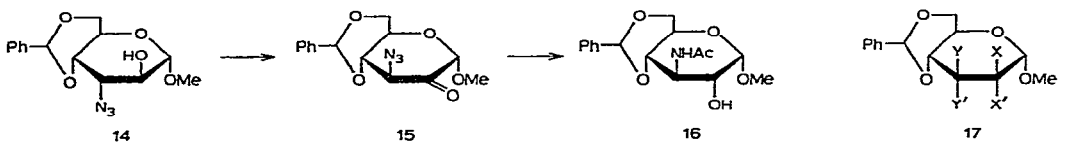


Fig. 1. N.m.r. spectrum of (*a*) methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hex-3-ulopyranoside and (*b*) its 2-deutero derivative.

glucoside, rather than the mannoside, by reduction of α-D-*arabino*-hexulopyranosides (*e.g.*, **15**) with borohydride has been observed by Baker and Buss[6]. It is probable that equatorial approach by borohydride is hindered by the axial methoxyl group, whereas axial approach suffers no such hindrance.



The reduction of azide groups to amino functions in these compounds prompted us to look more closely at this reagent to see whether it could be utilised generally for effecting this type of transformation. In addition to the azides referred to above, seven azide and diazide derivatives of the general type **17** have been reduced to the corresponding amines in 60–80% yields. In most cases, the amines have been characterised as *N*-acetyl derivatives. With methyl 3-azido-4,6-*O*-benzylidene-2-*O*-methanesulphonyl-α-D-altropyranoside, the amine was isolated after 1 h, but, on one occasion, when the reaction mixture was kept overnight, a 60% yield of the epimine, methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allopyranoside, isolated as the *N*-acetyl derivative, was obtained.

EXPERIMENTAL

Melting points were determined on a Kofler microscope hot-stage and are

uncorrected. Unless otherwise stated, optical rotations were determined in chloroform to an accuracy better than ±0.002° with a Bendix-N.P.L. automatic polarimeter, using a 2-cm cell at 21 ±2°. Thin-layer chromatography was carried out on microscope slides coated with silica gel (Whatman SG41), using chloroform–methanol (9:1) or ether; detection was effected with a 10% v/v solution of sulphuric acid in ethanol followed by heating. Unless otherwise stated, all named products gave single spots on chromatograms, and their infrared spectra were in accord with their structures.

Methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside. — Methanesulphonyl chloride (100 ml) was added slowly to a chilled solution of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (100 g) in dry pyridine (250 ml), and the resulting solution was kept overnight at *ca.* 5°. Decomposition of the reaction mixture with crushed-ice afforded the crude, solid disulphonate (150 g, 97%). This material was suitable for the next stage but could be recrystallised from chloroform to give needles, m.p. 187–188°, $[\alpha]_D$ +48.5° (*c* 0.5). Lit.[10], m.p. 188–189°, $[\alpha]_D$ +49°.

The disulphonate was then added to a solution prepared by adding sodium (16.25 g) to ethanol (1500 ml) (*i.e.*, 0.5N sodium ethoxide), and the resulting mixture was heated under reflux for 1 h with stirring. Addition of water to the cooled reaction mixture yielded the epoxide, which was washed well with water and ethanol and finally dried to give the product (66 g, 70% overall yield). Recrystallisation from chloroform–ether gave needles, m.p. 200°, $[\alpha]_D$ +140° (*c* 1). Lit.[14], m.p. 200°, $[\alpha]_D$ +140°. The infrared spectrum was identical with that of an authentic specimen of the epoxide[9].

In some preparations, the product was contaminated with some of the corresponding *manno*-2,3-epoxide, and we believe that this arises because of incomplete esterification during the first stage of the preparation. This can usually be overcome by the use of a larger proportion of the acid chloride or longer reaction times for the sulphonylation.

Methyl 2-azido-4,6-O-benzylidene-2-deoxy-α-D-altropyranoside (**5**). — A suspension of the *allo*-epoxide (40 g) in hot ethanol (500 ml) was treated with a solution of sodium azide (40 g) and ammonium chloride (40 g) in water (120 ml), and the mixture was heated under reflux for 22 h with stirring. After cooling, the reaction mixture was diluted with water (*ca.* 800 ml), and the solid was filtered off, washed well with water, and dried to give the azide (40 g, 85%). Recrystallisation from ether–light petroleum gave the product as plates, m.p. 77–80°, $[\alpha]_D$ +64.2° (*c* 1.0). Lit.[8], m.p. 79–80°, $[\alpha]_D$ +65°.

Methyl 2-azido-4,6-O-benzylidene-2-deoxy-α-D-ribo-hex-3-ulopyranoside (**7**). — (*a*) The 2-azido-altroside (**5**; 30 g) was dissolved in methyl sulphoxide (300 ml), and acetic anhydride (150 ml) was added. The resulting solution was kept at room temperature overnight. Addition of water to the reaction mixture initially precipitated an oil that soon crystallised. The product was then filtered off, washed well with water, and, without drying, recrystallised from ethanol to give ketone **7** (19 g, 64%), m.p. 153–155°, $[\alpha]_D$ +550° (*c* 0.44) (Found: C, 54.7; H, 5.5; N, 13.55. $C_{14}H_{15}N_2O_5$ calc.: C, 55.0; H, 5.6; N, 13.7%).

When the ketone (100 mg) was allowed to stand in a mixture of methyl sulphoxide (1 ml), acetic anhydride (0.5 ml), and deuterium oxide (0.32 ml) for 48 h and then re-isolated by addition of water to the reaction mixture, the n.m.r. spectrum of the product (75 mg) indicated (Fig. 1) that complete exchange of H-2 for deuterium had taken place.

(*b*) The 2-azido-alloside **9** (500 mg) was oxidised in a manner exactly similar to the above to give the azido-ketone (**7**) (60%), m.p. 151–152°, mixed m.p. with the product obtained from the altroside, 152–154°.

Methyl 2-azido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside (**9**). — To a stirred solution of ketone **7** (5 g) in *N,N*-dimethylformamide (10 ml) was added methanol (100 ml) followed by the portionwise addition of sodium borohydride (1 g). After 30 min, the mixture was diluted with water and extracted with chloroform (3 × 75 ml). The combined extracts were washed with water, dried ($MgSO_4$), and evaporated to a crystalline solid. Recrystallisation from ethanol gave the 2-azido-alloside (**9**) (4 g), m.p. 117.5–118.5°, $[\alpha]_D$ +139.2° (*c* 0.53) (Found: C, 54.9; H, 5.0; N, 13.8. $C_{14}H_{17}N_3O_5$ calc.: C, 54.7; H, 5.5; N, 13.7%).

Reduction of azides with sodium borohydride. — (*a*) Compound **7** (12.5 g) was dissolved in *N,N*-dimethylformamide (20 ml), and the solution was diluted with methanol (150 ml). Sodium borohydride (10 g) was then added portionwise to the stirred solution. After 45 min, the reaction mixture was diluted with water and extracted with chloroform (3 × 100 ml). In some cases, the reaction mixture was briefly boiled prior to dilution with water. The combined extracts were washed with water, dried ($MgSO_4$), and taken to dryness. The resulting, crystalline solid was dissolved in ethanol (50 ml), and acetic anhydride (7 ml) was added, causing immediate crystallisation of methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside (**10**) (10 g, 86%), which, after recrystallisation from ethanol, had m.p. 210.5–211.5°, $[\alpha]_D$ +64.7° (*c* 1.0). Lit.[5], m.p. 214–215°, $[\alpha]_D$ +64°.

(*b*) Compound **9** was reduced, in a manner exactly analogous to that described above, to give compound **10** (88%), m.p. 210–212°, $[\alpha]_D$ +63.8° (*c* 1.0), identical with the product of (*a*) above.

(*c*) Compound **5** was reduced as above to give methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside[15] (**17**; X = NH_2, Y′ = OH, X′ = Y = H) in 80% yield, m.p. 165–166°, $[\alpha]_D$ +105°. With benzoic anhydride in ethanol, the amine gave the *N*-benzoyl derivative, m.p. 161–163°, $[\alpha]_D$ −1° (*c* 1.0). Lit.[16], m.p. 162–164°, $[\alpha]_D$ −1°.

(*d*) Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside (**17**; Y′ = N_3, X = OH, X′ = Y = H) was reduced, as above, to give the 3-amine (**17**; Y′ = NH_2, X = OH, X′ = Y = H) in 60% yield. After recrystallisation from ethanol–light petroleum, it had m.p. 186–188°, $[\alpha]_D$ +91° (*c* 0.55). Lit.[15], m.p. 188°, $[\alpha]_D$ +89°.

(*e*) Methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-methanesulphonyl-α-D-altropyranoside (**17**; X = N_3, Y′ = OMs, X′ = Y = H) upon reduction, as above, with borohydride, gave the corresponding amine (**17**; X = NH_2, Y′ = OMs, X′ = Y = H) in 60% yield. The product, recrystallised from ethanol, had m.p. 128–129°, $[\alpha]_D$ +95° (*c* 0.7) (Found: C, 50.2; H, 5.75; N, 4.2. $C_{15}H_{21}NO_7S$ calc.: C, 50.1; H, 5.85; N, 3.9%).

With acetic anhydride in ethanol, the amine gave the *N*-acetyl derivative, m.p. 143–145°, $[\alpha]_D$ +74.5° (*c* 0.51). Lit.[16], m.p. 142–145°, $[\alpha]_D$ +64°.

(*f*) Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-2-*O*-methanesulphonyl-α-D-altropyranoside (**17**; Y′=N_3, X=OMs, X′=Y=H) afforded a syrup upon reduction as described above, which, with acetic anhydride in ethanol, gave the corresponding *N*-acetyl derivative (**17**; Y′=NHAc, X=OMs, X′=Y=H) in 60% yield, m.p. 168–170°, $[\alpha]_D$ +40.8° (*c* 0.71). Lit.[17], m.p. 161–162°, $[\alpha]_D$ +30°.

When the reduction reaction mixture was kept overnight, the product (60%), after *N*-acetylation, was shown to be methyl 2,3-acetylepimino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-allopyranoside, by comparison with an authentic sample[16].

(*g*) Methyl 3-azido-4,6-*O*- benzylidene-2,3-dideoxy-α-D-*arabino*-hexopyranoside (**17**; Y=N_3, X=X′=Y′=H) was reduced as above, and the product was treated with acetic anhydride in ethanol to give the corresponding, sparingly soluble *N*-acetyl derivative (**16**; Y=NHAc, X=X′=Y′=H) in 78% yield, m.p. 278–280° (subl.), $[\alpha]_D$ +62.4° (*c* 0.94) (Found: C, 62.1; H, 7.0; N, 4.3. $C_{16}H_{21}NO_5$ calc.: C, 62.6; H, 6.8; N, 4.5%). Lit.[18], m.p. 272–274° (subl.), $[\alpha]_D$ +65°.

(*h*) Methyl 2,3-diazido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-mannopyranoside (**17**; X=Y=N_3, X′=Y′=H) was reduced as above, and the syrupy diamine was treated with acetic anhydride in ethanol to give the corresponding di-*N*-acetyl derivative (**17**; X=Y=NHAc; X′=Y′=H) in 65% yield, m.p. 305–306° (subl.), $[\alpha]_D$ −36° (*c* 0.66, *N*,*N*-dimethylformamide) (Found: C, 58.9; H, 6.8; N, 7.4. $C_{18}H_{24}N_2O_6$ calc.: C, 59.3; H, 6.6; N, 7.7%). Lit.[19], m.p. 310–311° (subl.), $[\alpha]_D$ −36.2°.

(*i*) Methyl 2-acetamido-3-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranoside[4] (**17**; Y=N_3, X′=NHAc, Y′=X=H) was reduced, as described above, to give methyl 2-acetamido-3-amino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranoside (**17**; Y=NH_2, X′=NHAc, Y′=X=H), m.p. 261–262°, $[\alpha]_D$ +45.2° (*c* 0.62), in 75% yield (Found: C, 59.4; H, 6.9; N, 8.5. $C_{16}H_{22}N_2O_5$ calc.: C, 59.6; H, 6.6; N, 8.7%). With acetic anhydride in ethanol, the product gave the sparingly soluble di-*N*-acetyl derivative (93%), m.p. 324–330° (subl.), $[\alpha]_D^{50}$ +44.3° (*c* 0.56, *N*,*N*-dimethylformamide) (Found C, 58.9; H, 6.7; H, 7.6. $C_{18}H_{24}N_2O_6$ calc.: C, 59.3;H, 6.6; N, 7.7%).

Sequential oxidation and reduction of methyl 3-azido-4,6-O-benzylidene-3-deoxy-α-D-altropyranoside (**17**; Y′=N_3, X=OH, Y=X′=H). — The 3-azide (0.5 g) was oxidised with methyl sulphoxide–acetic anhydride, as described above for the 2-azide. The product was isolated as an impure syrup containing three components (t.l.c.). Reduction of this product, as described above, gave a syrup that was dissolved in ethanol (2 ml). Addition of acetic anhydride (0.2 ml) caused crystallisation of methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-glucopyranoside (100 mg, 19%), m.p. 292–295° (subl.), $[\alpha]_D$ +96.8° (*c* 0.46, *N*,*N*-dimethylformamide), identical by its infrared spectrum with an authentic sample. Lit.[20], m.p. 286–288° or[6] m.p. 311–313°.

ACKNOWLEDGMENT

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SUMMARY

Sodium borohydride has been shown to be a valuable reagent for the reduction of azides to amines in yields of 60–85%. Oxidation of methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside with methyl sulphoxide–acetic anhydride gave, *via* epimerisation at C-2, methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hex-3-ulopyranoside. It has been demonstrated that epimerisation occurs subsequent to oxidation, *via* an acid-catalysed enolisation. The ketone, upon reduction with borohydride and *N*-acetylation, gave an 86% yield of methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside, thus providing a convenient synthesis of this compound.

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