NITROGEN-CONTAINING CARBOHYDRATE DERIVATIVES

PART XXVIII* REACTION OF AZIDO SUGARS WITH HYDRAZINE AND METHYLHYDRAZINE

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ABSTRACT

Several azido derivatives of aldosides, having tosyloxy, hydroxy, and deoxy neighbouring-groups, have been treated with hydrazine, with its hydrate, and with methylhydrazine In general, complex mixtures of products resulted, and it is postulated that these were formed by simple reduction of the azido group to amine, and by decomposition of an intermediate di-imide derivative which gave olefins or deoxy compounds

INTRODUCTION

In earlier papers[1,2], some observations on the reactions of hydrazine with azido sugars were reported More-detailed examination of the reactions with a wider variety of azido sugars has now shown that they are much more complex than was previously believed, especially for those compounds bearing an equatorial azido group All the compounds studied had the azido group attached to C-2 or to C-3 of a methyl 4,6-*O*-benzylidene-α-D-glycopyranoside (*trans*-fused series), so that there was certainty of the conformation of the starting materials Parallel experiments were carried out, in some cases, with hydrazine hydrate and with methylhydrazine

RESULTS AND DISCUSSION

In many of the reactions, complex mixtures of products resulted and these were generally separated by preparative thin-layer chromatography The results obtained are summarized in Tables I–VI, and no other description of them will be given, apart from in the Experimental section Two of the common products were the unsaturated sugar **7** and its dideoxy analogue **8** It was shown that **8** can be derived from **7** if the reaction is carried out in air Thus, a 30-min reflux of a solution of **7** in hydrazine gave

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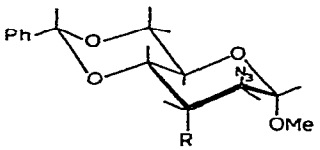
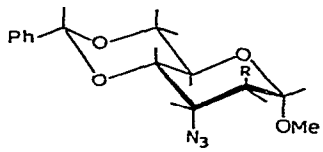
23% of **8**, whereas under a nitrogen atmosphere only a 3% conversion occurred The reduction of **7** by hydrazine in air is believed to be due to the formation of diimide *in situ* Compound **8** was unaffected by boiling hydrazine in air All the reactions described in Tables I–VI were carried out in an atmosphere of air, unless otherwise stated.



1 R = OTs
2 R = OH
3 R = H



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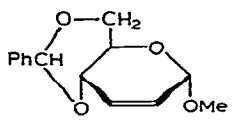
5 R = OH
6 R = OCH_2Ph



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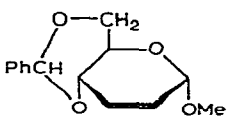

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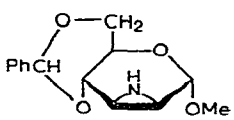

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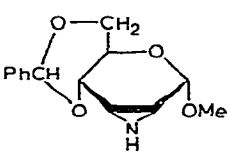

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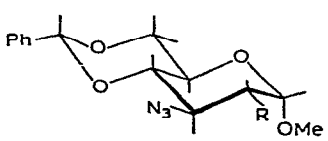
The findings reported in the Tables can be generalised as follows

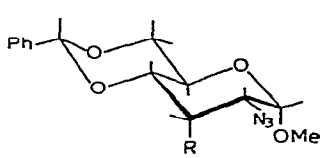
(*i*) With an *axial* azido group and a neighbouring, axially situated, good leaving-group (*e g* **1**), the corresponding olefin was formed as the predominant or only product Carrying out such reactions in the presence of a variety of substances failed to trap any active intermediates When the *axial* azido group was adjacent to an axially situated poor leaving-group, such as a hydroxyl group (*e g* **2**), or adjacent to a methylene group (*e g* **3**), the reaction was complex For both types, the 1,2-olefin and the reduction product ($N_3 \rightarrow NH_2$) were amongst the products, as well as the compound arising from loss of the azido group ($N_3 \rightarrow H$) In the azido-hydroxy case (*e g* **2**), the 2,3-olefin was also a product

(*ii*) With an *equatorial* azido group and a vicinal *equatorial* group, elimination of the latter did not occur, and the products resulted from the $N_3 \rightarrow NH_2$ and $N_3 \rightarrow H$ conversions

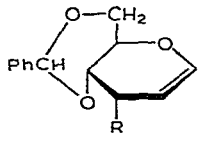
(*iii*) *cis*-Systems having an *equatorial* azido group gave complex mixtures of unsaturated compounds and those resulting from $N_3 \rightarrow NH_2$ and $N_3 \rightarrow H$ changes



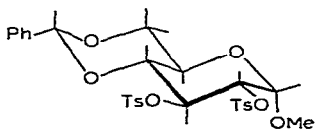
11 R = OTs
12 R = OH
13 R = H



14 R = OTs
15 R = OH



16 R = OH
17 R = H



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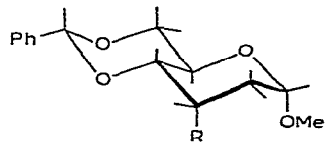
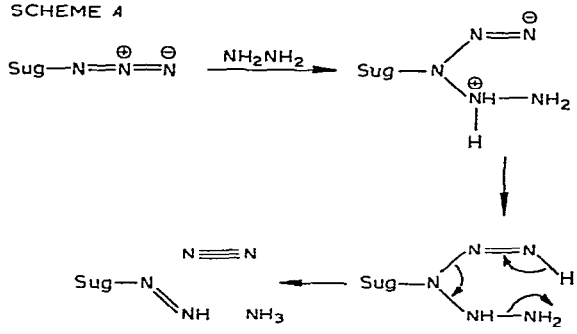


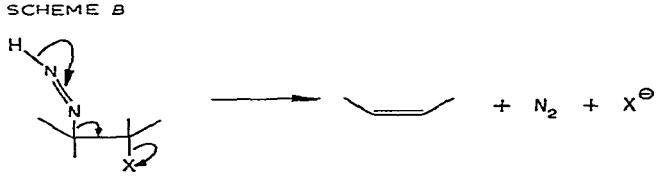
19 R = OTs
20 R = OH

The reduction mode (*i e* $N_3 \rightarrow NH_2$) is explicable from the known properties of hydrazine, but the interesting features are the eliminations and the $N_3 \rightarrow H$ conversion The results in Tables I–VI can be rationalised if it is considered that two reaction pathways are operating simultaneously These are firstly the reduction pathway, and secondly some other pathway (more than one can be envisaged) involving a di-imide structure (R–N = N–H) as an intermediate; a possible pathway is shown in Scheme *A* When in an axial situation, and next to an axial substituent, the azide group would tend to eliminate (Scheme *B*), thus, **1**, where the leaving groups could be tosyloxy or methoxy, gave the expected olefin **7**, whereas **2**, where the azide group is flanked by two possible leaving-groups of similar character (*i e* hydroxy and methoxy), gave both possible olefins When the intermediate was in other situations, it could react in a "Wolff–Kishner manner" (Scheme *C*) to give the corre-

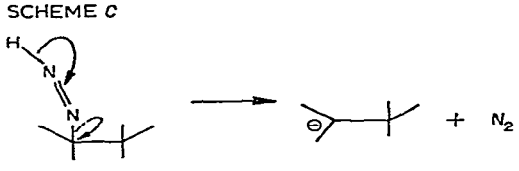
SCHEME *A*



SCHEME *B*



SCHEME *C*



sponding deoxy compound The reactions with hydrazine hydrate and with methylhydrazine followed the pattern of those with hydrazine In some cases, the former reactions went less readily

With compound **4** in hydrazine, the reduction mode proceeded to a considerable extent, as witnessed by the formation of the *allo*-epimine **10** which would be formed from an intermediate amino-tosyl derivative Compound **1** gave no epimine **9** with hydrazine, but did so with methylhydrazine This was consistent with the formation of more of epimine **10** from **4** with the latter reagent than with hydrazine

EXPERIMENTAL

T l c and p l c were performed on silica gel (Merck GF_{254}) All solvent extracts were washed, dried ($MgSO_4$), and evaporated *in vacuo* at <50° Compounds were identified by m p , $[\alpha]_D$, i r and n m r comparisons, and by t l c comparison with authentic samples whenever possible Optical rotations are for chloroform solutions, unless otherwise stated

*Methyl 3-azido-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-altropyranoside* (**6**) — The hydroxy analogue[3] **5** (5 g) was suspended in benzyl chloride (25 ml) and warmed to 50° in the presence of solid sodium hydroxide (15 g), the temperature rose rapidly to >80° and, after cooling, a temperature of 60° was maintained for a further 45 min The yellow solution was poured on to ice (400 ml) and extracted with ether Evaporation of the extracts gave a solid that was recrystallised from ether–light petroleum to give **6** (74%), m p 93–94 5°, $[\alpha]_D^{18}$ +26 6° (*c* 3 14) (Found C, 63 5, H, 5 8, N, 10 6 $C_{21}H_{23}N_3O_5$ calc . C, 64 1, H, 5 8, N, 10 5%)

*Methyl 3-acetamido-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-altropyranoside* — Compound **6** (0 4 g) was dissolved in *N*,*N*-dimethylformamide (1 ml) and methanol (5 ml), and sodium borohydride (0 4 g) was added in portions during 1 h Water was then added, and the mixture was extracted with chloroform Concentration of the extract gave a colourless syrup whose n m r was consistent with the corresponding amino sugar Acetylation with acetic anhydride–pyridine under the usual conditions gave, after recrystallisation from aqueous methanol, the title compound (84%), m p. 171–172°, $[\alpha]_D^{22}$ +46 2° (*c* 1 2) (Found C, 67 0, H, 6 7, N, 3 8 $C_{23}H_{27}NO_6$ calc C, 66 8; H, 6 6, N, 3.4%)

*Methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-*D*-allopyranoside* (**14**) — This compound was prepared by conventional tosylation of the corresponding alcohol[4] and had m p 197–198° (Found C, 55 0, H, 5 1, N, 9 1, S, 6 65 $C_{21}H_{23}N_3O_7S$ calc · C, 54 6, H, 5 0; N, 9 1; S, 6 95%)

*Methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-*D*-ribo-hexopyranoside*[5] (**19**) — The corresponding alcohol was tosylated by the standard procedure to give **19**, m p 144 5–145°, $[\alpha]_D^{20}$ +76 5° (*c* 0 84) (Found: C, 60 3, H, 6 2 $C_{21}H_{24}O_7S$ calc · C, 60 0, H, 5 8%)

Reactions with hydrazine (*i*). — Reaction times were 10 min at reflux, unless otherwise stated. The mixture was worked up by pouring into excess of water, and

evaporation by co-distillation with water to give the product which was subjected to chromatography

(*a*) *Methyl 2-azido-4,6-O-benzylidene-2-deoxy-3-O-tosyl-α-D-altropyranoside*[3] (**1**) [Hydrazine (5 ml), **1** (0.5 g)] The crystalline product (253 mg) was shown by t l c to be a mixture of methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**7**), m p 116–117°, and methyl 4,6-O-benzylidene-2,3-dideoxy-α-D-*erythro*-hexopyranoside (**8**), m p 83–84°, in yields of 81 and 13%, respectively (n m r. analysis)

TABLE I

REACTIONS OF METHYL 2-AZIDO-4,6-*O*-BENZYLIDENE-2-DEOXY-3-*O*-TOSYL-α-D-ALTROPYRANOSIDE (**1**) WITH HYDRAZINES

Conditions	*Products*		
	7 (%)	**8** (%)	*Other*
NH_2NH_2 + air (to cessation of effervescence)	91	[a]	
NH_2NH_2 + air (10-min reflux)	81	13	
NH_2NH_2 + air + heptane (2-h reflux)	87	[a]	
NH_2NH_2 + air + propan-1-ol (2-h reflux)	84	[a]	
NH_2NH_2 + air + pyridine (2-h reflux)	81	[a]	
NH_2NH_2 H_2O[2] (4-h reflux)	81	0	
$PhNHNH_2 + N_2$ (4-h at 100°)	0	0	Starting material (99%)
$MeNHNH_2$	71	0	Epimine **9**[b] (22%)

[a]Saturated product was not investigated [b]After exposure of **9** to refluxing NH_2NH_2 for 10 min, 99% of starting material was recovered

(*b*) *Methyl 2-azido-4,6-O-benzylidene-2-deoxy-α-D-altropyranoside*[3] (**2**) [**2** (1 5 g), hydrazine (25 ml), 20 min at reflux] The colourless syrup was fractionated by p l c (benzene–chloroform, 1 1, 3 passes, 2 3, 2 passes; 1·3, 2 passes, and then chloroform–methanol, 95 5, 2 passes) to give four bands *A–D*. Band *A* (95 mg) contained (t l c and n m r) compounds **7** and **8** in a ratio 29 71, *i e* in yields of 2 and 6%, respectively Band *B* (148 mg) was identified as 4,6-*O*-benzylidene-D-allal (**16**) (13%), m p 82–83°, $[\alpha]_D^{22}$ +201° (*c* 0 6, ethanol); lit [6] m p 84–84 5°, $[\alpha]_D^{25}$ +210° (*c* 0 44, ethanol) Band *C* (648 mg) was shown to be methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside (50%), m p 127–128°, lit [7] m p 126–129° Band *D* (260 mg) gave methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (17%), m p 168–170°, lit [8] m.p 168°, and two minor components.

(*c*) *Methyl 2-azido-4,6-O-benzylidene-2,3-dideoxy-α-D-arabino-hexopyranoside*[9] (**3**) [**3** (0 5 g), hydrazine (5 ml)] P l c (benzene, 4 passes; followed by benzene–chloroform, 9:1, 2 passes) gave four bands *A–D* Band *A* (36 mg) was identified as the

3-deoxy-1-ene derivative[10] **17** (10%) Band *B* (106 mg) was identified as the 2,3-dideoxy compound (**8**) (28%) Band *C* (22 mg) consisted of three components that were not further investigated A portion (240 mg) of band *D* (256 mg) was re-chromatographed (chloroform) to give bands *D 1* to *D 4* Three of these (2 mg, 3 mg, and 20 mg) were not considered further The third fastest band, *D 3* (215 mg), was re-chromatographed (chloroform, 2 passes, then chloroform–methanol, 99 1) to give two bands *D 3'* and *D 3''*, the first of which (4 mg) was ignored Band *D 3''* (156 mg) was identified as methyl 2-amino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*arabino*-hexopyranoside (36%), and was further characterised as its *N*-acetyl derivative, m p 174–175°, lit [9] m p 174–175°

(*d*) *Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-D-altropyranoside*[3] (**4**) [**4** (1 g), hydrazine (10 ml)] P l c (benzene–chloroform, 1 1, 3 passes) gave band *A* (320 mg) which was shown by n m r to be a mixture of **7** and **8** in a ratio of 3 1 Further elution (benzene–chloroform, 3 7, 2 passes) and removal of band *B* gave 24 mg of **8**, thus the yield of **7** was 42% and that of **8**, 22% Further elution (ether) gave band *C* (3 mg) which was ignored, and band *D* (209 mg), m p 152–154°, identified, after recrystallisation from propan-2-ol, as **10** (36%), m p 155–156°, lit [3] m p 156–157°

TABLE II

REACTIONS OF METHYL 3-AZIDO-4,6-*O*-BENZYLIDENE-3-DEOXY-2-*O*-TOSYL-α-D-ALTROPYRANOSIDE (**4**) WITH HYDRAZINES

Conditions	*Products*		
	(**7**) (%)	(**8**) (%)	(**10**) (%)[a]
NH_2NH_2 (10 min)	42	22	36
CH_3NHNH_2 (3-h reflux)	49	0	45

[a]Exposure of **10** to refluxing hydrazine for 10 min left 62% of starting material, **7** and **8** were not formed

(*e*) *Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside*[3] (**5**) [**5** (0 5 g), hydrazine (5 ml)] P l c of the mixture was carried out as for compound **2**, to give **8** (6%), methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside (63%), m p 185–187° (lit [11] m p 188°), and methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*ribo*-hexopyranoside (7%) No unsaturated compound **7** was detected

(*f*) *Methyl 3-azido-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside* (**6**) [**6** (1 g), hydrazine (10 ml)] P l c (benzene–chloroform, 1 1) gave band *A* (146 mg), shown (n m r) to be a mixture of **7** (12%) and **8** (4%) Further elution (ether) gave band *B* (708 mg), a portion of which was re-chromatographed (chloroform–ethanol, 25 5, 2 passes) to give syrupy methyl 3-amino-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside (67%), characterised as its *N*-acetyl derivative, m p 171–172°

(*g*) *Methyl 4,6-O-benzylidene-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside* (**7**) (*i*) *In an atmosphere of air* The unsaturated sugar (490 mg) was heated under reflux with hydrazine (5 ml) for 30 min Water was added to the solution which was worked up in the usual manner Recrystallisation of the product from ethanol gave white crystals (450 mg) which contained two close-moving components (t l c), corresponding to **7** and methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hexopyranoside (**8**) in yields (n m r) of 70 and 23%, respectively

(*ii*) *In an atmosphere of nitrogen* This reaction was performed under nitrogen with conditions otherwise identical to those in (*i*) A quantitative recovery of a white, crystalline material was obtained by the addition of water followed by evaporation of the reaction mixture The n m r spectrum showed a 97% recovery of **7** and 3% formation of the dideoxy sugar **8**

(*h*) *Methyl 4,6-O-benzylidene-2,3-dideoxy-α-D-erythro-hexopyranoside* (**8**) Compound **8** (0 5 g) was treated with hydrazine as in (*i*) above Cooling the solution and the addition of water (20 ml) gave white crystals (470 mg, 94%), m p 83–84°, which were washed well with water and dried The n m r spectrum showed no peaks which could be attributed to the unsaturated compound **7**

(*i*) *Methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino-α-D-mannopyranoside*[3] (**9**) Compound **9** (0 5 g) was heated with hydrazine (5 ml) for 10 min at reflux temperature Water (20 ml) was added to the solution, and the mixture was evaporated The white solid was washed with water and dried to give starting material (497 mg, 99%)

(*j*) *Methyl 3-azido-4,6-O-benzylidene-3-deoxy-2-O-tosyl-α-D-glucopyranoside*[3] (**11**) [**11** (0 5 g), hydrazine (5 ml)] A portion (300 mg) of the product mixture (367 mg) was chromatographed (benzene–chloroform, 1 1) to give bands *A–C* Band *A* (5 mg) was ignored Band *B* (167 mg) gave methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-D-glucopyranoside (44%), m p 146–147°, $[\alpha]_D^{22}$ +61 0° (*c* 1 39) (Found C, 58 4, H, 5 7, N, 3 4 $C_{21}H_{25}NO_7S$ calc C, 57 9, H, 5 8, N, 3 2%) This product was characterised as its *N*-acetyl derivative, m p 208°, $[\alpha]_D^{22}$ +24 6° (*c* 1 115), lit [12] m p 202–203° Band *C* (115 mg) was identified as methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-D-*ribo*-hexopyranoside (31%), m p 122–122 5°, $[\alpha]_D^{22}$ +55 9° (*c* 1 57), lit [13] m p 123 5–124°, $[\alpha]_D^{20}$ +60 1±2° (*c* 2 694)

(*k*) *Methyl 3-azido-4,6-O-benzylidene-3-deoxy-α-D-glucopyranoside*[3] (**12**) [**12** (1 g), hydrazine (10 ml)] P l c (benzene–chloroform, 1 1, 4 passes, and then 2 3, 1 pass) gave bands *A* (364 mg) and *B* (481 mg), the latter was identified as methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucopyranoside (53%), m p 190–191°, lit [12] m p 184–186°

Band *A* was re-chromatographed (benzene–chloroform, 1 1) to give bands *A-1* to *A-3*, the first (8 mg) was not further investigated Band *A-2* (181 mg) was identified as methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*ribo*-hexopyranoside (30%), m p 186–188°, lit [14] m p 187° Band *A-3* (68 mg) was identified as starting material (7%)

(*l*) *Methyl 3-azido-4,6-O-bensylidene-2,3-dideoxy-α-D-arabino-hexopyranoside*[15] (**13**) [**13** (0 5 g), hydrazine (5 ml)] P l c (benzene–chloroform, 1 1, 3 passes), with removal of the fastest moving band (113 mg), gave methyl 4,6-*O*-benzylidene-2,3-

TABLE III

REACTION OF NON DIAXIAL AZIDO-TOSYLOXY SYSTEMS WITH HYDRAZINES

Compound	*Reagent*	*Products* (%)				
		7	*8*	*NH_2/OTs*[a]	*H/OTs*[b]	*Others*
Methyl 3-azido-4,6-*O*-benzylidene-2-*O*-tosyl-α D-glucopyranoside (**11**)	NH_2NH_2	0	0	44	31	
	$NH_2NH_2 \cdot H_2O$	0	0	25	48	One unidentified component, plus starting material (5%)
	$MeNHNH_2$	0	0	53	22	
Methyl 2-azido-4,6-*O*-benzylidene-3-*O*-tosyl-α D-allopyranoside (**14**)	NH_2NH_2	19	17			[c]

[a] Starting-material structure, but with NH_2 in place of N_3. [b] Starting-material structure, but with H in place of N_3. [c] No other identifiable products

TABLE IV

REACTION OF HYDROXY-AZIDO SYSTEMS WITH HYDRAZINES

Compound	*Reagent*	*Products* (%)				
		7	*8*	*NH_2/OH*[a]	*H/OH*[b]	*Others*
Methyl 2-azido-4,6-*O*-benzylidene-α-D-altropyranoside (**2**)	NH_2NH_2	2	6	17	50	Allal **16** (13%)
Methyl 3-azido-4,6-*O*-benzylidene-α-D-altropyranoside (**5**)	NH_2NH_2	0	6	63	7	
	$NH_2NH_2 \cdot H_2O$	15	0	42	0	
	$MeNHNH_2$	0	0	80	0	Starting material (13%)
Methyl 3-azido-4,6-*O*-benzylidene-α-D-glucopyranoside (**12**)	NH_2NH_2	0	0	53	30	Starting material (7%)
Methyl 2-azido-4,6-*O*-benzylidene-α-D-allopyranoside (**15**)	NH_2NH_2	0	3	3	13	Allal **16** (9%), plus 3 components

[a] Starting material, but with NH_2 in place of N_3 [b] Starting material, but with H in place of N_3

TABLE V

REACTION OF AZIDO-DIDEOXY SYSTEMS WITH HYDRAZINES

Compound	*Reagent*	*Products* (%)		
		8	*H/NH₂*[a]	*Others*
Methyl 2-azido 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*ribo*-hexoside (**3**)	NH_2NH_2	28	36	3-Deoxy-allal **17** (10%) + 3 components
	$MeNHNH_2$	15	69	3-Deoxy-allal **17** (4%) + starting material (4%)
Methyl 3-azido 4,6-*O*-benzylidene-2,3-dideoxy-α D-*arabino*-hexoside (**13**)	NH_2NH_2	26	48	3 Minor components
	$NH_2NH_2 \cdot H_2O$	56	42	
	$MeNHNH_2$	9	61	Starting material (26%)

[a]Same as starting material, but with NH_2 in place of N_3.

TABLE VI

MISCELLANEOUS HYDRAZINE REACTIONS

Compound	*Reagent*	*Products* (%)			
		7	**8**	*NH₂/X*[a]	*Others*
Methyl 3 azido 2-*O*-benzyl-4,6-*O* benzylidene-α-D-altropyranoside (**6**)	NH_2NH_2	12	4	67	
	$NH_2NH_2\ H_2O$	0	0	0	S M[b] (50%)
Methyl 4,6-*O*-benzylidene 2,3-di *O*-tosyl-α-D-glucopyranoside (**18**)	NH_2NH_2	0	0		S M. (63%) + four components
	$NH_2NH_2 \cdot H_2O$	0	0		S M (90%)
Methyl 4,6-*O*-benzylidene-2-deoxy-2-*O* tosyl-α-D-*ribo*-hexopyranoside (**19**)	NH_2NH_2	45	13		S M (2%) + one component
Methyl 4,6-*O*-benzylidene 2-deoxy-α-D-*ribo*-hexopyranoside (**20**)	NH_2NH_2	0	0		S M. (91%)

[a]Same as starting material, but with NH_2 in place of N_3 [b]S M = Starting material.

dideoxy-α-D-*erythro*-hexopyranoside (**8**) (26%) Further elution (ether) gave band *B* (35 mg) which contained three components that were not investigated further Continued elution (ether, 3 passes) gave band *C* (217 mg), which was methyl 3-amino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*arabino*-hexopyranoside (48%), characterised as its *N*-acetyl derivative, m p (sublimed) 276–277°, lit [15], sublimation from 240–245°)

(*m*) *Methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-D-allopyranoside* (**14**) [**14** (0 5 g), hydrazine (5 ml)] P l c (ether–light petroleum, 1 1) gave six bands *A–F* Band *A* (98 mg) was shown (n m r , t l c) to be a mixture of **7** (19%) and **8** (17%) Bands *B–F* could not be identified, *B* (25 mg) and *C* (19 mg) were both crystalline, *D* (25 mg), *E* (23 mg), and *F* (270 mg) were dark-yellow syrups

(*n*) *Methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside*[4] (**15**) [**15** (0 95 g), hydrazine (10 ml)] P l c (benzene–chloroform, 1 1, four passes) gave band *A* (424 mg) Further elution with the same solvents (1 2) gave band *B* (23 mg), and with benzene–chloroform–ethanol (1 2 1) gave band *C* (370 mg) Band *A* was re-chromatographed (benzene–chloroform, 2 3, 2 passes) to give band *A 1* (64 mg), identified as the allal **16** (9%), m p 82–83°, band *A 2* (109 mg), shown to be methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside (13%), m p 126–128°, and band *A 3* (23 mg) that was not identified Band *B* was shown to be compound **8** (3%), and band *C* to be methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside (43%), m p 165–166°, lit [16] m p 165°

(*o*) *Methyl 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-α-D-glucopyranoside* (**18**) Compound **18** (1 g) was heated under reflux for 1 h with hydrazine (10 ml) A portion (650 mg) of the product (760 mg) was chromatographed (benzene–chloroform, 1 1) The fastest-moving band (535 mg) was shown to be starting material The remaining four components (86 mg) and the material obtained from the aqueous washings of the crude product (77 mg) were not further investigated

(*p*) *Methyl 4,6-benzylidene-2-deoxy-3-*O*-tosyl-α-D-*ribo*-hexopyranoside* (**19**), [**19** (0 5 g), hydrazine (5 ml)] P l c (benzene–chloroform, 1 1, 3 passes) gave three bands Band *A* (170 mg) was identified as a mixture of **7** (45%) and **8** (13%) Band *C* (10 mg) was shown to be starting material (2%) Band *B* (207 mg) was not identified

(*q*) *Methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside*[5] (**20**) [**20** (0 5 g) hydrazine (5 ml), 15 min at reflux] P l c (benzene–chloroform, 1 1, three passes) separated the mixture The fastest-moving band (455 mg, 91%) was starting material, m p 126–127 5° Two s ower-moving components were not further investigated, but neither appeared to be identical (t l c) with the allal **16**

Reactions with hydrazine hydrate — Reaction times were judged by disappearance (t l c) of starting material, the work-up was as for the hydrazine reactions

(*a*) *Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside* (**5**) Compound **5** (0 5 g) and hydrazine hydrate (10 ml) were refluxed for 2 5 h P l c (benzene–chloroform, 1 1, 3 passes) gave two bands, band *A* (60 mg) was identified as **7** (15%), and band *B* as methyl 3-amino-4,6-O-benzylidene-3-deoxy-α-D-altropyranoside (42%), m p 185–187°

(*b*) *Methyl 3-azido-2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-altropyranoside* (**6**) Compound **6** (0 5 g) and hydrazine hydrate (10 ml) were refluxed for 1 5 h The crude product was crystallised from ether–light petroleum and shown to be starting material (50%), m p 92–93°

(*c*) *Methyl 3-*azido-*4,6-*O*-benzylidene-2-*O*-tosyl-α-*D*-glucopyranoside* (**11**) Compound **11** (0 5 g) was refluxed with hydrazine hydrate (10 ml) for 3 h P l c (benzene–chloroform, 1 1) gave three bands, band *A* (219 mg) was shown to be methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-D-*ribo*-hexopyranoside (48%), m p 121–122 5°, band *B* (112 mg) was methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-D-glucopyranoside (25%), m p 144–145°

(*d*) *Methyl 3-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-*D*-*arabino*-hexopyranoside* (**13**) Compound **13** (0 5 g) was refluxed with hydrazine hydrate (10 ml) for 4 h P l c (benzene–chloroform, 1·1) gave two components that were identified as compound **8** (56%) and methyl 3-amino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*ribo*-hexopyranoside (42%), characterised as its *N*-acetyl derivative, m p 275–276°

(*e*) *Methyl 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-α-*D*-glucopyranoside* (**18**) Reaction of **18** (0 5 g) with hydrazine hydrate (10 ml) for 8 h at reflux gave only starting material (90%)

Reactions with methylhydrazine — The procedure was as for the hydrazine hydrate reactions

(*a*) *Methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-*D*-altropyranoside* (**1**) Compound **1** (1 g) and methylhydrazine (10 ml) were refluxed for 3 h P l c (benzene, 3 passes, benzene–chloroform, 9.1, 2 passes, chloroform, 2 passes; and finally chloroform–ethanol, 95 5) gave bands *A-C* Band *A* (380 mg) was shown to be **7** (71%), band *B* (140 mg) was identified as **9** (22%), band *C* (150 mg) was not carbohydrate in nature (n m r) and was not further investigated

(*b*) *Methyl 2-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-*D*-arabino-hexopyranoside* (**3**) Compound **3** (0 5 g) was refluxed for 8 h with methylhydrazine (5 ml) P l c (benzene) gave bands *A–D* Band *A* (15 mg) was identified as compound **17** (4%), band *B* (18 mg) was starting material (4%), and band *C* (63 mg) was compound **8** (15%) A portion (390 mg) of band *D* (405 mg) was re-chromatographed (benzene–chloroform, 1 1, 2 passes, 1 2, 2 passes) to give bands *D 1* (3 mg) and *D 2* (303 mg). The latter band was shown to be methyl 2-amino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*arabino*-hexopyranoside, characterised as its *N*-acetyl derivative (69%), m p 176–177°

(*c*) *Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-*D*-altropyranoside* (**4**) Compound **4** (1 g) was heated under reflux with methylhydrazine (10 ml) for 2 5 h A portion (320 mg) of the product mixture (540 mg) was chromatographed (p l c, benzene–chloroform, 1 1) and separated into two bands Band *A* (155 mg) was compound **7** (49%), and band *B* (152 mg) was methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allopyranoside (45%)

(*d*) *Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-α-*D*-altropyranoside* (**5**) Compound **5** (1 45 g) and methylhydrazine (15 ml) were heated for 20 h at reflux P l c.

(benzene–chloroform, 1 1, 3 passes) was carried out and band *A* removed Further elution (benzene–chloroform–methanol, 45 45 10, 4 passes, chloroform, 2 passes) gave band *B* Band *A* (193 mg) was identified as starting material (13%), and band *B* (1 085 g) was methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside (80%), m p 189–191°

(*e*) *Methyl 3-azido-4,6-O-benzylidene-3-deoxy-2-O-tosyl-α-D-glucopyranoside* (**11**). The glucoside **11** (0 5 g) was heated under reflux with methylhydrazine for 5 h The product was chromatographed (benzene–chloroform, 1 1) and separated into two main bands *A* and *B* Band *A* (126 mg) was a mixture of starting material and another component, and was rechromatographed The fastest-moving component (25 mg, 5%) was unreated starting material, and the other component was methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-D-*ribo*-hexopyranoside (100 mg, 22%), m p 121 5–122 5°

The white, crystalline material obtained from band *B* was methyl 3-amino-4,6-*O* benzylidene-3-deoxy-2-*O*-tosyl-α-D-glucopyranoside (250 mg, 53%), m p 145 5–146 5°, characterised as its *N*-acetyl derivative, m p 208°

(*f*) *Methyl 3-azido-4,6-O-benzylidene-2,4-dideoxy-α-D-arabino-hexopyranoside* (**13**) Compound **13** (1 0 g) and methylhydrazine (10 ml) were refluxed for 8 h P l c (benzene–chloroform, 1 2, 2 passes; chloroform, 2 passes, and chloroform–methanol, 9 1) gave bands *A–C* Band *A* (264 mg) was starting material (26%) Band *B* (75 mg) was the dideoxy compound **8** (9%) Band *C* (558 mg) was *N*-acetylated to give methyl 3-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*arabino*-hexopyranoside, m p 274–275° The yield ofthe amino compound from the reaction was 61%

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