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PHOTOCHEMISTRY OF GLYCOSYL AZIDES—II[a]

INVESTIGATION OF THE DUAL BEHAVIOR: FORMATION OF A REVERSIBLE INTERMEDIATE AND CHAIN-DEGRADATION

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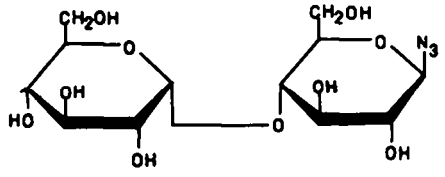
Abstract—The photochemistry of glycosyl azides has been studied. Some of the azides, for example, β-D-glucopyranosyl or α-D-mannopyranosyl azide, were found to afford in good yield, on irradiation with UV light, the corresponding next-lower aldose. In other cases, for example, β-maltosyl or β-D-ribofuranosyl azide, there was observed the formation of an intermediate which, on standing in the dark, reverts back to starting material. A rationalization of the two types of behavior is suggested.

In a previous communication[1] from this laboratory, some preliminary results of an investigation of the photochemistry of glycosyl azides were reported. It was found that irradiation with UV light of a methanolic solution of β-D-glucopyranosyl (1) or α-D-mannopyranosyl (3) azide afforded in good yield the next-lower aldose, namely, D-arabinose (2); analogously, β-D-galactopyranosyl azide (4) gave D-lyxose (5) in 65% yield. However, in the case of β-maltosyl (6), β-D-ribofuranosyl (7), or α-L-arabinopyranosyl (8) azide, there was observed the formation of an intermediate which, on standing in the dark, reverts back to starting material. Although the photochemistry of various types of organic azides has been extensively studied,[2,3] the two types of behavior exhibited by the glycosyl azides are unusual. In the present article, full details of the above work are described and, on the basis of the results of an investigation of the dual behavior, a rationalization of the phenomena is proposed.



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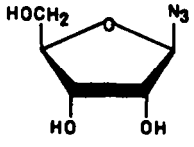

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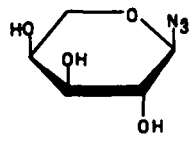

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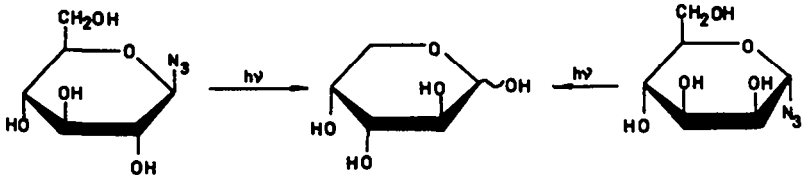
The unexpected result obtained with β-maltosyl azide (6, 4-O-α-D-glucopyranosyl-β-D-glucopyranosyl azide) prompted initially an investigation of the photochemistry of β-cellobiosyl azide (9, 4-O-β-D-glucopyranosyl-β-D-glucopyranosy azide). When compound 9



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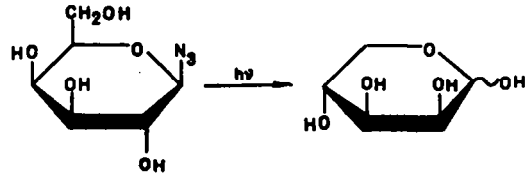

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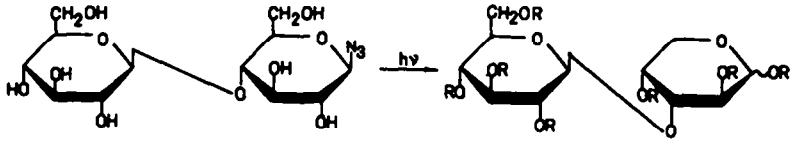
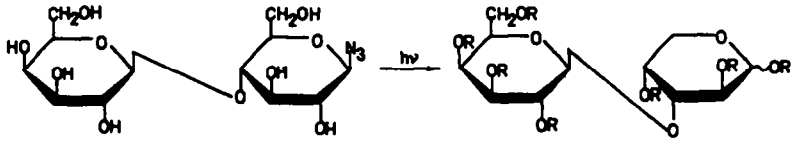
was irradiated in methanol, TLC indicated after 4 hr that all of the starting compound had been converted into a slower-moving material and a nonmigrating component; no change was observed, even after 24 hr. The slower-moving component was isolated by column chromatography and, on acid-catalyzed hydrolysis, yielded two compounds which were identified by paper chromatography as glucose and arabinose; thus, the component was, presumably, 3-O-β-D-glucopyranosyl-D-arabinose (**10**, R=H). In a separate experiment, β-cellobiosyl azide (**9**) was irradiated for ~3 hr, and the reaction mixture was treated with acetic anhydride-pyridine; a crystalline heptaacetate, presumably, 3-O-β-D-glucopyranosyl-D-arabinose heptaacetate (**10**, R=Ac), was obtained in 53% yield. Analogously, β-lactosyl azide (**11**, 4-O-β-D-galactopyranosyl-β-D-glucopyranosyl azide) underwent, on UV irradiation, a degradation to a hexopyranosylpentose (**12**, R=H); a heptaacetate (**12**, R=Ac) could again be obtained, in 51% yield.

irradiated. A particularly significant result was that obtained from the irradiation of 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl azide (**13**). It was found that treatment of the methanolic solution of the photoproduct with an acidic ion-exchange resin afforded, in 37% yield, crystalline methyl 2,3,4,6-tetra-O-acetyl-D-gluconate (**15**). The structure of **15** was assigned to the crystalline compound on the basis of its ^{1}H-NMR spectrum (Experimental). Moreover, the methyl ester had the same m.p., TLC mobility, and ^{1}H-NMR spectrum as the compound obtained by treatment with diazomethane of the acetylated gluconic acid derived[4] from D-glucono-1,5-lactone. The formation of compound **15** from the photoproduct can be reasonably explained by formulation of the latter as the D-gluconoimino-1,5-lactone **14**. Compound **14** might be considered to arise, on photolysis of the azide **13**, by elimination of molecular nitrogen and the intermediacy of a nitrene. Significantly, the formation of a reversible intermediate or a chain-degradation was also not observed on



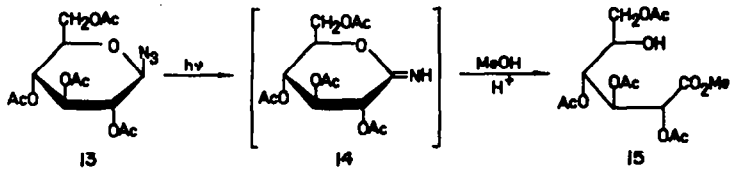
9 **10**



11 **12**

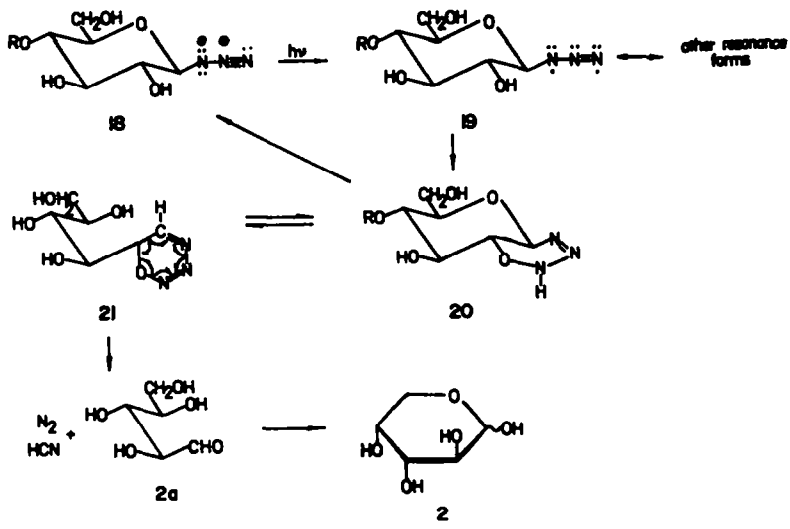
The above results indicate that the irradiation with UV light of appropriate glycosyl azides should be a convenient one-carbon, chain-shortening procedure in synthetic carbohydrate chemistry. However, the results obtained in the case of β-maltosyl (**6**), β-D-ribofuranosyl (**7**), or α-L-arabinopyranosyl (**8**) azide were clearly puzzling. In an effort to gain an insight into the structural features required for the photochemical degradation, a number of substituted, monomeric glycosyl azides were irradiated. A particularly significant result was that obtained from the irradiation of 2-deoxy-β-D-*arabino*-hexopyranosyl azide (**16**) or 2-O-methyl-β-D-glucopyranosyl azide (**17**). The results obtained with compounds **13**, **16**, and **17** suggested the involvement of a free OH group, on the carbon adjacent to that bearing the azido function, in the two processes observed with the other glycosyl azides.

An attractive rationalization of the two processes is outlined in Scheme 1, using β-D-glucopyranosyl (**18**, R=H) and β-maltosyl (**18**, R = α-D-glucopyranosyl)



13 **14** **15**

16 **17**

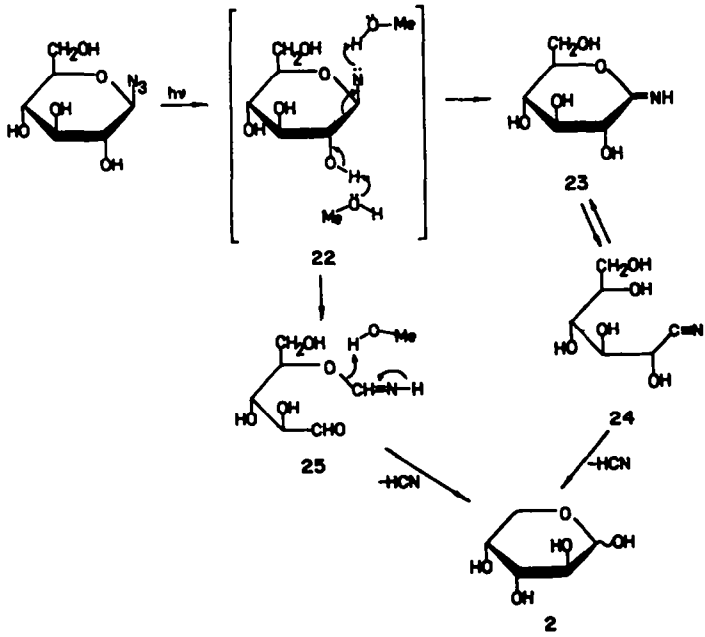


Scheme 1.

azides as examples. According to this suggestion, excitation of the azido group in **18** is followed by intramolecular azide insertion into the O–H bond of the hydroxyl group at C-2 to give the intermediate **20**.† This intermediate might revert to the starting azide, as in the case of β-maltosyl azide (**18**, R = α-D-glucopyranosyl), or might yield the next-lower aldose by way of fragmentation of the tautomer **21**, as in the case of β-D-glucopyranosyl azide (**18**, R=H). Support for this fragmentation was provided by the polarographic detection of hydrogen cyanide‡ during the irradiation of β-D-glucopyranosyl azide (**18**, R=H). The liberation of hydrogen cyanide, however, is also consistent with two other possible mechanisms for the degradation process, each involving the intermediacy of a β-hydroxy nitrene (**22**) (Scheme 2). In one pathway, **22** may rearrange by a 1,2-hydrogen migration to give D-gluconoimino-1,5-lactone (**23**), which undergoes a tautomeric ring-opening to afford D-gluconononitrile (**24**); loss of hydrogen cyanide from **24** yields D-arabinose (**2**). An analogous mechanism has been proposed by Binkley and Binkley[7] to account for the light-induced, one-carbon degradation of sugar oximes. In the second pathway, the nitrene **22** is considered to rearrange to **25**, which by loss of hydrogen cyanide gives D-arabinose (**2**). The intermediacy of a β-hydroxy nitrene has been postulated previously by

†Paulsen *et al.*[5] have recently shown that glycosyl azides, like methyl glycopyranosides, exhibit an *exo*-anomeric effect, the result being that the azido group, in the ground state, is oriented towards the ring oxygen; however, in the excited state the polarization is presumably the reverse of that indicated in **18**, *that is, the α-nitrogen is electron-deficient relative to the ground state* (Ref. 6).

‡We thank Prof. J. A. Page for these measurements.



Scheme 2.

Wechter[8] in photochemical reactions of 5α-hydroxy-6β-azido steroids. It is possible, however, to rationalize the formation of D-gluconoimino-1,5-lactone (**23**) and of **25** without invoking the nitrene **22**; instead, **23** and **25** may arise by synchronous processes involving the elimination of molecular nitrogen from the excited azide (see Refs. 3 and 6*c*). It is clearly very difficult to distinguish between the various mechanistic possibilities. Moreover, the effect responsible for either chain-degradation or the reversal to the starting azide in a particular case is not immediately apparent. However, the work described in this paper at least indicates that a free hydroxyl group on the carbon adjacent to that bearing the azido function is a requisite structural feature for the operation of the two processes.

EXPERIMENTAL

General. M.ps were determined on a Fisher–Johns m.p. apparatus and uncorrected. IR spectra were recorded with a Unicam SP 1000 spectrophotometer. UV spectra were recorded in methanol with a Unicam SP 800B spectrophotometer. Proton magnetic resonance (PMR) spectra were recorded at 60 MHz in chloroform-*d* with tetramethylsilane (TMS) as the internal standard, unless otherwise stated. Carbon-13 magnetic resonance (CMR) spectra were recorded in acetone-d_6 on a Bruker HX-60 spectrometer equipped with a FT60M Fourier transform accessory at 15.1 MHz, with TMS as the internal standard; chemical shifts (δ_C) are given in parts per million downfield from TMS. Optical rotations were measured with a Perkin–Elmer Model 141 automatic polarimeter at 20°. TLC was performed on Silica Gel G as the adsorbent. The air-dried plates were sprayed with 10% aqueous sulfuric acid containing 1% of cerium sulfate and 1.5% of molybdic acid, and heated at ~ 150°. Column chromatography was performed on Silica Gel 60 (70–230 mesh, Merck).

General procedure for the preparation of glycosyl azides

β-D-Glucopyranosyl azide (**1**). The general procedure is illustrated by the synthesis of **1**. Tetra-O-acetyl-α-D-glucopyranosyl bromide (147 g, 0.357 mole, 64%) was prepared from D-glucose (100 g, 0.555 mole) by the method of Lemieux.[9] The bromide (47 g, 0.114 mole) was added to a stirred mixture of dry acetonitrile (250 ml) and sodium azide (27 g, 0.415 mole), and the mixture was refluxed for 4–10 hr, when TLC [$CHCl_3$–MeOH, 97:3 (v/v)] showed that the bromide had all been consumed. The mixture was filtered, and the filtrate was evaporated under reduced pressure to yield a semi-crystalline residue (44.6 g). This material was recrystallized from EtOH to afford tetra-O-acetyl-β-D-glucopyranosyl azide (**13**) as white crystals (27.9 g, 0.075 mole, 65%), m.p. 127.5–129°, $[\alpha]_D$ − 31.5° (*c*, 2.0 in $CHCl_3$) [lit.:[10] m.p. 129°, $[\alpha]_D$ − 33° (*c*, 2.49 in $CHCl_3$)]; UV: λ_{max} 272 nm (ε 36.6); IR: ν_{max}^{Nujol} 2120 (N_3), 1760 cm^{-1} (C=O); PMR: δ 4.53–5.33 (m, 4H, H-1, -2, -3, -4), 3.77 (m, 1H, H-5), 4.17–4.32 (m, 2H, H-6, -6'), 2.00 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.09 (s, 3H, OAc).

Compound **13** (16.5 g, 0.044 mole) was added to a stirred NaOMe solution prepared from 0.25 g of sodium and 120 ml of dry MeOH. (Alternatively, the Na can be dissolved in 10 ml of dry MeOH and the soln added to the mixture.) After 45 min, all of compound **13** had dissolved, and TLC [$CHCl_3$–MeOH, 97:3 (v/v)] showed only the presence of nonmigrating material. The pale yellow soln was neutralized with Rexyn 102 (H^+ form) ion-exchange resin and filtered; the filtrate was evaporated to yield a syrup (9.5 g). Crystallization from 1-pentanol afforded **1** (7.5 g, 0.037 mole, 83%), m.p. 86–89°, $[\alpha]_D$ − 30.8° (*c*, 2.0 in H_2O) [lit.:[11] m.p. 89°, $[\alpha]_D$ − 29.6° (*c*, 1.6 in H_2O)]; UV: λ_{max} 274 nm (ε 34.5); IR: ν_{max}^{Nujol} 3440 (OH), 2120 cm^{-1} (N_3); CMR: δ_C 91.3 (C-1), 74.5 (C-2), 77.9 (C-3), 70.9 (C-4), 79.6 (C-5), 62.5 (C-6).

α-D-Mannopyranosyl azide (**3**). α-D-Mannopyranosyl azide (**3**) was prepared from D-mannose (50 g) according to the general procedure. TLC [benzene–EtOAc–MeOH, 3:2:2 (v/v)] revealed the resulting syrup as three components. Column chromatography afforded a sample (3.5 g) which was treated with NaOMe in the usual fashion; the product was chromatographed to afford a syrup (1.65 g). Crystallization from EtOH gave compound **3**, m.p. 120–121°, $[\alpha]_D$ + 223° (*c*, 1.0 in H_2O); UV: λ_{max} 273 nm (ε 29.4); IR: ν_{max}^{Nujol} 3460 (OH), 2130 cm^{-1} (N_3). (Found: C, 35.41; H, 5.32; N, 20.50. Calc. for $C_6H_{11}O_5N_3$: C, 35.12; H, 5.36; N, 20.49%).

β-D-Galactopyranosyl azide (**4**). β-D-Galactopyranosyl azide (**4**) was prepared from D-galactose according to the general procedure. Crystallization of the resulting syrup from acetonitrile gave the azide **4**, m.p. 152–153° (decomp), $[\alpha]_D$ + 7.8° (*c*, 2.3 in H_2O) [lit.:[12] m.p. 152°, $[\alpha]_D$ + 8.5° (H_2O)]; UV: λ_{max} 275 nm (ε 36.1); IR: ν_{max}^{Nujol} 3400 (OH), 2130 cm^{-1} (N_3).

The intermediate tetra-O-acetyl-β-D-galactopyranosyl azide was crystallized from acetonitrile to give a product having m.p. 93–94°, $[\alpha]_D$ − 18° (*c*, 1.0 in $CHCl_3$) [lit.:[13] m.p. 96°, $[\alpha]_D$ − 16.2° (*c*, 1.0 in $CHCl_3$)]; UV: λ_{max} 273 nm (ε 41.5); IR: ν_{max}^{Nujol} 2125 (N_3), 1755 cm^{-1} (C=O).

β-D-Maltosyl azide (**6**). Octa-O-acetyl-β-D-maltose was prepared by the method of Wolfrom and Thompson[14] from D-maltose. The acetate (5.0 g, 0.0074 mole) was dissolved in AcOH (17 ml), and the soln was cooled to 0°. A saturated soln (11 ml) of HBr in AcOH was added, and the soln was kept at 0° for 1 hr and at room temp. for 1.5 hr. The solution was poured into ice-water, and the mixture was extracted with $CHCl_3$ (70 ml). The extract was washed with ice-water, dried over $CaCl_2$, and evaporated under reduced pressure to yield a syrup. The syrup was dissolved in acetonitrile, and the soln was treated with sodium azide and processed according to the general procedure to yield a syrup. Column chromatography, using 3:2 (v/v) benzene–EtOAc as eluant, afforded crystals (3.1 g, 0.0047 mole, 64%) which, after recrystallization from 1:1 (v/v) water–MeOH, had m.p. 88–90° $[\alpha]_D$ + 50° (*c*, 5.0 in $CHCl_3$) [lit.:[10] m.p. 91°, $[\alpha]_D^{18}$ + 53° (*c*, 1.0 in $CHCl_3$)]; UV: λ_{max} 272 nm (ε 50.1); IR: ν_{max}^{Nujol} 2125 (N_3), 1750 cm^{-1} (C=O).

A sample of hepta-O-acetyl-β-D-maltosyl azide (4.2 g, 0.0063 mole) was treated with NaOMe soln, and the mixture was processed in the usual fashion as described in the general procedure to give **6** as a hygroscopic glass (1.8 g, 0.0049 mole, 78%) which had $[\alpha]_D$ + 75° (*c*, 1.0 in H_2O); UV: λ_{max} 274 nm (ε 35.7); IR: ν_{max}^{Nujol} 3500 (OH), 2125 cm^{-1} (N_3).

β-D-Ribofuranosyl azide (**7**). 1-O-Acetyl-2,3,5-tri-O-benzoyl-β-D-ribofuranose was prepared from D-ribose by the method of Recondo and Rinderknecht.[15] The 1-O-acetyl compound was converted into 2,3,5-tri-O-benzoyl-α,β-D-ribofuranosyl bromide by the method of Fletcher *et al.*[16] using a saturated soln of HBr in dry CH_2Cl_2. The crude bromide (25 g) was treated with sodium azide (15 g) according to the general procedure to give a syrup. Column chromatography, using 5:3:1 (v/v) EtOAc–petroleum ether (b.p. 60–80°)–MeOH as eluant, yielded 2,3,5-tri-O-benzoyl-β-D-ribofuranosyl azide as a colorless syrup, $[\alpha]_D$ − 41° (*c*, 1.0 in $CHCl_3$) [lit.:[17] m.p. 63–64°, $[\alpha]_D^{22}$ − 41.2° (*c*, 2.97 in $CHCl_3$)]; IR: ν_{max}^{Film} 2130 (N_3), 1750 cm^{-1} (C=O).

The compound (15 g) obtained above was O-debenzoylated with NaOMe in the usual fashion to afford a syrupy product. Column chromatography, using 3:2 (v/v) petroleum ether (b.p. 60–80°)–ethyl acetate as eluant, gave β-D-ribofuranosyl azide (**7**) as a pale yellow oil, $[\alpha]_D$ − 194° (*c*, 2.15 in H_2O) [lit.:[17] $[\alpha]_D$ − 193° (*c*, 1.77 in H_2O)]; UV: λ_{max} 275 nm (ε 41.9); IR: ν_{max}^{Nujol} 3480 (OH), 2120 cm^{-1} (N_3).

α-L-Arabinopyranosyl azide (**8**). According to the procedure of Brauns,[18] 2,3,4-tri-O-acetyl-α-L-arabinopyranosyl chloride was prepared from L-arabinose using acetyl chloride and zinc chloride; the product, recrystallized from ether, had m.p. 150–153° and gave a positive Beilstein test. The chloride (18 g, 0.061 mole) was dissolved in dry N,N-dimethylformamide (150 ml), and sodium azide (20 g) was added. The stirred mixture was heated at 110–125° for 6 hr, allowed to stand overnight, and then filtered. The filtrate was evaporated under reduced pressure to yield a black syrup. The syrup was dissolved in chloroform, and the soln was washed 3 times with water, dried over Na_2SO_4, and evaporated under reduced pressure to yield a syrup (15 g). Column chromatography, using 3:2 (v/v) petroleum ether (b.p. 60–80°)–ethyl acetate as eluant, afforded 2,3,4-tri-O-acetyl-α-L-arabinopyranosyl azide (7.28 g, 0.024 mole, 40%). After recrys-

tallization from MeOH, the compound had m.p. 86.5–88°, $[\alpha]_D$ − 18° (*c*, 4.05 in $CHCl_3$) [lit.:[10] m.p. 88–89°, $[\alpha]_D$ − 11.0° (*c*, 1.0 in $CHCl_3$)]; UV: λ_{max} 273 nm (ϵ 34.2); IR: ν_{max}^{Nujol} 2110 (N_3), 1750 cm^{-1} (C=O); PMR: δ 4.58 (bd, 1H, $J_{1,2}$ = 6.0 Hz, H-1), 5.05–5.43 (m, 3H, H-2, -3, -4), 3.73 (dd, 1H, $J_{5,5'}$ = 13.0 Hz, $J_{4,5'} \simeq$ 1.0 Hz, H-5), 4.15 (dd, 1H, $J_{4,5'}$ = 2.5 Hz, H-5'), 2.03 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.17 (s, 3H, OAc). (Found: C, 44.00; H, 4.94; N, 13.81. Calc. for $C_{11}H_{15}O_7N_3$: C, 43.85; H, 5.02; N, 13.95%).

A sample (7.0 g, 0.023 mole) of the compound prepared above was treated with NaOMe (see general procedure), and the resulting product was chromatographed, using 1:1 (v/v) benzene–EtOH as eluant, to afford a crystalline material (3.08 g, 0.018 mole, 76%). Recrystallization from 2-propanol gave **8**, m.p. 107–109°, $[\alpha]_D$ + 21.8° (*c*, 3.3 in H_2O); UV: λ_{max} 274 nm (ϵ 40.7); IR: ν_{max}^{Nujol} 3450 (OH), 2120 cm^{-1} (N_3). (Found: C, 34.17; H, 5.10; N, 23.77. Calc. for $C_5H_9O_4N_3$: C, 34.29; H, 5.18; N, 23.99%).

β-D-Cellobiosyl azide (**9**). Octa-O-acetyl-β-D-cellobiose (10.0 g, 0.015 mole) was converted into crystalline hepta-O-acetyl-D-cellobiosyl bromide (9.6 g, 0.014 mole, 91%) by the procedure established for the preparation of hepta-O-acetyl-β-D-maltosyl bromide (see above). After recrystallization from benzene, the bromide gave a positive Beilstein test and had m.p. 170–172°, $[\alpha]_D$ + 92° (*c*, 1.0 in $CHCl_3$) [lit.:[19] m.p. 184°, $[\alpha]_D$ + 93 ± 2° (*c*, 1.0 in $CHCH_3$)].

A soln of the bromide (5.0 g, 0.0071 mole) in N,N-dimethylformamide (30 ml) was treated with sodium azide (5 g) at 80–90° for 3.5 hr and at room temp. for 2 hr. The mixture was processed by the procedure established for 2,3,4-tri-O-acetyl-α-L-arabinopyranosyl azide (see above) to yield a crystalline material. Recrystallization from MeOH gave the acetylated azide (3.5 g, 0.0053 mole, 75%), m.p. 180–182° (decomp), $[\alpha]_D$ − 29.3° (*c*, 2.15 in $CHCl_3$) [lit.:[10] m.p. 182–182.5°, $[\alpha]_D^{16}$ − 30.9° (*c*, 1.0 in $CHCl_3$)]; UV: λ_{max} 272 nm (ϵ 37.7); IR: ν_{max}^{Nujol} 2120 (N_3), 1760 cm^{-1} (C=O). The PMR spectrum showed the presence of 7 acetyl groups (δ 1.95–2.23) and 14 sugar protons (δ 3.47–5.43).

A sample (9 g, 0.014 mole) of hepta-O-acetyl-β-D-cellobiosyl azide was treated with sodium azide (general procedure) to yield a syrupy product. Column chromatography, using 3:2 (v/v) chloroform–methanol as eluant, afforded compound **9** as a glass (4.1 g, 0.011 mole, 80%), $[\alpha]_D$ − 24° (*c*, 1.0 in H_2O), IR: ν_{max}^{Nujol} 3480 (OH), 2120 cm^{-1} (N_3).

β-D-Lactosyl azide (**11**). According to the procedure established for the preparation of **9** (see above), **11** was prepared from octa-O-acetyl-D-lactose. The product was recrystallized from MeOH and then had m.p. 167–168°, $[\alpha]_D$ − 8.7° (*c*, 1.26 in H_2O); UV: λ_{max} 275 nm (ϵ 35.9); IR: ν_{max}^{KBr} 3440 (OH), 2120 cm^{-1} (N_3). (Found: C, 39.57; H, 6.01; N, 11.17. Calc. for $C_{12}H_{21}O_{10}N_3$: C, 39.24; H, 5.76; N, 11.44%).

The intermediate hepta-O-acetyl-D-lactosyl bromide was crystallized from EtOAc-ether and had $[\alpha]_D$ + 102.1° ($CHCl_3$) [lit.:[20] m.p. 141–142°, $[\alpha]_D$ + 107.2° (*c*, 0.72 in $CHCl_3$)]. The intermediate hepta-O-acetyl-β-D-lactosyl azide was an amorphous powder, $[\alpha]_D$ − 20.5° (*c*, 3.82 in $CHCl_3$); UV: λ_{max} 273 nm (ϵ 64.7); IR: ν_{max}^{Film} 2105 (N_3), 1750 cm^{-1} (C=O); PMR: δ 3.67–5.47 (m, 14H, sugar protons), 1.95 (s, 3H, OAc), 2.05 (s, 12H, 4 OAc), 2.13 (s. 6H, 2 OAc).

Methyl 2,3,4,6-tetra-O-acetyl-D-gluconate (**15**). 2,3,4,6-Tetra-O-acetyl-D-gluconic acid (6 g) was prepared by the method of Major and Cook[4] by dissolving D-glucono-1,5-lactone (5 g) in a soln of $ZnCl_2$ and Ac_2O. The acid (0.72 g, 0.002 mole) was suspended in a mixture of ether and $CHCl_3$ and an excess of freshly prepared diazomethane was added to the mixture. The mixture was evaporated, and the residue was recrystallized from benzene to give **15** (0.68 g, 0.0018 mole, 90%), m.p. 112–113.5°, $[\alpha]_D$ + 16.9° (*c*, 3.2 in $CHCl_3$) [lit.:[21] m.p. 113–114°, $[\alpha]_D$ + 16.8° (*c*, 4.35 in $CHCl_3$)]; IR: ν_{max}^{Nujol} 3530, 3480 (OH), 1750 cm^{-1} (C=O); PMR (100 MHz, $CDCl_3$): δ 5.31 (d, 1H, $J_{2,3}$ = 4.0 Hz, H-2), 5.72 (t, 1H, $J_{3,4}$ = 4.0 Hz, H-3), 5.20 (dd, 1H, $J_{4,5}$ = 8.0 Hz, H-4), 3.86 (sextet, 1H, $J_{5,6}$ = 4.5 Hz, H-5), 4.13 (d, 2H, H-6, -6'), 3.73 (s, 3H, OCH_3), 2.09 (s, 6H, 2 OAc), 2.12 (s, 3H, OAc), 2.15 (s, 3H, OAc).

2-Deoxy-β-D-arabino-hexopyranosyl azide (**16**). Tri-O-acetyl-D-glucal (5.44 g, 0.02 mole) was dissolved in dry benzene and the soln was saturated with dry HBr for 1.5 hr. The soln was evaporated under reduced pressure, the residue was dissolved in benzene, and the soln evaporated again. The residue was dissolved in N,N-dimethylformamide (20 ml) containing sodium azide (5.2 g). The mixture was stirred overnight and then diluted with $CHCl_3$ (100 ml), washed twice with water, dried over $MgSO_4$, and evaporated under reduced pressure to yield a syrup (5.4 g) which was revealed as two components in TLC [petroleum ether (b.p. 60–80°)–$CHCl_3$–acetone, 7:2:1 (v/v)]. Column chromatography afforded 3,4,6-tri-O-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl azide (1.24 g, 0.004 mole, 20%). Two recrystallizations from ether–petroleum ether (b.p. 30–60°) afforded the product as colorless needles, m.p. 57–57.5°, $[\alpha]_D$ − 32.0° (*c*, 0.75 in $CHCl_3$); IR: ν_{max}^{KBr} 2100 (N_3), 1745 cm^{-1} (C=O); PMR (100 MHz, $CDCl_3$); δ 4.80 (dd, 1H, $J_{1,2ax}$ = 10.5 Hz, $J_{1,2eq}$ = 2.25 Hz, H-1), 1.58–1.88 (m, 1H, H-2ax), 2.20–2.41 (m, 1H, H-2eq), 4.92–5.10 (m, 2H, H-3, -4), 3.71 (octet, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 4.9 Hz, $J_{5,6'}$ = 2.5 Hz, H-5), 4.14 (dd, 1H, $J_{6,6'}$ = 12.5 Hz, H-6'), 4.33 (dd, 1H, H-6), 2.02 (s, 3H, OAc), 2.03 (s, 3, OAc), 2.08 (s, 3, OAc). (Found: C, 46.02; H, 5.68; N, 13.45. Calc. for $C_{12}H_{17}O_7N_3$: C, 45.71; H, 5.44; N, 13.33%).

A sample (0.323 g) of 3,4,6-tri-O-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl azide was dissolved in dry MeOH (25 ml), and a small lump of Na was added. After 40 min TLC [$CHCl_3$–MeOH, 95:5 (v/v)] showed the consumption of the starting material. The soln was neutralized with ion-exchange resin (H^+ form) and filtered. Azide **16** was not isolated; instead, the filtrate was employed in the irradiation experiment (see below) in order to obviate the possible elimination of hydrazoic acid.

2-O-Methyl-β-D-glucopyranosyl azide (**17**). Compound **1** (6.1 g, 0.03 mole), α,α-dimethoxytoluene (5.0 g, 0.033 mole), and *p*-toluenesulfonic acid monohydrate (0.5 g) were dissolved in dry N,N-dimethylformamide (20 ml) and the soln was heated, with stirring, at 55–60° for 2 hr; TLC [$CHCl_3$–MeOH, 95:5 (v/v)] showed that the reaction was complete. The mixture was diluted with CH_2Cl_2, washed with $NaHCO_3$ aq and water, dried over Na_2SO_4, and evaporated under reduced pressure. Crystallization of the residue from benzene afforded 4,6-O-benzylidene-β-D-glucopyranosyl azide (5.99 g, 0.02 mole, 67%), m.p. 158–159°, $[\alpha]_D$ − 57.7° (*c*, 1.75 in acetone); IR: ν_{max}^{KBr} 3420, 3280 (OH), 2110 cm^{-1} (N_3); PMR [$CDCl_3$–$(CD_3)_2C{=}O$]; δ 4.67 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 2.8–4.93 (m, 8H, H-2, -3, -4, -5, -6, -6', 2 OH), 7.33 (m, 5H, Ph), 5.55 (s, 1H, PhC<u>H</u>). (Found: C, 53.09; H, 5.23; N, 14.21. Calc. for $C_{13}H_{15}O_5N_3$: C, 53.24; H, 5.16; N, 14.33%).

A sample (1.914 g, 0.0065 mole) of 4,6-O-benzylidene-β-D-glucopyranosyl azide was dissolved in a soln of pyridine (5 ml) and CH_2Cl_2 (15 ml), and the soln was cooled in an ice-water bath. Benzoyl chloride (0.918 g, 0.0065 mole) dissolved in CH_2Cl_2 (5 ml) was added to the soln. The solution was kept at room temp. for 2 hr. TLC [benzene–EtOAc, 95:5 (v/v)] showed the presence of three new components and of a trace of starting material. The mixture was diluted with $CHCl_3$ (100 ml), and then was washed successively with 5% HCl aq, $NaHCO_3$ aq, and water, dried over $MgSO_4$, and evaporated under reduced pressure to yield a solid residue (2.386 g). Column chromatography, using 95:5 (v/v) benzene–EtOAc as eluant, afforded 3-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl azide (1.281 g, 0.0032 mole, 50%) which, after recrystallization from MeOH, was obtained as colorless needles, m.p. 180–181°, $[\alpha]_D$ − 107° (*c*, 2.2 in $CHCl_3$); IR: ν_{max}^{KBr} 3500 (OH), 2120 (N_3), 1735, 1715 cm^{-1} (C=O); PMR: δ 4.74 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 3.17–4.03 (m, 5H, H-2, -4, -5, -6ax, OH), 5.49 (t, 1H, $J_{2,3} = J_{3,4}$ = 9.0 Hz, H-3), 4.39 (dd, 1H, $J_{5,6eq}$ = 4.0 Hz, $J_{6ax,6eq}$ = 10.0 Hz, H-6eq), 5.52 (s, 1H, PhC<u>H</u>), 7.33 (m, 5, <u>Ph</u>CH), 7.17–8.25 (m, 5H, <u>Ph</u>C=O). Double-resonance experiments showed that signals at δ 4.74 and 5.49 were not coupled, and it was concluded, therefore, that the O-benzoyl group was attached to C-3. (Found: C, 60.46; H, 4.72; N, 10.55. Calc. for $C_{20}H_{19}O_6N_3$: C, 60.45; H, 4.82; N, 10.58%).

A sample (0.708 g, 0.0018 mole) of 3-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl azide was dissolved in MeI, and to the soln was added Ag_2O (1.0 g). The stirred mixture was heated at reflux temp. for 1 hr, then cooled, diluted with benzene, and filtered; the filtrate was evaporated under reduced pressure to yield a syrup. Column chromatography, using 9:1 (v/v) benzene–EtOAc as eluant, afforded a homogeneous (TLC) sample of 3 - O - benzoyl - 4,6 - O - benzylidene - 2 - O - methyl - β - D -

glucopyranosyl azide (0.65 g, 0.0016 mole, 88%). PMR: δ 4.73 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 3.27 (t, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 5.53 (t, 1H, $J_{3,4}$ = 9.0 Hz, H-3), 3.37–4.00 (m, 3H, H-4, -5, -6ax), 4.35 (m, 1H, H-6eq), 3.50 (s, 3H, OCH_3), 5.43 (s, 1H, PhCH), 7.27 (m, 5H, PhCH), 7.05–8.17 (m, PhC=O).

The above product (0.65 g, 0.0016 mole) was dissolved in dry MeOH (50 ml), and a small lump of Na was added. The soln was kept overnight, and then processed in the usual manner (see above) to yield a homogeneous (TLC, benzene–EtOAc, 9:1 (v/v)] sample of 4,6-O-benzylidene-2-O-methyl-β-D-glucopyranosyl azide (0.48 g, 0.00156 mole, 98%). After recrystallization from MeOH the compound had m.p. 98.5–99.5°, $[\alpha]_D$ – 49° (*c*, 1.95 in $CHCl_3$); IR: ν_{max}^{Nujol} 3450 (OH), 2110 cm^{-1} (N_3); PMR: δ 4.57 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 2.97 (t, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 3.27–3.93 (m, 5H, H-3, -4, -5, -6ax, OH), 4.33 (m, 1H, H-6eq), 3.62 (s, 3H, OCH_3), 5.50 (s, 1H, PhCH), 7.37 (m, 5H, Ph). Double-resonance experiments showed that the signals at δ 4.57 and 2.97 were coupled and thus confirming that the OMe group was attached to C-2.

A sample (0.40 g, 0.0013 mole) of 4,6-O-benzylidene-2-O-methyl-β-D-glucopyranosyl azide was dissolved in 2 ml of 1:1 (v/v) water–AcOH, and the soln was heated on a steam bath for 15 min; TLC [EtOAc–EtOH–water, 45: 5:3 (v/v)] indicated the consumption of starting material. Evaporation of the solution under reduced pressure afforded a syrup, which was dissolved in water. The aqueous solution was washed with petroleum ether (b.p. 60–80°) and evaporated to give 17 (0.27 g, 0.0012 mole, 94%) as a syrup, IR: ν_{max}^{Film} 3460 (OH), 2115 cm^{-1} (N_3). Compound 17 was characterized as its tri-O-acetyl derivative by treatment with a 1:1 mixture of Ac_2O–pyridine overnight. Two recrystallizations of the product from MeOH gave 3,4,6-tri-O-acetyl-2-O-methyl-β-D-glucopyranosyl azide as colorless needles which had m.p. 106–107.5°, $[\alpha]_D$ – 2.5° (*c*, 1.98 in $CHCl_3$); IR: ν_{max}^{Film} 2120 (N_3), 1755 cm^{-1} (C=O); PMR: δ 4.67 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1), 3.17 (t, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 4.85–5.35 (m, 2H, H-3, -4), 3.77 (m, 1H, H-5), 4.20 (m, 2H, H-6, -6'), 3.55 (s, 3H, OCH_3), 2.02 (s, 3H, OAc), 2.08 (s, 6H, 2 OAc). (Found: C, 45.18; H, 5.43; N, 12.03. Calc. for $C_{13}H_{19}O_8N_3$: C, 45.22; H, 5.51; N, 12.18%). The tri-O-acetyl derivative (0.5 g, 0.00145 mole) could be converted into 17 (0.31 g, 0.00141 mole, 98%) by treatment with NaOMe solution.

General procedure for the irradiation of glycosyl azides

The general irradiation procedure is illustrated by the irradiation of β-D-glucopyranosyl azide (1). Compound 1 (1.5 g, 0.0073 mole) was dissolved in dry MeOH (65 ml) and the soln was irradiated for 4 hr under N_2 in a borosilicate glass reaction-vessel in which was mounted a 450-W Hanovia medium-pressure mercury-arc lamp (Cat. No. 679A-36) contained in a water-cooled quartz immersion-well fitted with a Vycor 7010 filter-sleeve. After 4 hr, N_2 evolution ceased, and TLC [EtOH–benzene, 3:1 (v/v)] showed that all of the starting material had been consumed and the presence of a slower-moving component and a non-migrating component; the mixture was concentrated, and the former component was isolated by column chromatography to afford 2 (0.51 g, 0.0034 mole, 47%). After recrystallization from EtOH, the compound had m.p. 154–156°, $[\alpha]_D$ – 105° (*c*, 1.0 in H_2O). A commercial sample of L-arabinose had m.p. 156–160°, $[\alpha]_D$ + 105.1 ± 0.3° (*c*, 3.0 in H_2O) (after 22.5 hr). The PMR spectrum (D_2O) was identical with that of the commercial sample of L-arabinose.

Irradiation of β-D-mannopyranosyl azide (3). Compound 3 (1.5 g, 0.0073 mole) was irradiated, and the mixture was processed, according to the general irradiation procedure. Column chromatography of the product, using 3:2:2 (v/v) benzene–EtOAc–MeOH as eluant, afforded D-arabinose (0.65 g, 0.0043 mole, 60%) which, after recrystallization from EtOH, had m.p. 153–155°, $[\alpha]_D$ – 106° (*c*, 1.0 in H_2O). The PMR spectrum (D_2O) was identical with that of a commercial sample of L-arabinose.

Irradiation of β-D-galactopyranosyl azide (4). Compound 4 (1.5 g, 0.0073 mole) was irradiated, and the mixture was processed, according to the general irradiation procedure. Column chromatography of the product, using 3:2:2 (v/v) benzene–EtOAc–MeOH as eluant, afforded 5 (0.71 g, 0.0047 mole, 65%) which, after recrystallization from EtOH, had m.p. 110–112°, $[\alpha]_D$ – 14° (*c*, 1.0 in H_2O). A commercial sample of D-lyxose had m.p. 106 – 107°, $[\alpha]_D$ – 14° (*c*, 6 in H_2O). The PMR spectrum (D_2O) was identical with that of the commercial sample.

Irradiation of β-D-maltosyl azide (6). Compound 6 (1.5 g, 0.0041 mole) was irradiated as described in the general irradiation procedure. Although there as very little N_2 evolution during the 4 hr period of irradiation, TLC [EtOH–benzene, 3:2 (v/v)] indicated that all of the starting compound had been converted into a slower-moving material, which was revealed as an elongated spot suggestive of the presence of more than one compound, and a nonmigrating component. The IR spectrum of the mixture (determined with a smear obtained by rapidly evaporating a small aliquot) did not show any absorption at ~2130 cm^{-1} attributable to an azido group, but showed a broad band centered at ~1670 cm^{-1}. However, after the mixture had been kept for 2 hr in the dark, the IR spectrum showed a weak absorption at 2125 cm^{-1}. After 50 hr a very strong absorption attributable to an azido group was observed in the spectrum; moreover, TLC [EtOH–benzene, 3:2 (v/v)] indicated the presence of a considerable amount of starting material. Column chromatography, using 3:2 (v/v) EtOH–benzene as eluant, afforded 0.91 g of the starting azide 6 and 0.40 g of slower-moving material. The IR spectrum of the latter showed a broad band at ~1670 cm^{-1}. This material (0.40 g) was dissolved in dilute acid (37 ml water containing 0.5 ml conc. HCl), and the soln was heated at reflux temp. for 6 hr. The soln was neutralized with Dowex 1-X8 ion-exchange resin (OH^- form), filtered, and the filtrate was evaporated. The resulting oil was revealed by paper chromatography [n-BuOH–EtOH–water, 3:1:1 (v/v)] as two components which had the same mobilities as those of glucose and arabinose.

Irradiation of β-D-ribofuranosyl azide (7). Compound 7 (1.5 g, 0.0086 mole) was irradiated for 2 hr as described in the general irradiation procedure. TLC [EtOH–benzene, 3:1 (v/v)] and the IR spectrum (no azido absorption at ~2130 cm^{-1}) indicated that all of the starting material had been consumed. The mixture was evaporated, and column chromatography of the residual oil, using 3:1 (v/v) EtOH–benzene as eluant, afforded the starting material (0.6 g, 40%). In a separate experiment, the soln was irradiated for 2 hr and then kept in the dark. Aliquots were taken at intervals, evaporated, and their IR spectra were obtained. Initially there was no azido absorption but after 50 hr there was strong absorption at 2120 cm^{-1}.

Irradiation of α-L-arabinopyranosyl azide (8). Compound 8 (1.7 g, 0.0097 mole) was irradiated as described in the general irradiation procedure for 2.5 hr. The IR spectrum did not show an absorption at ~2130 cm^{-1} for the azido group, although there was only a small amount of gas evolved. Irradiation for a further 5.5 hr, addition of water (2 ml), and evaporation of the mixture yielded an oil whose IR spectrum showed a strong band at 2120 cm^{-1} (N_3) and a strong signal at 1650–1700 cm^{-1}.

Irradiation of β-D-cellobiosyl azide (9). Compound 9 (1.3 g, 0.0035 mole) was irradiated as described in the general irradiation procedure for 4 hr, at the end of which time gas evolution had ceased and TLC [$CHCl_3$–MeOH, 3:2 (v/v)] indicated that all of the starting compound had been converted into a slower-moving material and a nonmigrating component. Column chromatography, using 3:2 (v/v) $CHCl_3$–MeOH as eluant, afforded a homogeneous (TLC) sample of 10 (R=H) (0.53 g, 0.0017 mole, 48%) which had $[\alpha]_D$ – 53.5° (*c*, 5.2 in H_2O).

A crystalline hepta-O-acetyl derivative of 10 (R=H) was obtained in the following manner. A sample (0.33 g, 0.0009 mole) of 9 was irradiated for 2.75 hr, and the solvent was evaporated under reduced pressure to yield an amorphous material (0.302 g). The material was treated with pyridine (3 ml) and Ac_2O (3 ml) for 3 hr at room temp., and the mixture was evaporated then under reduced pressure. Column chromatography of the residue, using 4:1 (v/v) benzene–EtOAc as eluant, afforded a homogeneous (TLC) material (0.29 g, 0.00048 mole, 53%) which crystallized on trituration with ether. After recrystallization from MeOH the product (10, R=Ac) had m.p. 156–158°, $[\alpha]_D$ – 54.5° (*c*, 0.11 in $CHCl_3$) [lit.:[22] m.p. 196°, $[\alpha]_D^{25}$ – 16.8° (*c*, 4.5 in $CHCl_3$)]; the product was probably a mixture of anomers. (Found: C, 49.61; H, 5.37. Calc. for $C_{25}H_{34}O_{17}$: C, 49.50; H, 5.65%).

Irradiation of β-D-lactosyl azide (11). Compound 11 (0.441 g,

0.0012 mole) was irradiated as described in the general irradiation procedure for 1 hr. TLC [EtOAc–EtOH–water, 32:17:1 (v/v)] indicated that all of the starting compound had been consumed; no change was observed (TLC) to occur in the mixture during the course of its being kept for 1 day in the dark. The soln was evaporated, and the residue was treated with pyridine (5 ml) and Ac_2O (2.5 ml) for 2 hr. The mixture was evaporated under reduced pressure to give a syrup (0.841 g). Column chromatography, using 3:2 (v/v) benzene–EtOAc as eluant, afforded **12** (R=Ac) as a homogeneous (TLC) glass (0.372 g, 0.00061 mole, 51%), $[\alpha]_D - 8.7°$ (*c*, 3.83 in $CHCl_3$) [lit.:[23] m.p. 157°, $[\alpha]_D - 29.4°$ ($CHCl_3$)]; the product was probably a mixture of anomers. (Found: C, 50.10; H, 5.82. Calc. for $C_{25}H_{34}O_{17}$: C, 49.50; H, 5.65%).

Irradiation of 2,3,4,5-*tetra*-O-*acetyl*-β-D-*glucopyranosyl azide* (**13**). Compound **13** (1.152 g, 0.0031 mole) was irradiated as described in the general irradiation procedure for 30 min, at the end of which time gas evolution had ceased and TLC [benzene–EtOAc, 3:2 (v/v)] indicated that all of the starting compound had been consumed. Water (2 ml) and Rexyn 101 ion-exchange resin (H^+ form) were added, and the mixture was stirred for 2 hr. The mixture was filtered, and the filtrate was evaporated under reduced pressure. Column chromatography of the residue, using 4:1 (v/v) benzene–EtOAc as eluant, afforded **15** (0.435 g, 0.00115 mole, 37%) which crystallized from benzene and had m.p. 110–113°. The IR and PMR spectra were identical to those obtained for a sample of compound **15** prepared from D-glucono-1,5-lactone (see above). (Found: C, 47.27, H, 5.68. Calc. for $C_{15}H_{22}O_{11}$: C, 47.62; H, 5.86%).

Irradiation of 2-*deoxy*-β-D-*arabino-hexopyranosyl azide* (**16**). A soln (see above) of **16** in MeOH was irradiated as described in the general irradiation procedure for 1 hr, at the end of which time gas evolution had ceased and TLC [$CHCl_3$–MeOH, 3:1 (v/v)] indicated that all of the starting compound had been consumed. The soln was evaporated under reduced pressure, and the residue was treated with Ac_2O (2 ml) and NaOMe (0.15 g) on a steam bath for 110 min. The soln was diluted with $CHCl_3$, and the mixture was washed successively with $NaHCO_3$ aq and water. The isolated product was observed (TLC, PMR) to be very complex.

Irradiation of 2-O-*methyl*-β-D-*glucopyranosyl azide* (**17**). Compound **17** (0.348 g, 0.0016 mole) was irradiated as described in the general irradiation procedure for 1.5 hr, at the end of which time gas evolution had ceased and TLC [EtOAc–EtOH–water, 45:5.5:5 (v/v)] indicated that all of the starting compound had been consumed. Evaporation of the soln under reduced pressure gave a colorless gum (0.351 g) which was treated with Ac_2O (4 ml) and NaOAc (0.25 g) on a steam bath for 1 hr. The mixture was processed in the usual manner, and the product was chromatographed using 3:2:1 (v/v) benzene–EtOAc–MeOH as eluant. The major fraction (0.094 g) gave a complex PMR spectrum which showed an absorption attributable to a OMe group.

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