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CONVERSION OF A 2-(*N*-NITROSO)ACETAMIDO HEXOSE INTO A FIVE-CARBON, ACETYLENIC SUGAR DERIVATIVE*†

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ABSTRACT

Dinitrogen tetraoxide was used to convert 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (**1**) in high yield into the syrupy *N*-nitroso derivative **2**, and benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranose (**6**) into the crystalline *N*-nitroso analog **7**. The *N*-nitroso derivative **2** in acetonitrile underwent photolysis by pyrex-filtered, u.v. light to regenerate the starting acetamide **1** in high yield; spontaneous decomposition of **2** afforded β-D-glucopyranose pentaacetate (**3**) and other products. In ethereal solution, compound **2** reacted with potassium hydroxide in isopropyl alcohol with loss of the 2-substituent and C-1, to give a C_5 acetylene, 1,2-dideoxy-D-*erythro*-pent-1-ynitol, isolated in high yield as its triacetate **4** and characterized by conversion into the known, crystalline 1,2-dideoxy-3-*O*-(3,5-dinitrobenzoyl)-4,5-*O*-isopropylidene-D-*erythro*-pent-1-ynitol (**5**).

INTRODUCTION

This report is part of a more-general study of potentially useful reactions for specific structural modification of sugars and such complex, amino sugar-containing carbohydrates as the aminoglycoside antibiotics and various glycosaminoglycans, with a view to achieving modified biological response in the former[2] and developing improved, non-hydrolytic, fragmentation methods as tools for structural characterization with the latter[3]. Although the nitrous acid deamination of amino sugars and their derivatives continues to attract much interest on account of the mildness of the reaction and the great sensitivity of the reaction course to intra- and intermolecular features in the particular system investigated[4], the fact that most of the natural amino sugar derivatives contain acetamido groups, rather than free amino

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groups, prompted the evaluation of reactions specifically directed toward the acetamido group.

Although reactions for conversion of simple amides into *N*-nitroso derivatives are well established[5] and acetamido sugars have long been known[6], it is only recently that (*N*-nitroso)acetamido sugars have been prepared and studied; they have been obtained as unstable, yellow syrups by treating the fully acetylated acetamido sugar with nitrosyl chloride in chloroform[7].

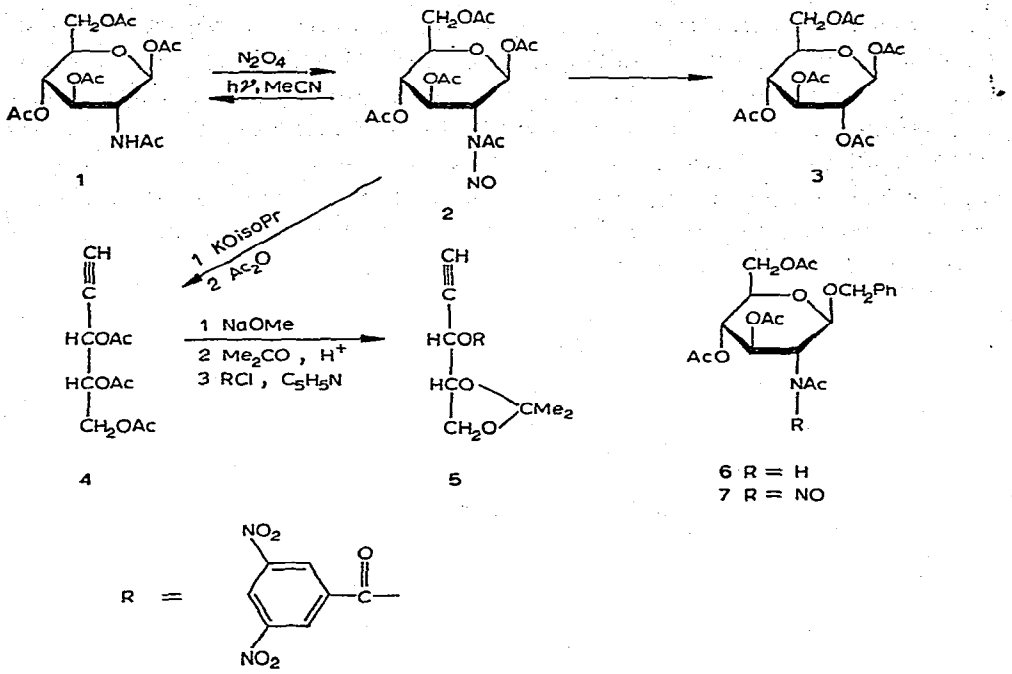
Dinitrogen tetraoxide is shown here to be a convenient reagent[5] for preparing *N*-(nitroso)acetamido sugar derivatives. Among the reactions of these products studied is a novel, base-catalyzed degradation leading to an acetylenic sugar derivative[8].

DISCUSSION

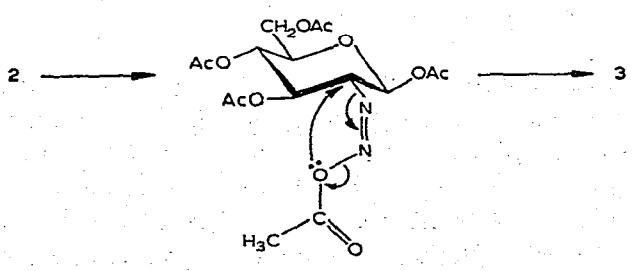
Following the general procedure of White[5], 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose[9] (**1**) in dichloromethane was treated at 0° with an excess of dinitrogen tetraoxide in the presence of sodium acetate, to give the *N*-nitroso derivative **2** as an oil in almost quantitative yield. Alternatively, pyridine could be used as the reaction solvent, in which case the sodium acetate was not required. The product **2** had properties closely resembling those of **2** prepared from **1** by action of nitrosyl chloride[7]. It was obtained as a chromatographically homogeneous, yellow oil that could be stored for at least several weeks at −80°; at room temperature, it underwent considerable decomposition after 1 day. Its 100-MHz n.m.r. spectrum in chloroform-*d* was essentially first-order, and resembled that[9,10] of **1**, except that the NH signal was absent, the NAc signal showed a distinctive[7], downfield shift to τ 7.34 from its position[11] (τ 8.09) in **1**, and the H-2 signal appeared ~0.4 p.p.m. downfield of its position in the spectrum[9,10] of **1**. The i.r. spectrum showed the anticipated[12] N=O absorption at 6.56 μm, and characteristic[7] absorption for the nitroso chromophore was observed in the u.v. spectrum.

Application of the same procedure to benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside[13] (**6**) gave a 92% yield of the crystalline, yellow *N*-nitroso derivative **7**. This compound gave an acceptable elemental analysis, showed N=O absorption in the i.r., and absorbed in the u.v. at 389, 406, and 426 nm; its n.m.r. spectrum in chloroform-*d* was essentially first-order, exhibiting in particular the N(NO)Ac methyl group absorption at characteristically low field with respect to the other acetyl-group resonances.

Photolysis of the *N*-nitrosoamide **2** in acetonitrile solution with pyrex-filtered u.v. light from a mercury lamp for 9 h at ~0° gave an 87% return of the starting acetamide **1**; evidently N–N cleavage occurs, followed by hydrogen capture from the solvent to regenerate the NHAc group. In contrast, when the *N*-nitroso derivative **2** was kept *in vacuo* for ~9 days at room temperature, there resulted a mixture of products from which β-D-glucopyranose pentaacetate (**3**), the major component by t.l.c., could be isolated pure in 31% yield. From the studies by White[14] on simple *N*-



nitrosoamides, it may be postulated that the reaction **2**→**3**, a net conversion of an *N*-nitrosoamide into an ester with retention of configuration, involves rearrangement of **2** to the diazoacetate[15], followed by extrusion of a nitrogen molecule (possibly with participation by O-5), and front-side (SNi) attack by acetate on C-2 as N_2 leaves. The last step could proceed by way of a 5-membered cyclic process as depicted, or by a 6-membered cyclic mechanism through attack at C-2 by the other oxygen atom of the acetate group.



This reaction course differs from that in a report[7] on the decomposition of **2** in various solvents, where it was stated that **3** is not an important product.

When treated at room temperature with an excess (~4 molar) of potassium hydroxide in isopropyl alcohol, an ethereal solution of the (*N*-nitroso)acetamide **2** showed rapid evolution of nitrogen. Acetylation of the reaction product gave a 70%

yield of a colorless, dextrorotatory oil that, by elemental analysis and n.m.r., mass, and i.r. spectroscopy, was identified as a C_5 acetylene, 3,4,5-tri-*O*-acetyl-1,2-dideoxy-D-*erythro*-pent-1-ynitol (**4**). In addition to the acetate-group signals anticipated, the n.m.r. spectrum (see Fig. 1) of **4** showed the high-field (τ 7.44), narrow doublet typical[8,16] of terminal acetylenes having H-1 coupled to a proton at C-3. The remaining couplings observed for protons along the chain were in essential accord[8,16] with the conformation depicted (in Fig. 1) for **4**. Mass-spectral fragmentations for **4** are listed in the Experimental section.

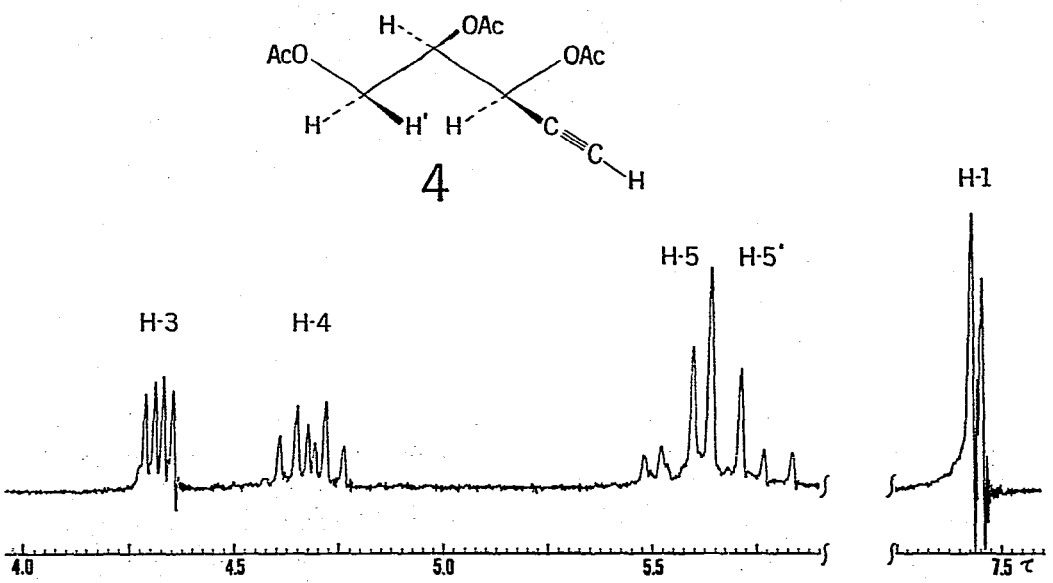
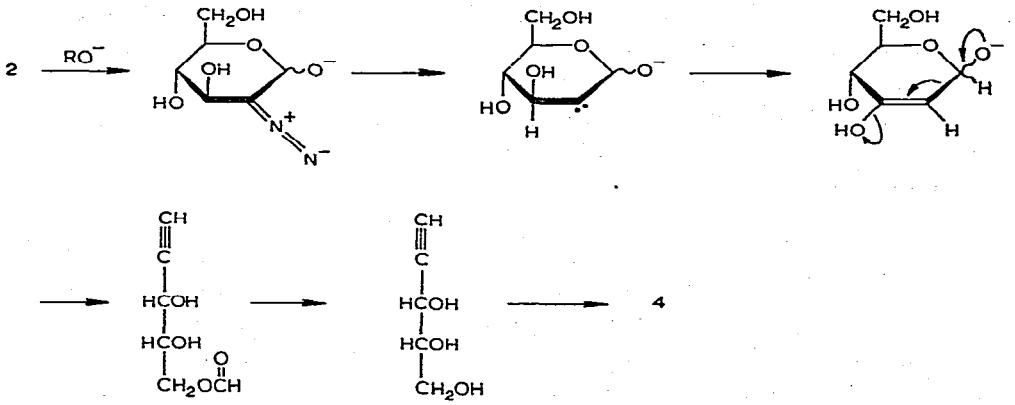


Fig. 1. The 100-MHz n.m.r. spectrum of 3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-*erythro*-pent-1-ynitol (**4**) in chloroform-*d* (acetate resonances omitted). [The small (4.2 Hz) $J_{3,4}$ coupling indicates that the stereo-electronic requirements of the 3-OAc group exceed those of the –C≡CH group, so that the 3-OAc group is oriented antiparallel to C-4 (see related examples in refs. 8 and 16).]

The characterizing data advanced for **4** leave little doubt as to the validity of the gross structural assignment, but the stereochemical designation on this evidence alone rests largely on the known stereochemistry of the precursor **1** and the assumption that stereochemical integrity at C-4 and C-5 in **1** is maintained through the sequence of transformations ending up with compound **4**. A classical proof of the structure of **4** was provided by successive Zemplén deacetylation, acetonation, and (3,5-dinitrobenzoyl)ation to yield the known[8] 1,2-dideoxy-3-*O*-(3,5-dinitrobenzoyl)-4,5-*O*-isopropylidene-D-*erythro*-pent-1-ynitol (**5**). The latter had been prepared in this laboratory[8] from 2,3-*O*-isopropylidene-D-glyceraldehyde by ethynylation, separation and degradative structural characterization of the epimeric products, and (3,5-dinitrobenzoyl)ation of the 3-epimers. The crystalline product **5** was identical with the independently prepared material in all respects, including the X-ray powder dif-

fraction pattern (see Experimental section). The sequence **4**→**5** involves initial Zemplén deacetylation, conditions under which the chiral propargylic alcohol group is known[17] to be stereochemically unaffected. The acetonation step could lead to two, isomeric monoacetals of the dioxolane type, and thus give low yields of **5**, but it was considered that the desired acetal incorporating the primary alcohol group would be the more stable; this premise was borne out by the 54% yield attained in the conversion **4**→**5**.

The mechanism of the conversion of **2** into **4** has not been investigated. Principal steps may be postulated to involve conversion of the (*N*-nitroso)acetamido group into a diazo group[15], together with saponification of the acetate groups; loss of N_2, and hydride migration in an incipient, carbenoid species[18,19] would generate an enolate that could suffer C-1–C-2 cleavage with expulsion of HO^- from C-3 and generate the acetylene having a base-labile, formic ester substituent. Other pathways, including routes by way of acyclic intermediates, are not excluded, and further work will be necessary to provide evidence in support of specific mechanistic steps.



The high-yielding conversion of the acetamido sugar **1** into the acetylene **4** provides a new and potentially useful route to acetylenic sugar derivatives, compounds whose value and versatility in synthetic sugar chemistry is well established[20].

EXPERIMENTAL

General methods. — Melting points were determined with a Thomas–Hoover "Unimelt" apparatus and are uncorrected. Optical rotations were measured in a 1-dm tube with a Perkin–Elmer model 141 recording polarimeter. I.r. spectra were recorded with a Perkin–Elmer model 457 grating i.r. spectrophotometer. N.m.r. spectra were recorded by using a Varian HA-100 spectrometer, with chloroform-*d* as the solvent and tetramethylsilane as the internal standard. Chemical shifts are given on the τ scale, and the J values recorded are first-order spacings. U.v. spectra were recorded with a Cary model 14 recording spectrophotometer. T.l.c. was per-

formed with 0.25-mm layers of Silica Gel G (E. Merck, Darmstadt, Germany); plates were activated at 110°. Column chromatography was conducted with Merck silica gel No. 7734. Spots were detected by spraying the plates with 5% (v/v) sulfuric acid in ethanol, and heating. X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The strongest lines are numbered in order (1, strongest). The camera diameter was 114.59 mm. Elemental analyses were performed by W. N. Rond. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-902 instrument at an ionization potential of 70 eV and an accelerating potential of 8 kV; the source temperature (direct-inlet system) was 150°.

*1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(*N*-nitroso)acetamido-β-*D*-glucopyranose* (**2**). — *Procedure A.* To 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose[9] (**1**, 973 mg, 2.5 mmoles) and anhydrous sodium acetate (615 mg, 7.5 mmoles) in dichloromethane (5 ml) at 0° was added dinitrogen tetraoxide[5] (1.38 g, 0.93 ml, 15 mmoles) in dichloromethane (10 ml) during 5 min at 0°, and the mixture was stirred for an additional 20 min at 0°. Dichloromethane (10 ml) was added, and the mixture was purged with nitrogen for 1 h at 0° to remove the excess of dinitrogen tetraoxide. Additional dichloromethane was added at intervals during the passage of nitrogen in order to keep the volume of the solution constant. The resulting yellow solution was successively washed with water (10 ml), an aqueous solution of sodium carbonate (2%, 10 ml), and water (10 ml), all washings being performed at 0°. The organic phase was dried with anhydrous magnesium sufate, and the solvent evaporated at 0° to give the pure *N*-nitrosoamide **2** as a yellow syrup; yield 940 mg (90%), $[\alpha]_D^{23}$ −1.1 ±0.2° (*c* 1.7, chloroform); R_F 0.76 (1:1 chloroform–ethyl acetate); λ_{max}^{film} 3.39, 5.72 (C=O), 6.56 (N=O)[5,12], 7.02, 7.31, 8.25, 9.35, 9.60, and 10.75 μm; λ_{max}^{EtOH} 390 (ε 46), 407 (66), and 425 nm (65) (lit.[7] $\lambda_{max}^{CHCl_3}$ 391, 407, and 426 nm); n.m.r. data: τ 3.75 (doublet, $J_{1,2}$ 9 Hz, H-1), 4.41 (doublet of doublets, $J_{2,3}$ 10 Hz, H-3), 5.00 (triplet, $J_{3,4}$ 10 Hz, H-4), 5.09 (triplet, H-2) (collapsed to a doublet when the H-1 resonance was irradiated), 5.77 (doublet of doublets, $J_{5,6}$ 4.5 Hz, $J_{6,6'}$ 12.5 Hz, H-6), 6.04 (doublet of doublets, $J_{5,6'}$ 2.3 Hz, H-6'), 6.18 (8-line pattern, $J_{4,5}$ 10 Hz, H-5), 7.34 [3-proton singlet, N(NO)Ac], 7.94, 8.00, 8.05, and 8.16 (each a 3-proton singlet, Ac).

Procedure B. To compound **1** (973 mg, 2.5 mmoles) in anhydrous pyridine (1 ml) at 0° was added dinitrogen tetraoxide (1.38 g, 0.93 ml, 15 mmoles) in dichloromethane (10 ml) during 5 min at 0°; the mixture was stirred for an additional 20 min at 0°, and then purged with nitrogen for 1 h at 0°. The subsequent procedure for isolation was identical to that given in procedure A; yield of *N*-nitrosoamide **2**, 920 mg (89%). If not required for immediate use, the product was stored at −80°, at which temperature it was stable for several weeks.

*Photolysis of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(*N*-nitroso)acetamido-β-*D*-glucopyranose* (**2**). — A solution of **2** (209 mg, 0.5 mmole) in acetonitrile (150 ml) in a 250-ml, Hanovia photochemical reactor (Engelhard Hanovia Lamps, Slough, Bucks., England) was irradiated under a nitrogen atmosphere at 0° through a pyrex filter with

light from a medium-pressure mercury lamp (~100 W) fitted with a high-purity, synthetic quartz envelope. The yellow solution became colorless as the irradiation proceeded, and, after ~9 h, t.l.c. showed only one spot, at R_F 0.20 (1:1 chloroform–ethyl acetate). The solution was evaporated to a syrup that crystallized spontaneously. Recrystallization from methanol–ether gave compound **1**; yield 170 mg (87%), m.p. 185–186°, $[\alpha]_D^{23}$ +2.2° (*c* 0.7, chloroform) (lit.[9] m.p. 186.0–186.5°, $[\alpha]_D$ +1.5 ±0.5° in chloroform).

The product was identical with an authentic sample of **1** by mixed m.p. and comparative i.r. and n.m.r. spectrum.

Spontaneous conversion of **2** *into β-*D*-glucopyranose pentaacetate* (**3**). — Syrupy compound **2** (1 g, 2.4 mmoles) was kept under diminished pressure (~5 torr) for 3 days at 25° and then at atmospheric pressure for 6 days at 25°. T.l.c. (1:1 chloroform–ethyl acetate) then indicated that the final product contained at least 6 components [R_F 0.75, 0.68 (major), 0.33–0.50 (streak), 0.13, and 0.00]. Column chromatography on silica gel with the t.l.c. solvent gave the component having R_F 0.68, contaminated to a minor extent with the two components having R_F 0.75 and 0.48. Crystallization from 95% ethanol gave colorless crystals of β-D-glucopyranose pentaacetate (**3**); yield 295 mg (31%), m.p. and mixed m.p. (with an authentic sample), 127–129°, $[\alpha]_D^{21}$ +4.4° (*c* 0.9, chloroform).

The other components (R_F 0.75, 0.33–0.50, 0.13, and 0.00) were not readily separated pure by column chromatography, and were not further studied.

Conversion of **2** *into 3,4,5-tri-*O*-acetyl-1,2-dideoxy-*D*-*erythro*-pent-1-ynitol* (**4**). — A solution of **2** (522 mg, 1.25 mmoles) in ether (10 ml) was stirred at ~25° in a 50-ml, round-bottomed flask equipped with a magnetic stirrer-bar. A solution of potassium hydroxide (310 mg, 5.5 mmoles) in isopropyl alcohol (10 ml) was added during 2 min while efficient stirring was maintained; nitrogen was evolved. The dark-brown mixture was then stirred for 10 min at 25° and, after evaporation of the solvents at 35° under diminished pressure, pyridine (6 ml) and acetic anhydride (2 ml) were added, and the mixture was stirred overnight at 25°. Ice and water (50 ml) were added, and the solution was extracted with three 10-ml portions of dichloromethane. The dark-brown extracts were combined, washed with water (10 ml), dried (anhydrous magnesium sulfate), and evaporated. T.l.c. (1:1 chloroform–ethyl acetate) revealed minute traces of unidentified material having R_F 0.57, 0.41, and 0.00. The main component (**4**, R_F 0.87) was separated by chromatography on a column (25 × 2 cm) of silica gel by using the t.l.c. solvent. Evaporation of the solvent gave **4** as a clear syrup; yield 210 mg (70%). An analytical sample was obtained by distillation onto a cold finger at 55° (bath)/10^{-5} torr; $[\alpha]_D^{24}$ +67.1 ±0.5° (*c* 1.2, chloroform); λ_{max}^{film} 3.06 (C≡CH), 3.38, 4.72 (C≡C), 5.74 (C=O), 6.97 (weak), 7.30, 8.20 (broad), 9.56, and 10.5 μm (weak); n.m.r. data: τ 4.32 (doublet of doublets, $J_{1,3}$ 2.2 Hz, $J_{3,4}$ 4.2 Hz, H-3), 4.69 (doublet of triplets, $J_{4,5}$ 4.2 Hz, $J_{4,5'}$ 6.8 Hz, H-4), 5.55 (doublet of doublets, $J_{5,5'}$ 11.8 Hz, H-5), 5.72 (doublet of doublets, H-5'), 7.44 (doublet, $J_{1,3}$ 2.2 Hz, H-1), 7.89 (6-proton singlet, OAc), and 7.93 (3-proton singlet, OAc); *m/e* (relative intensities and probable assignments given in parentheses): 183 (0.2, $M^+ - \cdot OAc$), 182 (0.2,

$M^{+}-AcOH$), 169 (0.2, $M^{+}-\cdot CH_2OAc$), 158 [0.2, $M^{+}-HC{\equiv}COAc$ (*m** 103, calc. 103.2)], 145 {15, Ac_3O^{+} and $[CH(OAc)CH_2OAc]^{+}$}, 140 (2), 127 (0.7), 103 [12, $(Ac_2OH)^{+}$ and $145-CH_2CO$ (*m** 73.2, calc. 73.2)], 98 [12, $(C_5H_6O_2)^{+}$], 97 (1), and 43 (100, Ac^{+}).

Anal. Calc. for $C_{11}H_{14}O_6$: C, 54.44; H, 5.79. Found: C, 54.53; H, 5.83.

Repetition of the procedure with **2** (209 mg, 0.5 mmole) in ether (5 ml) and a greater proportion of potassium hydroxide (185 mg, 3.3 mmoles) in isopropyl alcohol (5 ml) gave **4** in a lower yield; 70 mg (58%).

*1,2-Dideoxy-3-*O*-(3,5-dinitrobenzoyl)-4,5-*O*-isopropylidene-*D*-erythro-pent-1-ynitol* (**5**). — A solution of the 3,4,5-triacetate **4** (160 mg, 0.66 mmole) in abs. methanol (20 ml) was treated with a catalytic amount of sodium, and the mixture was stirred for 8 h at room temperature. The solution was made neutral with Dry Ice, and methanol was removed at 30° under diminished pressure. The residue was shaken with anhydrous copper(II) sulfate (100 mg) in acetone (40 ml) containing a catalytic amount of concentrated sulfuric acid for 6 h at room temperature. The acid was neutralized by stirring with anhydrous sodium carbonate (500 mg), the mixture was filtered, and the filtrate was evaporated. To the residue were added dry pyridine (5 ml) and 3,5-dinitrobenzoyl chloride (200 mg), and the mixture was stirred for 7 h at room temperature. Ice and water (50 ml) were then added, and the solution was extracted with three 10-ml portions of dichloromethane. The dried (anhydrous magnesium sulfate) extract was evaporated, and a solution of the product in chloroform was passed through a short column (6 × 2 cm) of silica gel. Evaporation of the effluent, and crystallization of the product from abs. methanol, gave **5** as a white solid; yield 124 mg (54%), m.p. 127–129°. Recrystallization from abs. methanol gave **5** as needles, m.p. 129–130°, $[\alpha]_D^{23}$ +47 ±1° (*c* 0.86, chloroform) [lit.[8] m.p. 133–133.5°, $[\alpha]_D^{23}$ +50 ±1° (*c* 2, chloroform)]; λ_{max}^{KBr} 3.07 (C=CH), 3.24, 4.73 (C≡C), 5.80 (C=O), 6.15, 6.47, 6.85, 7.45, 7.80, 8.05, 8.58, and 9.23 μm; n.m.r. data: τ 0.72–0.92 (3-proton multiplet, aryl protons; erroneously given as τ 1.8 in ref. 8), 4.20 (1-proton doublet of doublets, $J_{1,3}$ 2.2 Hz, $J_{3,4}$ 3.4 Hz, H-3), 5.40–6.10 (3-proton multiplet, H-4,5,5′), 7.34 (1-proton doublet, H-1), 8.59 (6-proton singlet, CMe_2); X-ray powder diffraction data: 11.62 m, 8.04 m, 6.75 m, 5.81 w, 5.57 vw, 5.18 w, 4.98 w, 4.69 m, 4.53 w, 4.40 w, 4.31 w, 4.12 m, 4.01 m, 3.70 vs (1), 3.62 w, 3.46 w, 3.42 w, 3.30 w, 3.03 w, 2.92 w, and 2.76 w. (The intensities of the lines at 4.01 and 3.70 were inadvertently reversed in ref. 8.)

The product gave an acceptable microanalysis, and was identical with an authentic sample of **5** by mixed m.p., comparative i.r. spectrum, and X-ray powder diffraction pattern.

*Benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(N-nitroso)acetamido-β-*D*-glucopyranoside* (**7**). — To benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside[13] (**6**, 874 mg, 2.0 mmoles) and anhydrous sodium acetate (492 mg, 6.0 mmoles) in dichloromethane (5 ml) at 0° was added dinitrogen tetraoxide (1.10 g, 0.74 ml, 12 mmoles) in dichloromethane (10 ml) during 5 min at 0°. After the mixture had been stirred for an additional 25 min at 0°, dichloromethane (10 ml) was added, and

the mixture was purged with nitrogen for 1 h at 0° to remove the excess of dinitrogen tetraoxide. The resulting yellow solution was successively washed with water (10 ml), an aqueous solution of sodium carbonate (2%, 10 ml), and water (10 ml), dried (magnesium sulfate), and evaporated at 0°, to give the pure *N*-nitrosoamide **7** as a yellow syrup that spontaneously solidified; yield 861 mg (92%), m.p. 84–85° (dec.). Recrystallization from methanol–hexane (plus a few drops of ether to give a homogeneous solution) gave **7** as large, yellow prisms, m.p. 90–91° (dec.), $[\alpha]_D^{23}$ −57.7 ±0.5° (*c* 0.71, chloroform); R_F 0.81 (1:1 chloroform–ethyl acetate), R_F 0.68 (3:1 chloroform–ethyl ether); λ_{max}^{KBr} 5.72 (C=O), 5.77 (C=O), 6.62 (N=O)[5,12], 6.88 (weak), 7.00 (weak), 7.30 (doublet), 7.96, 8.15, 8.26, 9.01, 9.38, 9.60, and 10.58 μm; λ_{max}^{EtOH} 389 (ε 59), 406 (93), and 426 (98) nm; n.m.r. data: τ 2.55–2.94 (5-proton multiplet, Ph), 4.38 (doublet of doublets, $J_{2,3}$ and $J_{3,4}$ 9, 10 Hz, H-3), 4.68 (doublet, $J_{1,2}$ 8.2 Hz, H-1), 4.86 (1-proton triplet, H-4), 4.97 (1-proton triplet, H-2), 5.20 (1-proton doublet, *J* 12.4 Hz, OCH_2Ph), 5.52 (1-proton doublet, OCH_2Ph), 5.64 (doublet of doublets, $J_{5,6}$ 4.6 Hz, $J_{6,6'}$ 12.3 Hz, H-6), 5.84 (doublet of doublets, $J_{5,6'}$ 2.7 Hz, H-6'), 6.21 (8-line pattern, $J_{4,5}$ 10 Hz, H-5), 7.44 [3-proton singlet, N(NO)Ac], and 7.93, 8.03, and 8.19 (3-proton singlets, OAc); X-ray powder diffraction data: 10.71 s, 6.88 vs (1), 6.39 m, 5.88 m, 5.26 m, 4.70 m, 4.44 s, 4.05 s, 3.82 s, 3.46 vw, 3.29 vw, 3.20 m, 3.05 vw, 2.92 w, 2.78 w, 1.96 w, and 1.89 vw.

Anal. Calc. for $C_{21}H_{26}N_2O_{10}$: C, 54.07; H, 5.62; N, 6.01. Found: C, 54.40; H, 5.47; N, 6.05.

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