Carbohydrate Research
Elsevier Publishing Company, Amsterdam
Printed in Belgium

SYNTHESIS OF TRIAZOLE DERIVATIVES OF SUGARS BY 1,3-DIPOLAR CYCLOADDITION FROM ACETYLENIC AND AZIDO PRECURSORS*†

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(Received July 23rd, 1970)

ABSTRACT

1,2,3-Triazoles having sugar chains at C-4, and others having the chain at N-1, were prepared. Condensation of 3-*O*-acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol (**1**) with phenyl azide, followed by removal of substituents, gave 1-phenyl-4-(D-*threo*-trihydroxypropyl)-1,2,3-triazole (**2**), whose structure was proved by oxidation to known derivatives of 1-phenyl-1,2,3-triazole. The 1-benzyl analog (**4**) of **2** was prepared similarly. The 4-*C*-substituted 1,2,3-triazole **12** was obtained in the same way from the acetylenic sugar derivative **11**. By condensing phenylacetylene with the sugar azides **13** (primary azide), **15** (secondary azide), and **17** (glycosyl azide), the 1-substituted 4-phenyl-1,2,3-triazoles **14**, **16**, and **18**, respectively, were obtained. The 4-substituted 1-phenyl-1,2,3-triazoles and 1-substituted 4-phenyl-1,2,3-triazoles here reported show $\pi \rightarrow \pi^*$ absorption near 246 nm, in contrast to the 4-substituted 2-phenyl-1,2,3-triazoles (phenylosotriazoles), which absorb near 268 nm. The optical rotatory dispersion spectrum of **2** shows a negative Cotton effect and is closely similar to that of the 2-phenyl analog (D-*threo*-pentulose phenylosotriazole).

INTRODUCTION

Heterocyclic bases having sugar chains attached, in numerous permutations and combinations, continue to attract the attention of the synthetic chemist in the quest for new chemotherapeutic compounds, especially as potential carcinostatic or antiviral agents. In addition to derivatives of the nucleoside type (*N*-glycosyl derivatives of aromatic, heterocyclic bases)[3], there has been considerable recent interest in *C*-substituted analogs, such as the naturally occurring antibiotics formycin, formycin B, and showdomycin[3,4]. Other derivatives of interest include types having a heterocycle attached to the ω-carbon atom of the sugar moiety[5].

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*Part IX in the series "Extension of Sugar Chains Through Acetylenic Intermediates". For a preliminary report, see ref. 1. For part VIII of this series, see ref. 2.

†Supported, in part, by the National Institutes of Health, Public Health Service, Department of Health, Education, and Welfare, Bethesda, Md. 20014; Grant No. GM-11976 (The Ohio State University Research Foundation Project 1820).

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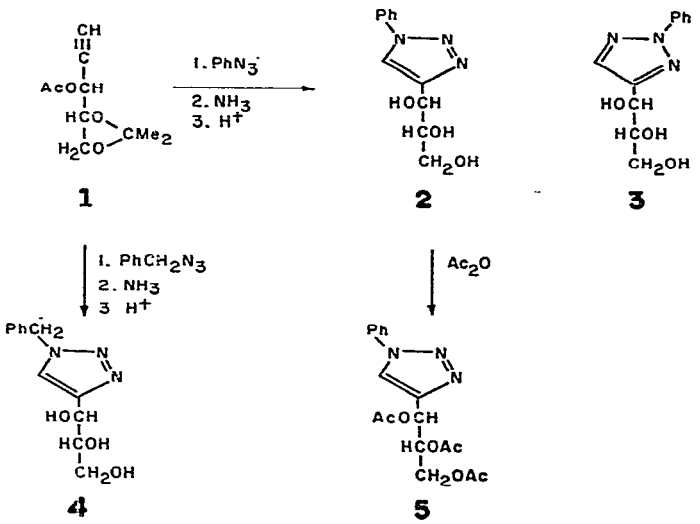
Earlier papers in this series[6] have documented the versatility of acetylenic derivatives of sugars (obtained by ethynylation of suitable carbonyl derivatives) for a wide range of useful synthetic transformations. The route to 1,2,3-triazoles by 1,3-dipolar cycloaddition of azides to acetylenes[7] has now been applied to representative examples of these acetylenic sugar derivatives, to give 4-*C*-substituted 1,2,3-triazoles having the sugar residue on C-4 and an aryl group on N-1. These products are isomeric with the osotriazoles obtained by oxidation of arylosazones[7], which have the sugar side-chain at C-4, but the aryl group at N-2, and which are related to the 1-(aroylamino)-1,2,3-triazoles obtained by oxidation of aroylosazones[8]. Also described in this paper is the preparation of 1,2,3-triazoles having a sugar residue attached to N-1; these triazoles were obtained by the action of phenylacetylene on primary and secondary azides of sugars. Another example having the sugar residue attached to N-1, but of the glycosylamine type and differing from the others by its susceptibility to hydrolytic cleavage of the heterocycle by acid, was obtained from a glycosyl azide and phenylacetylene; this reaction was first described in the D-glucose series by Micheel and Baum[10].

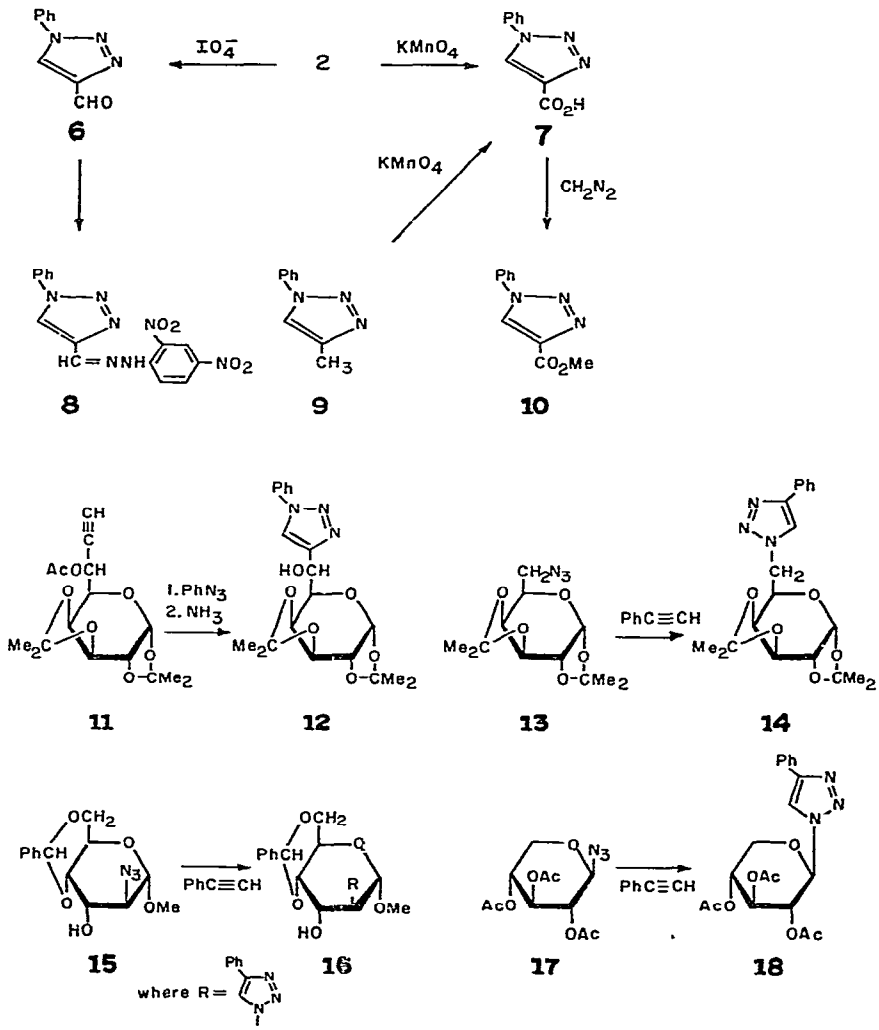
DISCUSSION

The acetylenic sugar 3-*O*-acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol[11] (**1**) reacted with phenyl azide at 100° to give, after saponification of the acetyl groups and acid hydrolytic cleavage of the isopropylidene acetal, the crystalline 1-phenyl-4-(D-*threo*-trihydroxypropyl)-1,2,3-triazole (**2**), m.p. 171°, in 68% yield. This product is a positional isomer of D-*threo*-pentulose phenylosotriazole[12] (**3**), which has the phenyl group at N-2 and melts at 88–90°.

The structure of **2** was confirmed by periodate oxidation. The side chain consumed the expected 2 moles of oxidant per mole of **2**, and the resultant 1-phenyl-



1,2,3-triazole-4-carboxaldehyde (**6**) was identified by comparison with a known[13] sample thereof and by conversion into the (2,4-dinitrophenyl)hydrazone (**8**). A second oxidative proof consisted in degradation of **2** with permanganate, which gave the crystalline 1-phenyl-1,2,3-triazole-4-carboxylic acid[14] (**7**), identical with a sample of **7** prepared by oxidation of 4-methyl-1-phenyl-1,2,3-triazole[15] (**9**); the derived methyl ester (**10**) of the acid **7** prepared from **2** was likewise identical with that prepared starting from **9**. These results clearly indicate that the sugar chain is acyclic and that the phenyl group is at N-1 in **2**; the mode of cycloaddition of phenyl azide to **1** is evidently controlled by a favored transition-state having the bulky substituent on the one addend remote from that on the other, so that the 1-phenyl derivative is the major product isolated. The possibility is not excluded that a small proportion of the 3-phenyl isomer may also be formed, as observed in the reactions of some glyco-



syl azides with phenylacetylene[10], but a sterically less favorable transition state having bulky substituents on vicinal atoms (C-4 and N-3) would be required for this.

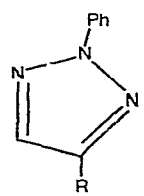
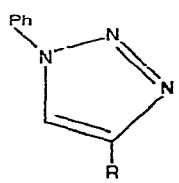
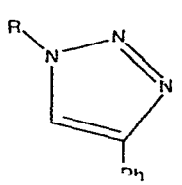
The triazole **2** is levorotatory ($[\alpha]_D$ −20° in ethanol) and shows a negative Cotton effect in its optical rotatory dispersion (o.r.d.) spectrum (inflection at 258 nm); in this respect, it closely resembles the corresponding 2-phenyl derivative **3**, which has $[\alpha]_D$ −32° in water[12] and shows a negative Cotton effect[16] with an inflection near 262 nm. The rules[17] relating rotation with configuration for the osotriazoles can likewise be expected to be operative with triazoles of the type **2**, and this feature may prove useful with acetylenic sugar derivatives[11,18] as a method for configurational assignment at the carbon atom (bearing a secondary alcohol group) adjacent to the triple bond.

The u.v. spectrum of the 4-substituted 1-phenyl-1,2,3-triazole **2** resembled those of the 4-carboxylic acid **7** and the 4-unsubstituted derivatives[19], in that each showed an absorption maximum (presumably a $\pi \rightarrow \pi^*$ transition) near 248 nm (see Table I). In this respect, they are clearly differentiated from the 2-phenyl analogs[20] (see Table I), which show this absorption near 268 nm.

The triacetate (**5**) of **2** gave an n.m.r. spectrum in chloroform-*d* entirely consistent[21] with the structure assigned (see Experimental section for full details); in addition to signals for the acetate and phenyl groups, the methylene protons (H-3,3′

TABLE I

ULTRAVIOLET SPECTRAL DATA FOR SOME 1,2,3-TRIAZOLE DERIVATIVES

Structural type	*Absorption maxima (λ_{max}), nm, for R group given*	
	R = H	210, 262[a]
	R = CO_2H	210, 270
	R = –(CHOH)$_2$CH$_2$OH (**3**)	210, 268
	R = H	209, 244[b]
	R = CO_2H	210, 248
	R = –(CHOH)$_2$CH$_2$OH (**2**)	208, 250
	R = 6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl (**14**)	209, 246
	R = methyl 4,6-*O*-benzylidene-2-deoxy-α-D-altropyranosid-2-yl (**16**)	216, 246
	R = tetra-*O*-acetyl-β-D-xylopyranosyl (**18**)	207, 242

[a]See ref. 19. [b]See ref. 20.

of the side chain) gave rise to the eight-line pattern of the AB portion of an ABX system, H-1 of the side chain gave a doublet, H-2 of the side chain gave the expected octet, and the methine proton at C-5 of the triazole ring gave the low-field singlet anticipated.

The acetylenic derivative **1** was also condensed with benzyl azide, and removal of the protecting groups gave the crystalline triazole **4**, the 1-benzyl analog of **2**. In a third example, 6-*O*-acetyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-oct-7-ynopyranose[22] (**11**) reacted with phenyl azide to give, after saponification of the acetyl group, the crystalline triazole **12**. The benzyl group in **4**, and the phenyl group in **12**, are assumed to be at N-1 by analogy with the conversion of **1** into **2**, and because of the usual stereoselectivity of this reaction[7] when bulky groups are present; the improbable N-3-substituted structures were not, however, excluded by direct, degradative evidence.

To prepare 1,2,3-triazoles having a sugar residue at N-1 and a phenyl group at C-4, various azidodeoxy sugars were condensed with phenylacetylene. From 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[23] (**13**), there was obtained the crystalline triazole **14** in 63% yield, and a high yield of the crystalline triazole **16** was likewise obtained from methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside[24] (**15**), despite the fact that the azido group is secondary in the latter example. This reaction has promise as a general method for attaching a heterocycle to a sugar by a C–N bond that is not susceptible to hydrolytic cleavage, and offers possibilities for the design of molecules for use in enzyme-inhibition studies. In the final example, 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl azide[25] (**17**) was condensed with phenylacetylene to give a 61% yield of the crystalline triazole **18**. This product, like the known[10] D-glucose analog, is a glycosylamine, and can be expected to undergo cleavage by acid.

The triazoles **14**, **16**, and **18** are all formulated with the sugar chain attached at N-1 rather than at N-3, for the same steric reasons[7] as those advanced for the triazole derivatives **2**, **4**, and **12**, although a formal proof of structure by degradation was not performed.

The u.v. spectra of the 1-substituted 4-phenyl-1,2,3-triazoles **14**, **16**, and **18** show maxima near 246 nm (see Table I), thus closely resembling the 4-substituted 1-phenyl-1,2,3-triazoles **2** and **7**; the spectra are clearly differentiated from those of the 4-substituted 2-phenyl-1,2,3-triazoles (phenylosotriazoles).

1,3-Dipolar cycloaddition reactions to acetylenic sugar derivatives offer wide scope for synthesis of heterocycles having sugar residues attached, by use of diazoalkanes to give pyrazoles, of nitrile oxides to give oxazoles, and of numerous related examples; many variants are also possible in the cycloaddition of triply bonded species to azidodeoxy sugar derivatives.

EXPERIMENTAL

General methods. — Solutions were evaporated below 50° under diminished pressure. Melting points were determined with a Thomas–Hoover "Unimelt"

apparatus and are uncorrected. I.r. spectra were recorded with a Perkin–Elmer Model 137 i.r. spectrophotometer. U.v. spectra were recorded with a Bausch & Lomb Model 505 u.v. spectrophotometer. Optical rotations were measured in 1-dm tubes with a Perkin–Elmer Model 141 polarimeter. O.r.d. measurements were made with a Jasco ORD/UV-5 recording spectropolarimeter. N.m.r. spectra were recorded at 60 and 100 MHz with Varian A-60 and HA-100 n.m.r. spectrometers. Chemical shifts are given on the τ scale, with tetramethylsilane (τ = 10.00) as the internal standard. Microanalyses were performed by W. N. Rond. 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 (1, strongest), and double numbers indicate approximately equal intensities. The camera diameter was 114.59 mm.

1-Phenyl-4-(D-threo-*trihydroxypropyl*)-*1,2,3-triazole* (**2**). — 3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol[11] (**1**, 1.0 g, 5 mmoles) was heated with phenyl azide[26] (1.2 g, 10 mmoles) for 2 h under reflux on a steam bath. The syrupy product was then treated with 10% methanolic ammonia (100 ml) for 24 h at room temperature. The solution was evaporated, the resultant syrup was dissolved in 1:1 ethanol–water (100 ml), and the solution was stirred with Amberlite IR-120 (H^+) cation-exchange resin (10 g) for 24 h at 50°. After removal of the resin, the solution was evaporated, and the residue crystallized from methanol–water to give **2** as needles; yield 0.8 g (68%), m.p. 171°, $[\alpha]_D^{25}$ −20° (*c* 1, ethanol); o.r.d. data at 20° (*c* 0.4, ethanol): [α] −72°, 240 nm; [α] 0°, 258 nm; [α] +250°, 226 nm; [α] 0°, 224 nm; and [α] −100°, 195 nm; λ_{max}^{EtOH} 208 (ε 3,500), 232 (sh) (2,100), and 250 nm (2,100); λ_{min}^{EtOH} 220 (ε 1,700), and 240 (sh) nm (1,700); X-ray powder diffraction data: 11.35 m, 7.16 m, 5.90 m, 4.92 w, 4.45 s (1), 4.08 s (2,2), and 3.82 s (2,2).

Anal. Calc. for $C_{11}H_{13}N_3O_3$: C, 56.17; H, 5.56; N, 17.87. Found: C, 56.59; H, 5.88; N, 18.05.

Oxidation of **2** (2.4 mg, 10 μmoles) with 10mM aqueous sodium metaperiodate (3 ml, 30 μmoles), for 24 h at room temperature, led to the uptake of 2.08 moles of oxidant per mole of **2**, as measured by the Müller–Friedberger method[27].

1-Phenyl-4-(D-threo-*1,2,3-triacetoxypropyl*)-*1,2,3-triazole* (**5**). — A mixture of the triazole **2** (0.3 g, 1.4 mmoles) and acetic anhydride (10 ml) in dry pyridine (5 ml) was kept for 24 h at room temperature and then poured onto crushed ice. The mixture was extracted with ether, and the extract was washed with water, dried, and evaporated, to give the acetate **5**; yield 0.4 g (82%), b.p. 100° (bath)/1 torr, $[\alpha]_D^{25}$ −10° (*c* 0.2, chloroform); λ_{max}^{KBr} 5.75 μm (OAc); n.m.r. data (100 MHz, chloroform-*d*): τ 1.90 (1-proton singlet, CH of triazole), 2.10–2.75 (5-proton multiplet, phenyl), 3.68 (1-proton doublet, $J_{1,2}$ 7.0 Hz, H-1 of side chain), 4.16 (1-proton octet, H-2 of side chain), 5.50 (1-proton quartet, $J_{3,3'}$ 12 Hz, $J_{2,3}$ 3.7 Hz, H-3 of side chain), 5.88 (1-proton quartet, $J_{2,3'}$ 5.6 Hz, H-3′ of side chain), and 7.74 (6 protons) and 7.90 (3 protons) (acetyls).

Anal. Calc. for $C_{17}H_{19}N_3O_6$: C, 56.50; H, 5.30; N, 11.63. Found: C, 56.71; H, 5.56; N, 11.30.

1-Phenyl-1,2,3-triazole-4-carboxaldehyde (**6**). — To a suspension of the triazole **2** (200 mg, 0.85 mmole) in water (100 ml) was added sodium metaperiodate (0.8 g), and the mixture was kept, with occasional shaking, for 24 h at room temperature. The resultant aldehyde **6** was filtered off, washed thoroughly with water, and recrystallized from water–methanol as needles; yield 120 mg (85%), m.p. 99–100° (lit.[13] m.p. 98°); λ_{max}^{KBr} 5.95 μm (CHO).

Anal. Calc. for $C_9H_7N_3O$: C, 62.42; H, 4.04; N, 24.27. Found: C, 62.36; H, 4.17; N, 24.12.

1-Phenyl-1,2,3-triazole-4-carboxaldehyde (2,4-dinitrophenyl)hydrazone (**8**). — A solution of the aldehyde **6** (100 mg, 0.57 mmole) in 2M hydrochloric acid (20 ml) was treated with (2,4-dinitrophenyl)hydrazine (100 mg, 0.5 mmole) and boiled for 1 h under reflux. The hydrazone **8** separated as the solution cooled; yield 130 mg (54%); it was recrystallized from ethanol as red needles, m.p. 298° (dec.).

Anal. Calc. for $C_{15}H_{11}N_7O_4$: N, 27.76. Found: N, 28.08.

1-Phenyl-1,2,3-triazole-4-carboxylic acid (**7**). — *A. By oxidation of* **2**. A suspension of the triazole **2** (200 mg, 0.85 mmole) in water (100 ml) was boiled under reflux, and potassium permanganate (3 g) was added in portions during 1 h. The mixture was filtered while hot, and the filtrate was decolorized with sulfur dioxide. Acidification of the solution caused the acid **7** to separate; yield 100 mg (62%). Recrystallization from water gave pure **7** as needles, m.p. 151°, alone or in admixture with an authentic[14] sample; λ_{max}^{EtOH} 210 (ε 2,900) and 248 nm (1,500); λ_{min}^{EtOH} 232 nm (ε 1,000); λ_{max}^{KBr} 5.9 μm (CO_2H); X-ray powder diffraction data: 8.54 m, 7.24 m, 6.53 vw, 5.54 s (2), 5.02 w, 4.31 vs (1), 3.74 s (3,3), 3.43 s (3,3), 3.18 s (3,3), 3.05 m, 2.93 w, 2.75 vw, and 2.68 m.

Anal. Calc. for $C_9H_7N_3O_2$: C, 57.14; H, 3.70; N, 22.22. Found: C, 56.98; H, 3.88, N, 22.54.

B. From 4-methyl-1-phenyl-1,2,3-triazole[15] (**9**). A suspension of **9** (300 mg, 1.8 mmoles) in water (100 ml) containing potassium permanganate (10 g) was boiled for 4 h under reflux. The hot mixture was filtered, and the filtrate was decolorized with sulfur dioxide, acidified, and extracted with ether; the acid **7** contained in this extract was secured by extraction with 50% aqueous potassium hydroxide (50 ml). The aqueous extract was washed with ether, acidified, and extracted with ether; the extract was evaporated to dryness, and the residue was recrystallized from water to give the acid **7**, yield 180 mg (50%), m.p. and mixed m.p. 150–151°.

The n.m.r. spectrum of the starting compound (**9**) in chloroform-*d* showed a 6-proton multiplet (aryl H and C-5 methine) at τ 2.18–2.78, and a 3-proton singlet at τ 7.58 (Me).

Methyl 1-phenyl-1,2,3-triazole-4-carboxylate (**10**). — A solution of the acid **7** (200 mg, 1.06 mmoles) in ether (50 ml) was treated with 5% diazomethane in ether (100 ml), and the mixture was allowed to evaporate slowly at room temperature. After 24 h, the resultant ester (**10**) was recrystallized from water as needles; yield 150 mg (71%), m.p. 121° (lit.[14] m.p. 120°); X-ray powder diffraction data 8.09 s (2),

6.36 m, 5.86 m, 5.08 s (3,3), 4.85 w, 4.62 vw, 4.27 s (3,3), 3.96 m, 3.68 vs (1), 3.63 w, 3.28 m, 3.13 w, 2.88 m, and 2.75 m.

Anal. Calc. for $C_{10}H_9N_3O_2$: N, 20.70. Found: N, 20.39.

1-Benzyl-4-(D-threo-*trihydroxypropyl)-1,2,3-triazole* (**4**). — A mixture of 3-*O*-acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol[11] (**1**, 1.0 g, 5 mmoles) and benzyl azide[28] (1.0 g, 7.6 mmoles) was heated for 4 h at 100° under reflux. The product was treated with 100 ml of 10% methanolic ammonia for 24 h, and the mixture was evaporated. The residue was dissolved in 1:1 ethanol–water (100 ml), and the solution was stirred with Amberlite IR-120 (H^+) resin for 24 h at room temperature. After removal of the resin, the solution was evaporated to give the triazole **4**; yield 600 mg (50%), crystallized from water as needles, m.p. 132°, $[\alpha]_D^{25}$ −24° (*c* 0.5, ethanol); λ_{max}^{EtOH} 209 nm (ε 1,700).

Anal. Calc. for $C_{12}H_{15}N_3O_3$: C, 57.83; H, 6.00; N, 16.86. Found: C, 57.82; H, 5.96; N, 16.55.

*1,2:3,4-Di-*O-*isopropylidene-6-*C-(*1-phenyl-1,2,3-triazol-4-yl*)-D-glycero-α-D-galacto-*hexopyranose* (**12**). — 6-*O*-Acetyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-oct-7-ynopyranose[22] (**11**, 1.0 g, 3 mmoles) was heated with phenyl azide (1.1 g, 9.3 mmoles) for 4 h under reflux on a steam bath. The resultant syrup was treated with 100 ml of 10% methanolic ammonia for 24 h at room temperature. Concentration of the solution gave the triazole **12**, which was recrystallized from water–methanol as needles; yield 0.6 g (50%), m.p. 193°, $[\alpha]_D^{25}$ −45° (*c* 0.2, ethanol).

Anal. Calc. for $C_{20}H_{25}N_3O_6$: C, 59.55; H, 6.20; N, 10.42. Found: C, 59.79; H, 6.32; N. 10.82.

*6-Deoxy-1,2:3,4-di-*O-*isopropylidene-6-*C-(*4-phenyl-1,2,3-triazol-1-yl*)-α-D-*galactopyranose* (**14**). — A mixture of 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[23] (**13**, 1 g, 3.5 mmoles) and 1 g (8.5 mmoles) of phenylacetylene (Aldrich Chemical Co., Inc.) was heated for 4 h under reflux on a steam bath, and the mixture was then kept overnight at room temperature. The triazole **14** separated as a crystalline mass, which was recrystallized from methanol to give needles; yield 850 mg (63%), m.p. 142°, $[\alpha]_D^{25}$ −31.7° (*c* 1.6, pyridine); λ_{max}^{EtOH} 209 (ε 6,500) and 246 nm (6,600); λ_{min}^{EtOH} 218 nm (ε 2,500); n.m.r. data (60 MHz, in pyridine-d_5): τ 1.25 (1-proton singlet, H-5 of triazole), 1.80–2.85 (5-proton multiplet, phenyl), 4.25 (1-proton doublet, $J_{1,2}$ 5 Hz, H-1), 5.05–5.75 (6-proton multiplet, H-2,3,4,5,6,6'), and 8.44, 8.46, 8.68, and 8.74 (3-proton singlets, CMe_2); X-ray powder diffraction data: 14.71 vw, 11.03 vs (1), 7.88 m, 7.00 w, 5.25 s (2,2), 4.95 s (2,2), 4.74 m, 4.50 s (3,3), 4.24 s (3,3), 3.97 m, 3.70 m, 3.61 w, 3.53 m, 3.36 w, 3.17 w, 2.92 vw, and 2.74 w.

Anal. Calc. for $C_{20}H_{25}N_3O_5$: C, 62.01; H, 6.45; N, 10.85. Found: C, 62.14; H, 6.48; N, 10.77.

*Methyl 4,6-O-benzylidene-2-deoxy-2-*C-(*4-phenyl-1,2,3-triazol-1-yl*)-α-D-*altropyranoside* (**16**). — A mixture of methyl 2-azido-4,6-O-benzylidene-2-deoxy-α-D-altropyranoside[24] (**15**, 1 g, 3.25 mmoles) and phenylacetylene (1 g, 8.5 mmoles) was

heated for 4 h under reflux on a steam bath. The crystalline triazole that separated after 24 h at room temperature was washed with methanol, yield 950 mg (72%); it was recrystallized from hot ethanol as needles, m.p. 204°, $[\alpha]_D^{25}$ −69.3° (*c* 1.1, pyridine); λ_{max}^{EtOH} 210 (ε 10,000) and 246 nm (13,500); λ_{min}^{EtOH} 218 nm (ε 1,800); n.m.r. data (60 MHz, pyridine-d_5): τ 1.70–2.85 (10-proton multiplet, phenyl), 4.15 (1-proton singlet, H-5 of triazole), 4.55 (1-proton doublet, $J_{1,2}$ 3 Hz, H-1), 4.75 (1-proton singlet, H-benzylidene), 5.0–6.25 (6-proton multiplet, H-2,3,4,5,6,6'), and 6.58 (3-proton singlet, OMe); X-ray powder diffraction data: 12.61 s (2), 10.76 vw, 8.65 w, 6.39 m, 5.44 s (3,3), 5.19 s (3,3), 4.75 m, 4.41 vs (1,1), 3.94 vs (1,1), 3.70 m, 3.44 m, 3.29 w, and 3.15 vw.

Anal. Calc. for $C_{22}H_{23}N_3O_5$: C, 64.30; H, 5.62; N, 10.24. Found: C, 64.51; H, 5.61; N, 9.98.

4-Phenyl-1-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-1,2,3-triazole (**18**). — A mixture of 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl azide[25] (**17**, 1 g, 3.3 mmoles) and phenylacetylene (1 g, 8.5 mmoles) was heated for 4 h under reflux on a steam bath. The cooled mixture, which began to solidify after 1 h, was kept for 24 h, and the solid was filtered off and washed with methanol. Recrystallization from boiling ethanol gave pure **18** as needles; yield 0.8 g (61%), m.p. 268° (dec.), $[\alpha]_D^{25}$ −54.0° (*c* 1, pyridine); λ_{max}^{EtOH} 207 (ε 16,000) and 242 nm (9,000); λ_{min}^{EtOH} 218 nm (ε 4,000); X-ray powder diffraction data: 11.61 m, 7.61 s (2), 6.89 w, 5.49 vw, 4.96 vw, 4.33 vs (1), 3.80 m, 3.53 w, and 3.27 vw.

Anal. Calc. for $C_{19}H_{21}N_3O_7$: C, 56.57; H, 5.21; N, 10.42. Found: C, 56.89; H, 5.27; N, 10.69.

ACKNOWLEDGMENTS

The authors thank J. K. Thomson and Dr. J. D. Wander for n.m.r. spectral measurements, Miss Willa Hsueh for measurements of o.r.d. spectra, and P. L. Durette, S. Walker, J. K. Thomson, and Dr. R. Hems for samples of acetylenic and azido sugars.

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