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Synthesis of propargyl *C*-glycosides using allenyltributylstannane

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Abstract—Protected propargyl *C*-glycosides have been prepared by activation of the anomeric centres of 2,3,4,6-tetra-*O*-benzyl-derivatives of D-glucose and D-galactose, followed by treatment with allenyltributylstannane in the presence of Lewis-acid. Activation was by formation of the anomeric acetates, trichloroacetimidates or fluorides; boron trifluoride etherate and trimethylsilyl trifluoromethanesulfonate were particularly effective Lewis-acids. Attempts to perform similar reactions on 1,2,3,4,6-penta-*O*-acetyl-D-glucose led to participation by the C-2 acetate group and formation of 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(prop-2-ynyl)ethylidene]-α-D-glucopyranose.

1. Introduction

There is much interest in the synthesis of *C*-glycosides for use as nonhydrolyzable carbohydrate isosteres.[1] Reactions of allylsilanes at the anomeric positions of carbohydrate esters, anhydro derivatives and trichloroacetimidates provide allyl *C*-glycosides;[2] this chemistry has been extended to the preparation of allenyl *C*-glycosides from propargylsilanes.[3] However, we are aware of only a few studies involving propargyl *C*-glycosides: thus van Boom has reported the conversion of the epoxide **1** into *C*-glycoside **2** using allenyllithium generated in situ from allenyltributylstannane[4] and recently the preparation of the ring-unsaturated species **3** by Lewis-acid induced reaction of $^{i}Pr_3SiC{\equiv}CCH_2SiMe_3$ with 3,4,6-tri-*O*-acetyl-D-glucal was described (Fig. 1).[5] Terminal alkynes offer great scope for further transformation under mild conditions, as is evident from the use of other acetylenic carbohydrate derivatives, such as ethynyl *C*-glycosides[6] and propargyl *O*-, *S*- or *N*-glycosides,[7] in the synthesis of sugar analogues. Propargyl *C*-glycosides would be a valuable addition to this group of synthetic building blocks.

In the presence of a Lewis-acid, allenylstannanes can convert aldehydes into homopropargyl alcohols.[8] We now report that anomeric esters, trichloroacetimidates and fluorides can all react with allenyltributylstannane, leading directly to the formation of propargyl *C*-glycosides.

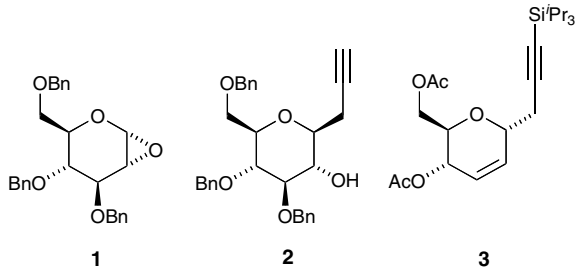

Figure 1.

2. Results and discussion

At first we examined the reaction of β-D-glucose pentaacetate (β-**4**) with excess allenyltributylstannane and trimethylsilyl trifluoromethanesulfonate (TMSOTf) in dichloromethane (0 °C to room temperature, CH_2Cl_2, 20 h; Scheme 1). Much of **4** remained unreacted, but we were able to isolate a single stereoisomer of a propargyl derivative in 43% yield. This product was the cyclic acetal **6**, rather than the desired *C*-glycoside. The configuration at the acetal stereocentre was assigned on the basis of NOESY correlations; thus the trioxabicyclo-[4.3.0]nonane system has the methyl substituent in an *endo*-orientation, whereas the somewhat larger propargyl group is *exo*-directed. When we used boron trifluoride etherate as the Lewis-acid in place of TMSOTf we again isolated the acetal **6** (38%). This product could arise by participation of the *O*-acetyl protecting group at C-2, followed by nucleophilic attack

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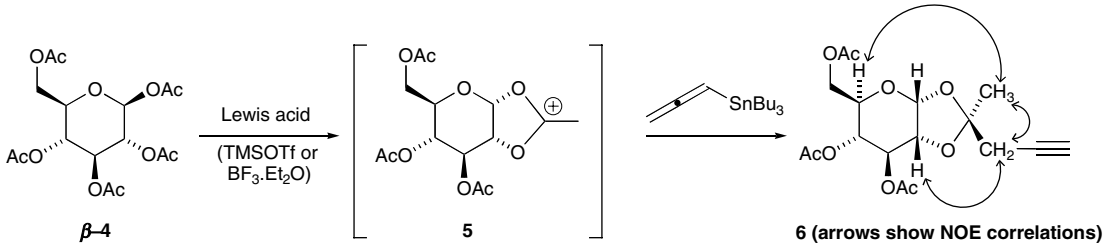


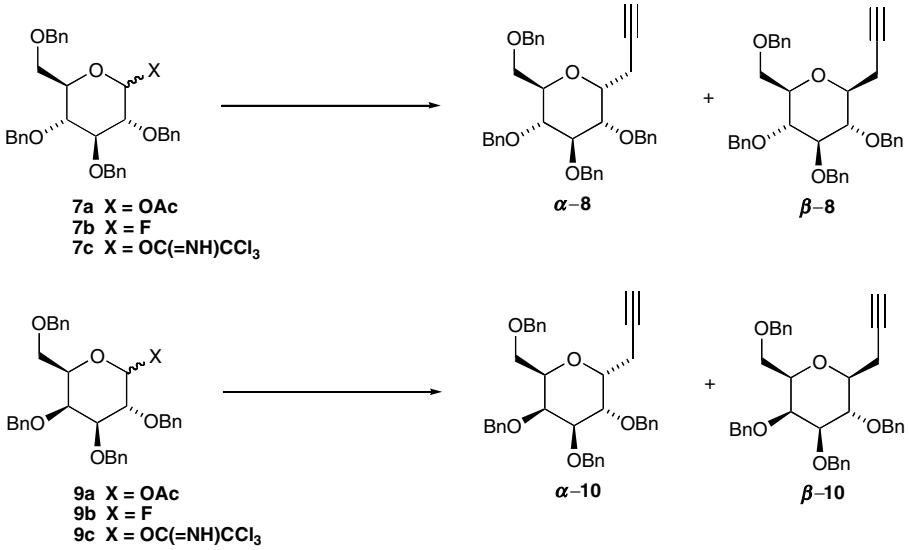
Scheme 1.

on the intermediate cation **5**: analogous bicyclic acetals have been observed from reactions of 2-*O*-acetyl glycosyl phosphates with cyanotrimethylsilane.[9]

In order to avoid the possibility of participation by an ester at C-2, we next turned our attention to the Lewis-acid induced reactions of allenyltributylstannane with 2,3,4,6-tetra-*O*-benzylglucopyranose derivatives that contained leaving groups at C-1 (Scheme 2, Table 1). Thus in the presence of excess TMSOTf the mixture of anomeric acetates **7a** was converted into a 55:45 mixture of two anomeric propargyl *C*-glycosides (α-**8** and β-**8**) in a combined yield of 40%. These isomers could not be separated from one another by TLC or flash chromatography, but they were distinguishable by their ^{1}H NMR spectra (400 MHz, $CDCl_3$). In particular, the acetylenic protons of the α- and β-anomers appeared as two triplets (J 2.6 Hz) with chemical shifts of 1.99 and 2.02, respectively. The 'anomeric' H-1 hydrogen atom of the minor (β-) isomer gave rise to a distinctive ddd (δ 3.40, J = 9, 5 and 3.5 Hz); homonuclear decoupling of the CH_2C≡ protons caused the H-1 signal to simplify to a doublet with J 9 Hz, consistent with an axial orientation of this hydrogen in a $^4C_1$, conformation. On the other hand, the multiplet corresponding to the H-1 signal of the major (α-) anomer was much further downfield (δ 4.26) and collapsed to a doublet with a J value of only 5 Hz when the CH_2C≡ protons were decoupled.

Propargylation of the corresponding benzyl-protected galactosyl acetates **9a** gave propargyl *C*-galactosides (α-**10** and β-**10**), which were separable by flash chromatography and could easily be distinguished by the appearance of their 'anomeric' H-1 protons in ^{1}H NMR (α-anomer $\delta_{H\text{-}1}$, 4.10, td J 7 and 3 Hz; β-anomer $\delta_{H\text{-}1}$ 3.38, ddd, J 10, 7 and 3 Hz).

The propargyl *C*-glycosides could be obtained by using other C-1 activated derivatives (fluorides **7b** and **9b**, trichloroacetimidates **7c** and **9c**) with various Lewis-acids [$BF_3{\cdot}Et_2O$, $SnCl_4$ and $Yb(OTf)_3$, as shown in Table 1]. The use of the sugar fluorides together with boron trifluoride was found to give the cleanest reaction, allowing tin residues to be removed by dissolution in acetonitrile and washing with light petroleum. Most of the experiments showed little or no stereoselectivity, but a preference for forming the α-anomer of the product was sometimes evident, particularly when boron trifluoride etherate was used in the glucose series. Experiments conducted using pure α-**9b** and β-**9b** (or a mixture of the two) as starting materials all gave the same anomer composition in the product **10**, as would be expected if the reaction involves an initial loss of leaving group followed by attack of allenyltin reagent on the resultant cation and/or if the anomers of the starting material are equilibrated under the reaction conditions. The successful reactions were done in the solvent dichloromethane; attempts to use acetonitrile as solvent led to



Scheme 2.

Table 1. Reactions of 2,3,4,6-tetra-*O*-benzylhexopyranose derivatives with allenyltributylstannane

Starting material (α:β ratio)[a]	Lewis acid (equiv)	Reaction conditions	α:β Ratio of *C*-glycosides **8** or **10**[a]	Yields of *C*-glycosides **8** or **10**[b]
7a (80:20)	TMSOTf (5.3)	CH_2Cl_2, 20 °C, 20 h	55:45	40% (α+β)
7a (80:20)	$BF_3{\cdot}Et_2O$ (1.05)	CH_2Cl_2, −15 °C → 20 °C, 6 h	—	0%
7a (80:20)	$BF_3{\cdot}Et_2O$ (5.2)	CH_2Cl_2, 25 °C, 20 h	55:45	17%
7b (60:40)	**$BF_3{\cdot}Et_2O$ (1.04)**	**CH_2Cl_2, −15 °C → 20 °C, 5 h**	**65:35**	**57% (α+β)**
7c (100:0)	TMSOTf (1.7)	CH_2Cl_2, −15 °C → 20 °C, 24 h	50:50	39%
7c (100:0)	$BF_3{\cdot}Et_2O$ (2.0)	CH_2Cl_2, −15 °C → 20 °C, 20 h	78:22	32% (α+β)
7c (100:0)	$Yb(OTf)_3$ (1.0)	CH_2Cl_2, −15 °C → 20 °C, 20 h	50:50	30% (α+β)
7c (100:0)	$SnCl_4$ (1.0)	CH_2Cl_2, 25 °C, 20 h	50:50	30% (α+β)
7c (100:0)	TMSOTf (1.9)	MeCN, 25 °C, 20 h	—	0%
7c (100:0)	$BF_3{\cdot}Et_2O$ (1.0)	MeCN, 25 °C, 20 h	—	0%
9a (50:50)	TMSOTf (2.0)	CH_2Cl_2, −15 °C → 20 °C, 6 h	50:50	28% (α)+35% (β)
9b (10:90)	**$BF_3{\cdot}Et_2O$ (1.05)**	**CH_2Cl_2, −15 °C → 20 °C, 5 h**	**55:45**	**39% (α)+34% (β)**
9b (10:90)	TMSOTf (1.05)	CH_2Cl_2, −15 °C → 20 °C, 5 h	55:45	[d]
9b (100:0)	$BF_3{\cdot}Et_2O$ (1.07)	CH_2Cl_2, −15 °C → 20 °C, 7 h	55:45	[d]
9b (0:100)	$BF_3{\cdot}Et_2O$ (1.05)	CH_2Cl_2, −15 °C → 20 °C, 6 h	55:45	[d]
9b (10:90)	$BF_3{\cdot}Et_2O$ (1.5)	MeCN, −15 °C → 20 °C, 7 h	—	0%
9c (10:90)	TMSOTf (1.0)	CH_2Cl_2, −15 °C → 20 °C, 24 h	50:50	34% (β)[c]
9c (10:90)	$BF_3{\cdot}Et_2O$ (1.05)	CH_2Cl_2, −15 °C → 20 °C, 5 h	50:50	[d]

[a] Anomer ratios were determined by 400 MHz ^{1}H NMR.
[b] The α- and β-*C*-glucosides **8** did not separate on TLC or flash chromatography, whereas separation of the corresponding α- and β-galactosides **10** was achieved.
[c] α-Anomer could not be separated from by products.
[d] Chromatographic isolation of the individual product anomers was not performed.

greatly diminished reactivity and failure to form the *C*-glycosides, presumably because the Lewis basicity of the nitrile function is sufficient to deactivate the Lewis acids.

3. Conclusions

Glucose and galactose derivatives with an acetate, fluoride or trichloroacetimidate leaving group at C-1 and 'nonparticipating' benzyl ether protecting groups at C-2 react with allenyltributylstannane under mild conditions, in the presence of Lewis acids, to yield mixtures of anomeric propargyl *C*-glycosides. The highest yielding reactions and cleanest conversions were observed for reactions of the glycosyl fluorides in dichloromethane, in the presence of boron trifluoride etherate, which gave some preference for forming the α-glucosides and galactosides. Such compounds are potentially important intermediates for the synthesis of metabolically stable carbohydrate analogues because methylene groups are good mimics of the oxygen atom present in *O*-glycosides,[10] whilst the reactivity of the terminal alkyne unit provides access to a structurally diverse range of derivatives. The use of these propargyl *C*-glycosides in Sonogashira and cycloaddition reactions is currently under investigation in our laboratory.

4. Experimental

Technical grade allenyltributylstannane of 80% purity is available from Aldrich or Lancaster. We prepared allenyltributylstannane by the method of Tagliavini and co-workers[11] and obtained a sample of 73% purity by weight based on ^{1}H and ^{13}C NMR analysis; the balance of the material was unreacted tributyltin chloride, which did not appear to interfere with the propargylation process when an excess of tin reagent was used. Glycosyl fluorides were prepared by treatment of the corresponding anomeric hydroxyl derivatives with 2-fluoro-1-methylpyridinium tosylate.[12]

Example propargylation procedure: preparation of the α- and β-anomers of 2,3,4,6-tetra-*O*-benzyl-1-(prop-2-ynyl)-1-deoxy-D-galactopyranose (10) from fluoride 9b

1-Fluoro-1-deoxy-2,3,4,6-tetra-*O*-benzyl-D-galactopyranose (**9b**) (α:β = 10:90 by NMR; 136 mg, 0.25 mmol) was dissolved in dry CH_2Cl_2 (4 mL), followed by the addition of allenyltributylstannane (73% purity; 0.149 mL, 0.365 mmol). The mixture was cooled to −15 °C (benzyl alcohol–liquid nitrogen bath) and treated with $BF_3{\cdot}Et_2O$ (0.033 mL, 0.26 mmol) dropwise over 1 min. The mixture was allowed to warm up to 20 °C over 2 h and maintained at this temperature for a further 3 h. CH_2Cl_2 (20 mL) was added and the solution was poured into ice-cold saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated, dried (Na_2SO_4) and evaporated to give the crude product, which was dissolved in MeCN (20 mL) and washed with petrol (bp 40–60 °C; 4 × 20 mL). Evaporation of the MeCN gave an oily residue (139 mg), which was analysed by ^{1}H NMR (400 MHz, $CDCl_3$). The only species observed were the α and β anomers of 2,3,4,6-tetra-*O*-benzyl-1-(prop-2-ynyl)-1-deoxy-D-galactopyranose (**10**), which were present in a ca. 55:45 ratio. These isomeric products were separated by flash chromatography [gradient from CH_2Cl_2–petrol (2:1) to CH_2Cl_2] to give first β-**10** (47.6 mg, 34%) and then α-**10** (54.9 mg, 39%).

2,3,4,6-Tetra-*O*-benzyl-1-(prop-2-ynyl)-1-deoxy-α-D-galactopyranose(α-10)

Colourless oil, $[\alpha]_D^{25} + 44.8$ (*c* 1.16, CH_2Cl_2); ν_{max} (film)/cm^{-1} 3294 (≡C–H) and 2122 (C≡C); δ_H (400 MHz, $CDCl_3$, assignments confirmed by COSY) 1.95 (1H, t, *J* 2.6 Hz, ≡C–H), 2.51 (1H, ddd, *J* 16.8, 7.1, 2.6 Hz, C*H*C≡), 2.58 (1H, ddd, *J* 16.8, 7.7, 2.6 Hz, C*H*C≡), 3.68–3.73 (2H, m, H-3 + H-6_a), 3.80 (1H, dd, *J* 5.5 and 2.9 Hz, H-2), 3.96–4.01 (2H, m, H-4 + H-6_b), 4.10 (1H, td, *J* 7.3, 2.9 Hz, H-1), 4.17 (1H, dt, *J* 8.0, 4.0 Hz, H-5), 4.50–4.65 (8H, m, 4 × OC*H*$_2$Ph) and 7.22–7.32 (20H, m, 4 × Ph); δ_C (100 MHz, $CDCl_3$, assignments by HSQC) 19.6 (CH_2), 66.9 (C-6), 69.2 (C-1), 70.5 (H*C*≡), 72.9 (Ph*C*), 73.5 (Ph*C*), 73.6 (Ph*C*), 73.9 (Ph*C*), 74.1 (C-4), 74.3 (C-5), 75.8 (C-3), 76.0 (C-2), 81.4 (C*C*≡), 127.94, 128.00, 128.03, 128.11, 128.19, 128.25, 128.33, 128.54, 128.80, 128.86, 138.5, 138.8, 138.9 and 139.0; *m*/*z* (ES) found: 563.2789 (M+H^+); $C_{37}H_{39}O_5$ requires 563.2792.

2,3,4,6-Tetra-*O*-benzyl-1-(prop-2-ynyl)-1-deoxy-β-D-galactopyranose (β-10)

Colourless oil, $[\alpha]_D^{25} + 9.8$ (*c* 1, CH_2Cl_2); ν_{max} (film)/cm^{-1} 3290 (≡C–H) and 2122 (C≡C); δ_H (400 MHz, $CDCl_3$) 1.96 (1H, t, *J* 2.5 Hz, ≡C–H), 2.50 (1H, ddd, *J* 16.9, 6.9, 2.6 Hz, C*H*C≡), 2.67 (1H, dt, *J* 17.0, 2.9 Hz, C*H*C≡), 3.38 (1H, ddd, *J* 9.7, 6.9, 2.9 Hz, H-1), 3.57–3.62 (4H, m, H-3, H-5, H-6_a, H-6_b), 3.87 (1H, t, *J* 9.4 Hz, H-2), 3.99 (1H, d, *J* 4.0, H-4), 4.43 (1H, d, *J* 11.9 Hz, C*H*Ph), 4.50 (1H, d, *J* 11.9 Hz, C*H*Ph), 4.61 (1H, d, *J* 11.7 Hz, C*H*Ph), 4.67 (1H, d, *J* 11.8 Hz, C*H*Ph), 4.68 (1H, d, *J* 10.9 Hz, C*H*Ph), 4.75 (1H, d, *J* 11.7 Hz, C*H*Ph), 4.94 (1H, d, *J* 10.9 Hz, C*H*Ph), 4.95 (1H, d, *J* 11.7 Hz, C*H*Ph) and 7.09–7.36 (20H, m, 4 × Ph); δ_C (100 MHz, $CDCl_3$, assignments by HSQC) 22.6 (CH_2), 69.2, 70.3 (H*C*≡), 72.6 (Ph*C*), 74.0 (Ph*C*), 74.1 (C-4), 74.8 (Ph*C*), 75.9 (Ph*C*), 77.7, 78.1 (C-1), 78.2 (C-2), 81.5 (C*C*≡), 85.0, 127.9, 128.0, 128.1, 128.20, 128.25, 128.4, 128.60, 128.61, 128.84, 128.86, 128.89, 138.4, 138.7, 138.8 and 139.3; *m*/*z* (ES) found: 580.3053 (M+NH_4^+); $C_{37}H_{42}NO_5$ requires 580.3057.

The following other propargylation products were prepared by similar methods.

3,4,6-Tri-*O*-acetyl-1,2-*O*-[1-(prop-2-ynyl)ethylidene]-α-D-glucopyranose (6), prepared from **4**, white solid, mp 69–71 °C, $[\alpha]_D^{25} + 26$ (*c* 1.1, CH_2Cl_2); ν_{max} (film)/cm^{-1} 3303 (≡C–H), 2119 (C≡C) and 1745 (C=O); δ_H (400 MHz, $CDCl_3$) 1.67 (3H, s, C*H*$_3$C, correlated with signal at δ 2.50 in NOESY spectrum), 2.0–2.1 (10H, m, 3 × OAc + ≡C–H), 2.50 (2H, d, *J* 2.7 Hz, C*H*$_2$C≡, correlated with signals at δ 1.67 and 4.36 in NOESY spectrum), 4.09 (1H, ddd, *J* 9.0, 5.0, 3.0 Hz, H-5), 4.17 (1H, dd, *J* 12.1, 3.0 Hz, H-6_a), 4.24 (1H, dd, *J* 12.1, 5.4 Hz, H_{6b}), 4.36 (1H, dd, *J* 4.9, 3.5 Hz, H-2), 4.90 (1H, dd, *J* 9.6, 3.5 Hz, H-4), 5.23 (1H, t, *J* 3.5 Hz, H-3), 5.76 (1H, d, *J* 4.9 Hz, H-1); δ_C (100 MHz, $CDCl_3$, assignments supported by HSQC spectrum) 20.7 (3 × CH_3), 24.3 (CH_3), 30.0 (*C*H_2C≡), 63.0 (C-6), 67.2 (C-5), 68.1 (C-4), 70.6 (C-3), 71.1 (≡*C*–H), 74.0 (C-2), 79.2 (*C*≡C–H), 97.2 (C-1), 109.8 (CH_3*C*), 169.2 (C=O), 169.6 (C=O) and 170.6 (C=O); *m*/*z* (ES) found: 388.1604 (M+NH_4^+); $C_{17}H_{26}NO_9$ requires 388.1602.

2,3,4,6-Tetra-*O*-benzyl-1-(prop-2-ynyl)-1-deoxy-D-glucopyranose (8), mixture of α- and β-anomers), prepared from **7a**,**b** or **7c**, colourless oil, ν_{max} (film)/cm^{-1} 3290 (≡C–H) and 2122 (C≡C); δ_H (400 MHz, $CDCl_3$) 1.99 (<1H, t, *J* 2.6 Hz, ≡C–H of α-anomer), 2.02 (<1H, t, *J* 2.6 Hz, ≡C–H of β-anomer), 2.56–2.72 (2H, m, C*H*$_2$C≡ of both anomers), 3.40 (<1H, ddd, *J* 9.1, 5.3, 3.5 Hz, H-1 of β-anomer, simplifies to d, *J* 9.3 Hz on homonuclear decoupling of C*H*$_2$C≡ protons at δ 2.64), 3.47 (<1H, ddd, *J* 9.6, 4.1, 2.3 Hz, H-5 of β-anomer), 3.57–3.80 (>5H, m, H-2, 3, 4, 6_a, 6_b, both anomers, H-5 of α-anomer), 4.26 (<1H, dt, *J* 9.7 and 5.2 Hz, H-1, α-anomer, simplifies to d, *J* 5.3 Hz on homonuclear decoupling of C*H*$_2$C≡ protons at δ 2.64), 4.47–4.93 (8H, m, 4 × PhC*H*$_2$O, both anomers) and 7.10–7.88 (20H, m, 4 × Ph); δ_C (100 MHz, $CDCl_3$) 17.3, 22.4, 69.30, 69.33, 70.5, 70.8, 72.3, 73.1, 73.7, 73.88, 73.90, 75.3, 75.5, 75.7, 75.8, 76.0, 77.2, 78.1, 79.0, 79.6, 79.8, 80.9, 81.07, 81.13, 82.2, 87.4, 127.96, 128.07, 128.09, 128.14, 128.21, 128.27, 128.34, 128.38, 128.39, 128.46, 128.77, 128.83, 128.86, 128.90, 128.93, 138.4, 138.54, 138.55, 138.6, 138.8, 139.00 and 139.02; *m*/*z* (ES) found: 580.3058 (M+NH_4^+); $C_{37}H_{42}NO_5$ requires 580.3057.

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