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REACTION OF BUTYLLITHIUM WITH BENZYLIDENE ACETALS OF ALDOPYRANOSIDES AND 1,5-ANHYDROALDITOLS*

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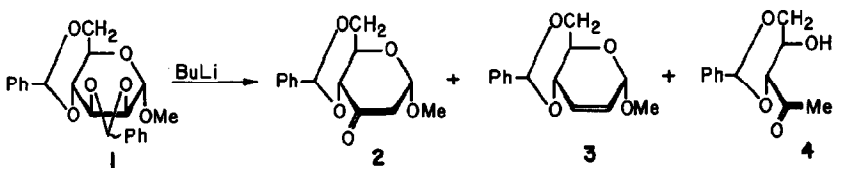
ABSTRACT

Under suitable conditions, butyllithium selectively cleaves 5-membered benzylidene acetals (1,3-dioxolane ring) leaving the 6-membered analogs (1,3-dioxane ring) intact in aldopyranoside and 1,5-anhydroalditol derivatives. The usual course of the reaction involves expulsion of the elements of benzaldehyde to give an enolate anion and thence a vicinal deoxyketone. The reaction is strongly regioselective and may be interpreted as proceeding *via* abstraction of the quasi-axial hydrogen atom on the sugar ring that is also part of the 1,3-dioxolane ring. Controlled routes of considerable synthetic utility are thereby feasible. In certain situations, an alternative reaction-pathway prevails that involves expulsion of the elements of benzoate anion with the formation of an alkene, the corresponding ring-unsaturated pyranose derivative.

INTRODUCTION

In 1974, Klemer and Rodemeyer reported[1] the reaction of methyl 2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside (**1**) with 2 mol. equiv. of butyllithium at −30° in oxolane to yield regiospecifically the 2-deoxy-3-ketone **2**; the only side-product was a trace of the 2,3-unsaturated compound **3**. Subsequently, this reaction was utilized on a large scale, employing a modified isolation procedure, in high-yielding syntheses of daunosamine[2] (3-amino-2,3,6-trideoxy-L-*lyxo*-hexose) and related compounds[3]. In our hands, the original procedure[1], in scaled-up preparations, did not lead to **2** but to complex mixtures from which 3,5-*O*-benzylidene-1-



*Dedicated to Professor Hans Paulsen.
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deoxy-D-*erythro*-pentulose (**4**) was isolated[2] in modest yield and subsequently identified[4] as a degradation product of **2**.

The base-induced decomposition of the 1,3-dioxolane ring in **1** (the 1,3-dioxane ring is unaffected) is an illustration of a general type of process observed with 1,3-dioxolanes[5] (Fig. 1). Initial removal of a proton from C-2, C-4, or C-5 of the dioxolane ring, and subsequent fragmentation, affords either the alkene or one or both of the positionally isomeric, vicinal deoxyketones. The fragmentation of **1** evidently follows almost exclusively only one of the three possible pathways outlined in Fig. 1, namely, initial proton abstraction[6] at C-3 to give **2**. It was therefore of interest to examine how related compounds having a different mode of substitution would react with butyllithium, as preparatively useful products could be expected through selective or exclusive operation of any one of these three pathways.

RESULTS AND DISCUSSION

The required dioxolane derivatives were prepared by benzylidenation[7] of appropriate aldopyranosides or 1,5-anhydroalditols with α,α-dimethoxytoluene. Throughout, the products were obtained in high yields as crystalline *endo/exo* mixtures diastereomeric at the acetal position of the 1,3-dioxolane ring. Purification to give a single diastereomer was not necessary for the subsequent reaction with butyllithium. In some instances, however, the individual isomers were isolated pure and were fully characterized (see Experimental). In these examples, the configuration at C-2 of the dioxolane ring was assigned[8] on the basis of ^{1}H-n.m.r. data.

When the butyllithium reaction, under the conditions applied previously to the *manno* dibenzylidene acetal, was applied to the *allo* isomer **5**, 86% of the crystalline 3-deoxy-2-ketone **6** was obtained, the structure of which was established by ^{1}H-n.m.r. spectroscopy and by comparison of its physical data with those reported[9] for this compound prepared by an independent route. In this reaction, fragmentation of the dioxolane ring evidently involved initial abstraction of H-2

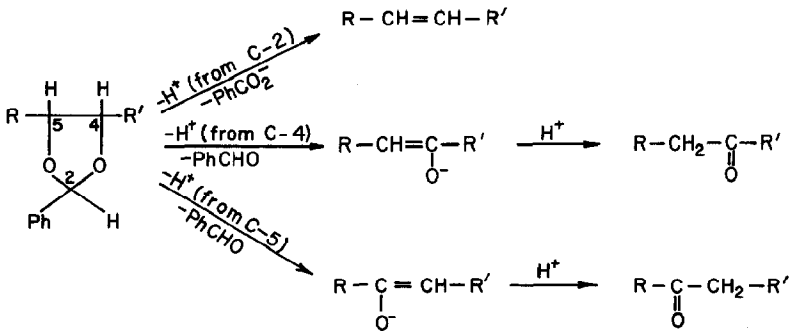
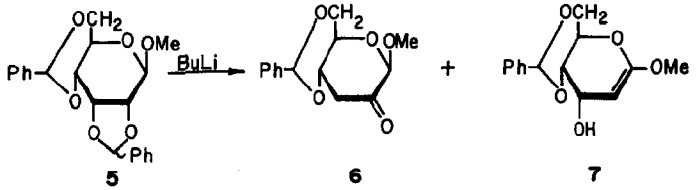
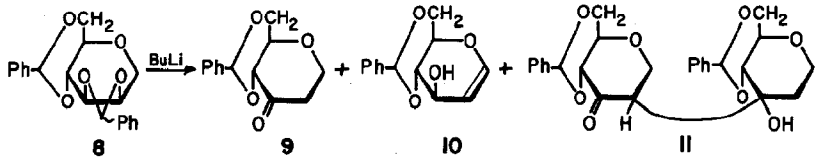


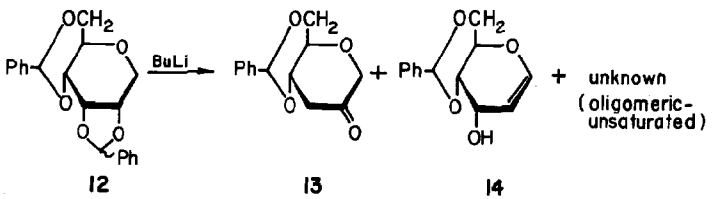
Fig. 1. Possible fragmentation-modes of a 5-membered ring benzylidene acetal (2-phenyl-1,3-dioxolane) to give an alkene (top) or regioisomeric deoxyketones (middle and lower).

(quasiaxial orientation) to generate the regioisomer **6** of the 2-deoxy-3-ketone **2** obtained from the *manno* dibenzylidene acetal **1**.

Accompanying **6** were traces of a side-product that was not fully purified, but which was probably the 1,2-unsaturated product **7** formed through initial abstraction of the axial H-1 of **5**, from the evidence of ^{1}H-n.m.r. spectroscopy. That **7** was not the 2,3-unsaturated glycoside was established by direct comparison with a reference sample of methyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside[10], nor was it the 2-deoxy-3-ketone.





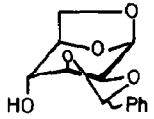


The butyllithium reaction was applied next to analogs of **1** and **5** that lack the glycosidic methoxyl group. Thus, 1,5-anhydro-2,3:4,6-di-*O*-benzylidene-D-mannitol (**8**) reacted with butyllithium at 0° (at −30°, the reaction proceeded too sluggishly) to give 66% of the crystalline 2-deoxy-3-ketone **9**, evidently by the same process that was observed for **1**. A dimeric side-product (**11**) was also encountered, which, presumably, arose from self-addition of **9**. A minor side-product was the glucal derivative **10**, the assigned structure of which is supported by analytical and spectroscopic data as well as by comparison with an authentic sample[11]. Again, the formation of **10** can be attributed to initial abstraction of the axial H-1 followed by expulsion of the elements of benzaldehyde.

The reverse course of the foregoing reaction was observed when 1,5-anhydro-2,3:4,6-di-*O*-benzylidene-D-allitol (**12**) was treated with butyllithium at 0° in oxolane. The major product, isolated crystalline, was the 3-deoxy-2-ketone **13**, which was fully in line with observations with the corresponding allose glycoside **5**.

Again, a glycal derivative (**14**) was isolated (3%) as a minor side-product and characterized by comparison with an authentic sample[11,13]. Another minor, side-product was also encountered; it could not be purified and characterized, but probably arose from aldol addition/condensation of the ketone **13**.

In 1,6-anhydro-β-D-mannopyranose (**15**), in which conformational rigidity is conferred by the 1,6-anhydro bridge, H-2 and H-3 are, respectively, quasiaxial and quasiequatorial in a (distorted) chair conformation. It had been expected that treatment of **15** with butyllithium would cause preferential abstraction of H-2 and lead to the 3-deoxy-2-ketone. However, no reaction occurred at −30°, but at 0° with 5 mol of butyllithium, a complex mixture of products was encountered, which was not examined further.



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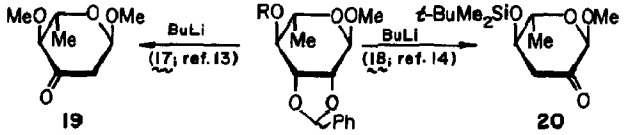
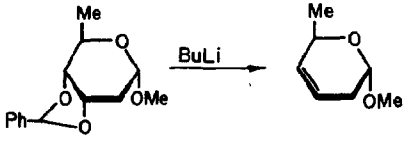
When the *conformationally flexible* system, methyl 2,3-*O*-benzylidene-6-deoxy-α-L-mannopyranoside (**16**) was treated[13] with butyllithium in the conventional way, the expected 2-deoxy-3-ketone was not obtained, probably because of the rather forcing conditions required. The corresponding 4-methyl ether **17**, however, led[13] to the *expected* product **19**. In contrast, protection of the alcohol at O-4 with a bulky silyl group (→ **18**) resulted[14] in deoxygenation at C-3 to form the *isomeric* 3-deoxy-2-ketone **20**.

The butyllithium reaction was applied next to methyl 3,4-*O*-benzylidene-2,6-dideoxy-α-D-*ribo*-hexopyranoside (**21**; in this instance, a pure diastereomer was used). In view of the conformational distortion and flexibility anticipated for **21**,



19 **20**

16 R = H
17 R = Me
18 R = *t*-BuMe$_2$Si



21 **22**

both fragmentation products, the 4-deoxy-3-ketone and/or the 3-deoxy-4-ketone[15] (methyl glycoside of cinerulose A[16]) might have been expected. However, **21** reacted with butyllithium at 0° (at −30°, the reaction proceeded insufficiently rapidly) to give, after column chromatography and in modest yield, only the 3,4-unsaturated derivative **22**, the assigned structure of which was supported by spectroscopic data. Evidently, with no proton properly disposed axially, abstraction of the benzylic proton (*cf.* Fig. 1) with subsequent loss of benzoate anion is the most favorable pathway for the fragmentation, leading, albeit in low yield, to the alkene **22**.

Thus, the synthetic utility of the reaction of butyllithium with a variety of 5-membered benzylidene acetal rings fused to a pyranose ring has been demonstrated. For compounds having a rigid chair conformation (**1, 5, 8**, and **12**), abstraction of the quasiaxial proton of the precursor diol proceeds with concomitant expulsion of the elements of benzaldehyde to afford deoxyketones (**2, 6, 9**, and **13**) having the ketone function *at the position of the former axial proton.* The outcome of the reaction with conformationally flexible or distorted-chair systems is more difficult to predict. In these situations, when no ring proton is constrained to a (quasi)axial disposition, more-vigorous reaction conditions may be required. Fragmentation originating with abstraction of the benzylidene proton (usually only a very minor side-reaction; *cf.* **1** → **3**) may then be an alternative or preponderant pathway leading to the corresponding alkene (reaction of **16** with butyllithium[13], and **21** → **22**) with expulsion of a benzoate anion. Occasionally, as in the reactions of **5, 8**, and **12** with butyllithium, fragmentation products (**7, 10**, and **14**) are observed that cannot have been formed through one of the three pathways outlined in Fig. 1. In these situations, a proton in the α-position (that is, at C-1 in the examples cited) of the 1,3-dioxolane ring evidently is sufficiently labile[17] to be abstracted in the initial step, with subsequent expulsion of benzaldehyde, to furnish the allylic alcohol derivatives **7, 10**, and **14**, respectively.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Specific rotations were measured, unless otherwise stated, for solutions in $CHCl_3$ with a Perkin–Elmer Model 141 polarimeter. ^{1}H-N.m.r. spectra were recorded, unless otherwise noted, for solutions in $CDCl_3$ (internal Me_4Si) at 100 MHz with a Varian HA-100 instrument. The R_F values refer to t.l.c. performed on Silica Gel 60 (Merck) with detection by u.v. light and by spraying with H_2SO_4 or $HClO_4$ and subsequent heating. Column chromatography was performed with silica gel (Merck 7734, 63–200 μm). Microanalyses were performed by W. N. Rond of this laboratory. Mass spectra were recorded by C. R. Weisenberger with an A.E.I. MS-9 instrument. All compounds gave spectra in accord with their assigned structures.

Preparation of O-benzylidene derivatives. — A mixture of the appropriate pyranose derivative (20 mmol), α,α-dimethoxytoluene (3.8 g, 25 mmol for

monobenzylidenation; 7.6 g, 50 mmol for dibenzylidenation), and *p*-toluenesulfonic acid monohydrate (20 mg) in dry $HCONMe_2$ (50 mL) was heated, under a water aspirator vacuum, for 3 h at 65–75°, and then poured into ice–water (200 mL) containing $NaHCO_3$ (2 g). The precipitate was collected and dried *in vacuo*. The products thus obtained were sufficiently pure for the following reaction with BuLi, and were mixtures of the *endo*/*exo*-diastereomers. In some instances, one or both diastereomers could be isolated pure.

*(a) Methyl 2,3:4,6-di-*O*-benzylidene-β-*D*-allopyranoside* (**5**). The yield of the crude mixture of diastereoisomers [~1:6 according to ^{1}H-n.m.r. spectroscopy: δ 6.42 and 5.95 (2 s, H-2′,2′ of dioxolane ring), 5.56 and 5.58 (2 s, H-2′,2′ of 1,3-dioxane ring)] was quantitative, melting range 90–120°, $[\alpha]_D^{22}$ +29° (*c* 1.2). The major isomer (2′-*R*), isolated by column chromatography (4:1 ether–light petroleum), had m.p. 125–127° (from 2-propanol), $[\alpha]_D^{21}$ +58° (*c* 0.8). ^{1}H-N.m.r. data: δ 5.92 and 5.55 (2 s, 2 PhC*H*).

Anal. Calc. for $C_{21}H_{22}O_6$ (370.41): C, 68.10; H, 5.99. Found: C, 68.10; H, 5.91.

*(b) 1,5-Anhydro-2,3:4,6-di-*O*-benzylidene-*D*-mannitol* (**8**). The mixture (96%) of diastereoisomers (~3:1, 2′-*R*/2′-*S*), after recrystallization from ethanol, had m.p. 145–148°, $[\alpha]_D^{22}$ −149° (*c* 1.5). Preparative t.l.c. (3:7:10 $CHCl_3$–Et_2O–light petroleum) afforded the 2′-*R* isomer (major component; R_F 0.2), double m.p. 160–161° and 164–165° (from EtOH), $[\alpha]_D^{22}$ −183° (*c* 0.8). ^{1}H-N.m.r. data: δ 5.95 (s, H-2′ of dioxolane ring) and 5.50 (s, H-2′ of dioxane ring).

Anal. Calc. for $C_{20}H_{20}O_5$ (340.38): C, 70.58; H, 5.92. Found: C, 70.52; H, 5.92.

The 2′-*S* isomer (minor component; R_F 0.4) had m.p. 186–187° (from EtOH), $[\alpha]_D^{22}$ −84° (*c* 0.8). ^{1}H-N.m.r. data: δ 6.35 (s, H-2′ of dioxolane ring) and 5.64 (s, H-2′ of dioxane ring).

Anal. Found: C, 70.70; H, 6.06.

*(c) 1,5-Anhydro-2,3:4,6-di-*O*-benzylidene-*D*-allitol* (**12**). The yield of the mixture of diastereoisomers (~4:1 in favor of the 2′-*S* isomer), after recrystallization from EtOH, was 56%; melting range 113–125°, $[\alpha]_D^{21}$ +82° (*c* 1.3). ^{1}H-N.m.r. data: δ 6.35 and 6.02 (2 s, H-2′,2′ of dioxolane ring), and 5.38 and 5.56 (2 s, H-2′,2′ of dioxane ring).

*(d) 1,6-Anhydro-2,3-*O*-benzylidene-β-*D*-mannopyranose* (**15**). Trituration of the crude reaction product (quantitative yield) with $CHCl_3$ afforded 24% of one diastereomer, m.p. 198–199° (from EtOH), $[\alpha]_D^{22}$ −122° (*c* 0.5, acetone). ^{1}H-N.m.r. data [$(CD_3)_2SO$]: δ 7.76–7.30 (m, 5 H, Ph), 5.69 (s, 1 H, PhC*H*), 5.60 (d, 1 H, $J_{4,OH}$ 3.8 Hz, OH), 5.40 (dd, 1 H, $J_{1,2}$ 2, $J_{1,3}$ 1.2 Hz, H-1), 4.51 (m, 1 H, $J_{4,5}$ 1.5, $J_{5,6}$ 1.5, $J_{5,6'}$ 6 Hz, H-5), 4.15–4.05 (m, 2 H, H-2,3), 3.91 (m, 1 H, H-4), 3.85 (dd, 1 H, $J_{6,6'}$ 7.5 Hz, H-6), and 3.64 (dd, 1 H, H-6′).

Anal. Calc. for $C_{13}H_{14}O_5$ (250.25): C, 62.40; H, 5.64. Found: C, 62.31; H, 5.72.

*(e) Methyl 3,4-*O*-benzylidene-2,6-dideoxy-α-*D*-ribo-hexopyranoside* (**21**). Col-

umn chromatography (4:1 Et_2O–light petroleum) of the mixture of products gave 34% of a diastereomer the configuration of which at C-2′ could not be assigned unambiguously. The compound had m.p. 58–59° (from ethanol–water). ^{1}H-N.m.r. data: δ 7.60–7.25 (m, 5 H, Ph), 5.77 (s, 1 H, PhC*H*), 4.69 (t, 1 H, $J_{1,2} = J_{1,2'} = 5.2$ Hz, H-1), 4.26 (m, 1 H, $J_{2,3}$ 5.2, $J_{2',3} = J_{3,4} = 6$ Hz, H-3), 4.07–3.70 (m, 2 H, H-4,5), 3.35 (s, 3 H, OMe), and 1.30 (d, 3 H, $J_{5,6}$ 6 Hz, H-6).

Anal. Calc. for $C_{14}H_{18}O_4$ (250.30): C, 67.18; H, 7.25. Found: C, 66.95; H, 7.18.

Reaction of benzylidene derivatives with butyllithium. — To a solution of the benzylidene acetal in dry oxolane at −30° under nitrogen was added butyllithium in hexane (2.4M, 2.2 mol). The specified temperature was maintained until t.l.c. indicated the reaction to be complete (~1.5 h). The mixture was then poured into ice–water containing NH_4Cl and processed. Invariably, 1-phenyl-1-pentanol (R_F 0.6; 4:1 ether–light petroleum) was encountered as a by-product from the reaction of benzaldehyde with butyllithium.

(a) Reaction of **5** *with butyllithium.* The mixture obtained from **5** (4.1 g, 11 mmol) at −30° was poured into ice–water containing NH_4Cl and the oxolane was removed *in vacuo* at ~30° (bath). The precipitate was collected and recrystallized from 2-propanol to afford methyl 4,6-*O*-benzylidene-3-deoxy-β-D-*erythro*-hexopyranosid-2-ulose (**6**, 720 mg). More (1.8 g; total yield, 86%) **6** was obtained by column chromatography (4:1 ether–light petroleum) of the material in the mother liquor. Compound **6** had m.p. 155–156° (from 2-propanol), $[\alpha]_D^{22}$ −26° (*c* 0.7); lit.[9] m.p. 153–155°, $[\alpha]_D$ −30° (chloroform).

Column chromatography also furnished a syrupy fraction (**7**; R_F 0.4; 100 mg) which could not be purified; it was tentatively identified as methyl 4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enopyranoside.

(b) Reaction of **8** *with butyllithium.* Following the reaction of **8** (5 g, 14.7 mmol) at 0°, the oxolane–water mixture was extracted with CH_2Cl_2, and the extract was washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. Trituration of the residue with EtOH afforded the dimer **11** (615 mg), more (200 mg) of which was obtained after column chromatography (see later); total yield, 24%; m.p. 254–255° (from EtOH), $[\alpha]_D^{23}$ −49° (*c* 0.7); R_F 0.1 (4:1 Et_2O–light petroleum). Mass spectrum: *m/z* 468 (M^+ 30% of base peak).

Anal. Calc. for $C_{26}H_{28}O_8$ (468.41): C, 66.66; H, 6.02. Found: C, 66.49; H, 6.03.

Column chromatography (4:1 Et_2O–light petroleum) of the material in the mother liquor afforded, first, 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-hex-1-enitol[11] (**10**; 180 mg, 5%), R_F 0.6, m.p. 145–146° (from hexane), $[\alpha]_D^{22}$ −19° (*c* 0.6).

Eluted second was 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*erythro*-hex-3-ulose (**9**; 2.26 g, 66%), R_F 0.4, m.p. 164–165° (from EtOH), $[\alpha]_D^{22}$ +19° (*c* 0.8). Mass spectrum: *m/z* 234 (M^+ 6% of base peak).

Anal. Calc. for $C_{13}H_{14}O_4$ (234.26): C, 66.66; H, 6.02. Found: C, 66.71; H, 6.31.

Elution with 4:1 $CHCl_3$–Me_2CO gave **11**.

(c) Reaction of **12** *with butyllithium.* Reaction of **12** (4 g, 11.8 mmol) at 0° and column chromatography (4:1 Et_2O–light petroleum) of the products afforded a fraction (R_F 0–0.1) that could not be purified or characterized, and a 2-component mixture (R_F 0.5). Column chromatography (2:1:1 C_6H_6–$CHCl_3$–Et_2O) of the latter fraction gave 1,5-anhydro-4,6-*O*-benzylidene-3-deoxy-D-*erythro*-hex-2-ulose (**13**; 1.4 g, 51%), m.p. 129–131° (from 2-propanol), $[\alpha]_D^{21}$ +20° (*c* 1.1). ^{1}H-N.m.r. data: *inter alia* δ 5.52 (s, 1 H, PhC*H*), 4.02 (d, 1 H, $J_{1e,1a}$ 10 Hz, H-1*e*), 3.66 (d, 1 H, H-1*a*), 3.03 (dd, 1 H, $J_{3e,3a}$ 16, $J_{3e,4}$ 6 Hz, H-3*e*), and 2.56 (dd, $J_{3a,4}$ 11 Hz, H-3*a*).

Anal. Calc. for $C_{13}H_{14}O_4$ (234.26): C, 66.66; H, 6.02. Found: C, 66.48; H, 5.86.

The fraction having R_F 0.3 was shown, by comparison with an authentic sample[11,12], to be 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enitol (**14**; 75 mg, 3%), m.p. 83–84° (from hexane), $[\alpha]_D^{21}$ +196° (*c* 1) and +214° (*c* 1.1, ethanol).

(d) Reaction of **21** *with butyllithium.* The reaction of **21** (1.0 g, 4.0 mmol) at −30° was sluggish but, at 0°, all **21** had disappeared after 30 min (t.l.c.). Column chromatography (4:1 Et_2O–light petroleum) of the product gave syrupy methyl 2,3,4,6-tetradeoxy-α-D-*glycero*-hex-3-enopyranoside (**22**; 200 mg, 39%), R_F 0.3. ^{1}H-N.m.r. data: δ 5.9 (dd, 1 H, $J_{3,4}$ 10, $J_{4,5}$ 1 Hz, H-4), 5.65 (ddd, 1 H, $J_{2,3}$ 3, $J_{2',3}$ 2 Hz, H-3), 4.8 (bd, $J_{1,2}$ 2, $J_{1,2'}$ <1 Hz, H-1), 3.0–4.0 (m, 3 H, H-2,2',5), 3.36 (s, 3 H, OMe), and 1.25 (d, 3 H, $J_{5,6}$ 7 Hz, H-6). Mass spectrum; *m/z* 128 (M^+, 15% of base peak). The compound could not be induced to crystallize, and elemental analytical data were not secured.

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