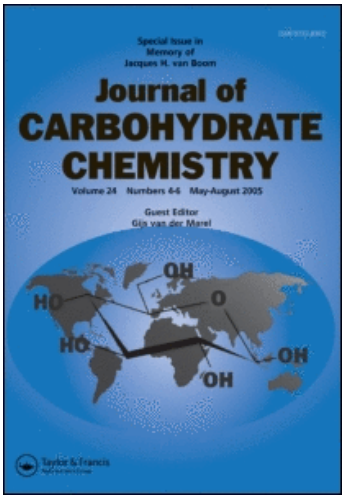

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Functionalized *C*-Glycosyl Compounds. III. Reaction of Tertiary Nucleophiles with Unsaturated Carbohydrates. Mechanism of the Anomerization

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FUNCTIONALIZED *C*-GLYCOSYL COMPOUNDS. III. REACTION OF TERTIARY NUCLEOPHILES WITH UNSATURATED CARBOHYDRATES. MECHANISM OF THE ANOMERIZATION.

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ABSTRACT

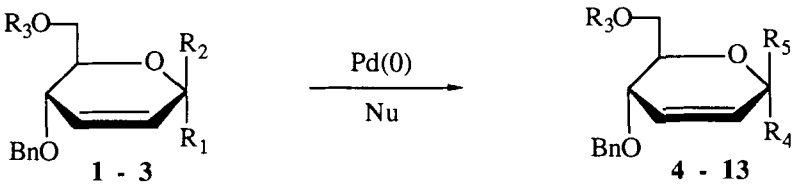
Phenyl 2,3-dideoxy-4,6-di-*O*-benzyl-D-*erythro*-hex-2-enopyranoside **1**α (or **1**β) is alkylated regio- and stereospecifically at the anomeric center by stabilized tertiary nucleophiles in the presence of Pd(0) as a catalyst, leading to the *C*-glycoside of α- (or β-) configuration. The observed loss of stereoselectivity using secondary stabilized nucleophiles is mainly due to a retro Michael reaction. The assignment of the α- (or β-) configuration at the anomeric center was accomplished using ^{13}C NMR and NOE experiments.

INTRODUCTION

C-glycosides are important chiral building blocks in the synthesis of natural compounds [2-7] and during the last few years several methods have been developed for their preparation.[8] The high stereochemical control offered by transition-metal-mediated transformations prompted several groups to investigate these methods for *C*-glycosyla-

* For part II, see ref. 1.

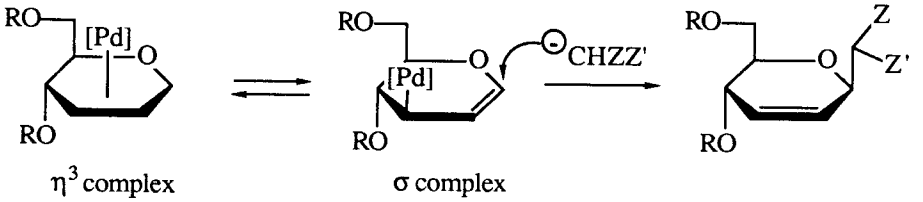
Scheme 1



1α	$R_1 = OPh$, $R_2 = H$, $R_3 = Bn$
1β	$R_1 = H$, $R_2 = OPh$, $R_3 = Bn$
2	$R_1 = OPh$, $R_2 = H$, $R_3 = t\text{-}BuMe_2Si$
3	$R_1 = OPh$, $R_2 = H$, $R_3 = Ph_3C$
4α	$R_4 = CH(CO_2C_2H_5)_2$, $R_5 = H$, $R_3 = Bn$
4β	$R_4 = H$, $R_5 = CH(CO_2C_2H_5)_2$, $R_3 = Bn$
5α	$R_4 = CH(COCH_3)_2$, $R_5 = H$, $R_3 = Bn$
5β	$R_4 = H$, $R_5 = CH(COCH_3)_2$, $R_3 = Bn$
6α	$R_4 = CH(NO_2)CO_2C_2H_5$, $R_5 = H$, $R_3 = Bn$
6β	$R_4 = H$, $R_5 = CH(NO_2)CO_2C_2H_5$, $R_3 = Bn$
7α	$R_4 = C(COCH_3)_2CO_2CH_3$, $R_5 = H$, $R_3 = Bn$
7β	$R_4 = H$, $R_5 = C(COCH_3)_2CO_2CH_3$, $R_3 = Bn$
8	$R_4 = C(CO_2C_2H_5)_2CH_3$, $R_5 = H$, $R_3 = Bn$
9	$R_4 = C(CO_2C_2H_5)_2CH_2CH{=}CH_2$, $R_5 = H$, $R_3 = Bn$
10	$R_4 = C(CO_2CH_3)_2CH_2C{\equiv}CH$, $R_5 = H$, $R_3 = Bn$
11α	$R_4 = C(NO_2)(CO_2C_2H_5)(CH_2CH{=}CH_2)$, $R_5 = H$, $R_3 = Bn$
11β	$R_4 = H$, $R_5 = C(NO_2)(CO_2C_2H_5)(CH_2CH{=}CH_2)$, $R_3 = Bn$
12	$R_4 = CH(NO_2)CO_2C_2H_5$, $R_5 = H$, $R_3 = t\text{-}BuMe_2Si$
13	$R_4 = CH(NO_2)CO_2C_2H_5$, $R_5 = H$, $R_3 = Ph_3C$

tion.[7, 9-13] We recently reported the palladium(0) catalyzed introduction, under neutral conditions, of a number of carbon nucleophiles at the anomeric position of 2,3-unsaturated phenyl glycoside **1** in excellent to moderate yields.[14] Alkylation of the β-anomer occurred with complete retention of configuration at the anomeric center, no matter which nucleophile was used. However, the stereospecificity of the reaction in the case of the α-anomer was dependent on the nucleophile used with β-dicarbonyl nucleophiles giving near 20-25 % of inversion. As part of our continuing interest in *C*-glycosyl compounds and to extend the synthetic utility of this reaction, we now report our results concerning the

Scheme 2



mechanism leading to the loss of stereospecificity in this reaction and the use of other β-dicarbonyl compounds as nucleophiles.

RESULTS AND DISCUSSION

We previously reported that the alkylation of the anomer **1β** occurred with complete retention of configuration at the anomeric center independant of the nucleophile employed.[14] In contrast, with the anomer **1α**, the reaction was only stereospecific using enolate type nucleophiles (acetyl acetone, ethyl malonate, methyl acetylacetate), ethyl nitromalonate and even ethyl nitroacetate only giving stereospecifically the *C*-glycoside of α-configuration.[14] The observed isomerization could be rationalized by a mechanism involving an S_N2' attack (syn) by the nucleophile on the σ-alkylpalladium complex (**Scheme 2**),[15] or more simply by a mechanism taking place under basic reaction conditions, i.e. a retro Michaël reaction. Isomerizations of this type with saturated *C*-glycosides have been previously explained in this way.[16,17] To determine what mechanism occurred in our case, we made a more detailed study of this reaction. The results are summarized in **Table 1**.

In alkylation with ethyl malonate or acetyl acetone, the use of an excess of the ligand (dppb or PPh_3) (entries 1-4) decreases the selectivity in the formation of the α-isomer, the β *C*-glycoside being only obtained in the presence of a large excess of PPh_3 (entry 4).

In the case of ethyl nitroacetate, an increase of the reaction temperature decreases the selectivity (entries 6-9). Even the phenyl glycoside **1β** gives a mixture of *C*-glycosides in a β/α = 64/36 ratio.

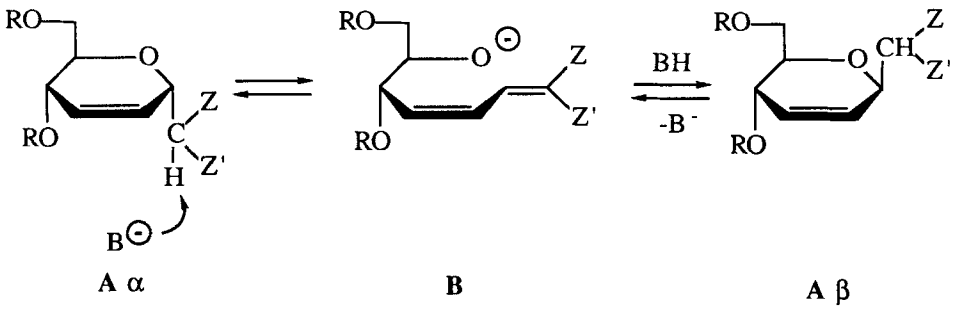
This isomerization could be well rationalized by a retro Michaël reaction (**Scheme 3**) better than by a S_N2' mechanism. In the presence of a base (PhO^- liberated in the reaction medium during the catalytic cycle), the α (or β) *C*-glycoside **A** leads to the linear interme-

TABLE 1. Alkylation of Glycals 1-3 with Various Nucleophiles.[a]

Entry	Glycal	Nucleophile	Ligand[b]	Solvent /T °C /Time (h)	Product (Yield %)[c]	α/β[d]
1	**1α**	$CH_2(CO_2C_2H_5)_2$	dppb	CH_3CN/60/6	**4** (60)	75/25
2	**1α**	$CH_2(CO_2C_2H_5)_2$	dppb + 3 PPh_3	CH_3CN/60/4	**4** (67)	75/25
3	**1α**	$CH_2(COCH_3)_2$	dppb	CH_3CN/60/6	**5** (67)	75/25
4	**1α**	$CH_2(COCH_3)_2$	PPh_3[e]	CH_3CN/60/6	**5** (40)	24/76
5	**1α**	$CH_2(COCH_3)_2$	dppb + 8 PPh_3	CH_3CN/60/5	**5** (40)	0/100
6	**1α**	$NO_2CH_2CO_2C_2H_5$	dppb	CH_3CN/60/2	**6** (80)	100/0
7	**1α**	$NO_2CH_2CO_2C_2H_5$	dppb	CH_3CN/80/3	**6** (80)	79/21
8	**1β**	$NO_2CH_2CO_2C_2H_5$	dppb	CH_3CN/60/2	**6** (80)	0/100
9	**1β**	$NO_2CH_2CO_2C_2H_5$	dppb	CH_3CN/80/3	**6** (80)	36/64
10	**1α**	$CH(COCH_3)_2CO_2CH_3$	dppb	THF/60/3	**7** (60)	100/0
11	**1α**	$CH(COCH_3)_2CO_2CH_3$	dppb	CH_3CN/80/4	**7** (64)	100/0
12	**1α**	$CH(COCH_3)_2CO_2CH_3$	$2PPh_3$	CH_3CN/80/3	**7** (61)	100/0
13	**1β**	$CH(COCH_3)_2CO_2CH_3$	dppb	CH_3CN/80/4	**7** (70)	0/100
14	**1α**	$NaC(CO_2C_2H_5)_2CH_3$	dppb	THF/60/12	**8** (88)	100/0
15	**1α**	$NaC(CO_2C_2H_5)_2CH_2$-$CH{=}CH_2$	dppb	THF/60/12	**9** (92)	100/0
16	**1α**	$NaC(CO_2CH_3)_2CH_2C{\equiv}CH$	dppb	THF/60/12	**10** (95)	100/0
17	**1α**	$NO_2CH(CO_2C_2H_5)CH_2CH{=}CH_2$	dppb	THF/60/12	**11** (90)	100/0
18	**2**	$NO_2CH_2CO_2C_2H_5$	dppb	CH_3CN/60/6	**12** (87)	100/0
19	**3**	$NO_2CH_2CO_2C_2H_5$	dppb	CH_3CN/60/6	**13** (87)	100/0

a. [glycal]:[NuH]:[Pd]:[phosphine] = 20:30:1:1.1; b. dppb: 1,4-bis(diphenylphosphino)butane; c. Isolated yield after column chromatography and not optimized; d. Determined by ^1H and ^{13}C NMR spectroscopy; e. $Pd(PPh_3)_4$ was used.

Scheme 3



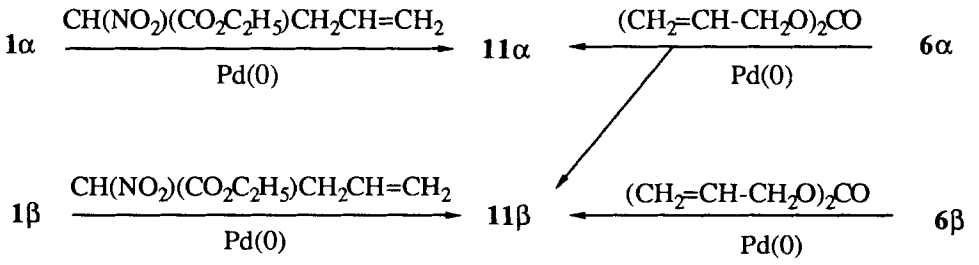
diate **B** which could cyclise to the β or the α *C*-glycoside Aβ or Aα, the β anomer being the thermodynamically more stable. Higher temperature increases also the ease of abstraction of the acidic hydrogen. This mechanism of isomerization is also consistent with the results observed in the synthesis of compounds **11α** and **11β** (**Scheme 4**). Alkylation of **6α** by diallyl carbonate in the presence of Pd(0) as the catalyst leads to the formation of the alkylated compound **11** as a mixture of α and β *C*-glycoside in a 60/40 ratio. Reversely alkylation of compound **6β** gives only the β *C*-glycoside **11β**. In this catalytic alkylation using carbonate as the leaving group, the nucleophile is formed *in situ* by abstraction of the acidic hydrogen from Aα or Aβ (Z = NO_2, Z' = $CO_2C_2H_5$) by CH_2=CH-CH_2O^-; the Aα anomer isomerizes to a mixture of α- and β- anomers by the above mechanism, which is not the case for the Aβ anomer. However, pure **11α** could be obtained by the alkylation of the phenylglycoside **1α** by ethyl 2-allyl-2-nitroacetate, a tertiary nucleophile, in the presence of a catalytic amount of palladium (0).

The observation that ethyl nitromalonate[14] and ethyl 2,2-diacetylacetate give no isomerized products in the alkylation of the phenyl glycoside **1α** even at 80 °C is also in agreement with this mechanism (entries 10-11).

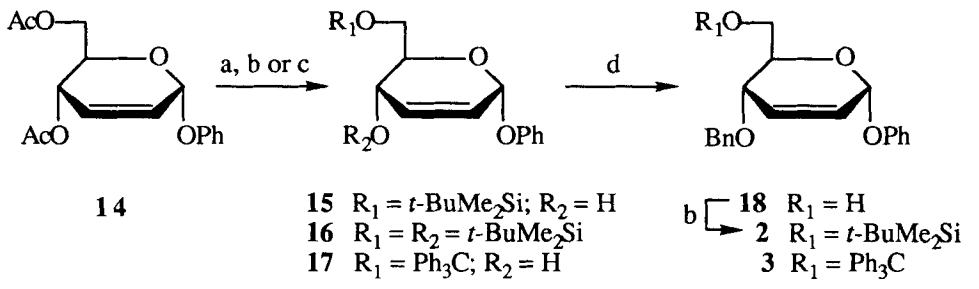
These observations prompted us to use ethyl alkylmalonates as nucleophiles in this reaction. Howewer, anions of these tertiary nucleophiles are needed for completion of the reaction, and as expected phenyl glycoside **1α** gives stereospecifically and very cleanly the α *C*-glycosides in good yields with no isomerized product being observed. Compounds **9**, **10** and **11** are interesting starting materials for the synthesis of homochiral cyclopentanes, an analog of compound **9** having been used recently in a palladium-mediated cyclisation.[18]

The unsaturated glycosides **2** and **3** were also used in this reaction. They were obtained from phenyl glycopyranoside **14** using conventional procedures (**Scheme 5**).

Scheme 4



Scheme 5



Reagents : a: CH_3ONa/CH_3OH; b: *t*-$BuMe_2SiCl$/imidazole, for **15** and **16**; c: Ph_3CCl/C_5H_5N for **17**; d: BnBr/KOH.

Deacetylation of **14** followed by tritylation and benzylation of the secondary hydroxyl function gave the trityl derivative **3**. Deacetylation of compound **14** followed by *t*-butyldimethylsilylation gave the monosilylated or the disilylated compounds **15** or **16**, using one or two equivalents of *t*-$BuMe_2SiCl$. Benzylation of compound **15** led to the formation of the hydroxy compound **18**, by the cleavage of the *t*-butyldimethylsilyl group; this compound was very easily transformed into the expected compound **2** by treatment with *t*-$BuMe_2SiCl$. The structure of compound **18** was determined by ^1H and mainly ^{13}C NMR (see Experimental Part). It is known that alkylation of a primary or a secondary alcohol shifts the carbon α to the oxygen downfield ~ 10 ppm and ~ 7 ppm, respectively, whereas the influence of a *t*-butyldimethylsilyl group is very low.[19] *t*-Butyldimethylsilyl ethers are also known to be cleaved by base.[20]

TABLE 2. Spectral Data Pertinent to Stereochemical Assignments of Compounds 4 - 13.[a]

Compound	(% epimer)	$J_{4',5'}$	δ C-1'	δ C-5'
4α		7.0	71.22	71.93
4β		8.2	73.25	77.75
5α		7.2	71.66	72.15
5β		8.4	73.57	77.28
6α	75 %	7.0	71.13	72.27
	25 %	7.0	70.16	72.84
6β	60 %	9.2	72.96	77.63
	40 %	9.2	72.89	78.05
7α		4.4	69.51	74.17
7β		8.7	74.77	77.74
8		4.3	72.36	73.65
9		4.2	71.22	73.18
10		4.9	70.96	73.65
11α	63 %	5.2	71.26	73.58
	37 %	4.9	71.26	73.25
11β	63 %	8.5	75.77	77.99
	37 %	8.5	74.64	78.38
12	75 %	7.7	70.03	73.48
	25 %	7.7	70.85	74.49
13	75 %	8.2	71.40	72.63
	25 %	8.2	70.32	73.55

a . δ in ppm; J in hertz.

The unsaturated phenyl glycosides **2** and **3** reacted with ethyl nitroacetate in the presence of palladium(0) as the catalyst to give stereospecifically the *C*-glycoside of α-configuration, as a mixture of *R* and *S* epimers at C-2 (75/25) [-$CHNO_2CO_2C_2H_5$)].

The structures of the *C*-glycosides were determined mainly on the basis of ^1H and ^{13}C NMR (**Table 2**). Having two anomers in hand (for compounds **7** and **11**), we observed larger coupling constants $J_{4',5'}$ for the β-anomer ($J_{4',5'}$ values of 8.7 and 8.5 Hz,

respectively) than for the α-anomer ($J_{4',5'}$ values of 4.4 and 4.9 -5.2 Hz, respectively). This is consistent with a stable $^0H_5$ conformation for the β-anomer and an equilibrating mixture of the $^0H_5$ and $^5H_0$ conformations for the α-anomer.

The assignment of configuration at the anomeric center could also be made from ^{13}C NMR data, mainly the chemical shift of C-5'. The α-anomer shows a C-5' signal at 74.17 ppm for compound **7α** and two signals at 73.58 and 73.25 ppm for **11α**, at higher field than the β-anomer (respectively at 77.74 and 77.99 and 78.38 ppm). This is due to the γ-gauche effect.[19] It is to be noticed that the C-5' signal for all the α-anomers is about 71.9-74.5 ppm, and for the β-anomers about 77.3-78.4 ppm. This chemical shift could be used for the determination of the α- or β-configuration.

However, the most suitable method for the determination of the configuration at C-1' was the use of NOE experiments. For example, irradiation at the C-1' methine proton of **7β** at δ = 5.02 ppm at 300 MHz ($CDCl_3$), showed an enhancement of 10 % in the C-5' methine proton signal at δ = 3.60-3.80 ppm. Similar experiments, made on compound **11β** by irradiation of the C-1' methine proton at δ = 5.01 ppm, showed an enhancement of 11 % for the C-5' methine signal at 3.58-3.75 ppm. A NOE experiment on compound **7α**, using the C-1' and the C-5' signals at 4.32 and 4.37 ppm, showed no enhancement of, respectively, the C-5' and C-1' signals.

In the case of **11α**, irradiation of the C-1' methine proton at 4.86 ppm showed no enhancement of the C-5' methine signal at 3.81 ppm. This behaviour was found for all the α-anomers. In our opinion the NOE experiments allowed the unambiguous assignment of the α or β configuration at the anomeric center.

CONCLUSION

In summary, alkylation of unsaturated phenyl glycosides with stabilized nucleophiles in the presence of Pd (0) occurs regio- and stereospecifically at the anomeric center. The observed inversion of configuration is due to a retro Michaël reaction arising under the experimental conditions described. The use of tertiary nucleophiles suppresses this isomerization. The assignments of the α or β configuration at the anomeric center of these unsaturated *C*-glycosides was based upon results from NOE experiments.

EXPERIMENTAL

Thin-layer and column chromatography were carried out on silica gel GF_{254} (230-400 mesh Merck). Proton and carbon NMR spectra were recorded on a Bruker MSL 300

spectrometer with $CDCl_3$ as solvent and Me_4Si as internal standard. Heteronuclear chemical shift correlation (COSY) experiments were carried out using furnished software. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Microanalyses were performed by the Laboratoire Central de Microanalyse du CNRS, Vernaison, France. All solvents were distilled from an appropriate drying agent and stored under nitrogen. All air-sensitive reactions were performed under an atmosphere of nitrogen. Phenyl 2,3-dideoxy-4,6-di-*O*-benzyl-D-*erythro*-hex-2-enopyranoside **1**α and **1**β were prepared according to the literature.[14] Compounds **4**α and **4**β, **5**α and **5**β, **6**α and **6**β have been already described.[14]

General Procedure for Pd(0)-Catalyzed *C*-Glycosylation. To a solution of 36 mg (0.062 mmol) of $Pd(dba)_2$ and 0.07 mmol of diphosphine (or 0.14 mmol of triphenylphosphine) in 3 mL of THF or CH_3CN was added 502 mg (1.25 mmol) of the unsaturated sugar. To the above mixture was added 2.5 mmol of the nucleophile, and the mixture was stirred at the desired temperature until no more starting material was visible on TLC. In entries 14-16, the anions of the nucleophiles were prepared from 2.5 mmol of the nucleophile and 2.7 mmol of NaH in THF (or CH_3CN). Concentration and column chromatography in the indicated solvents furnished the *C*-glycosides.

Phenyl 2,3-Dideoxy-6-*O*-*t*-butyldimethylsilyl-α-D-*erythro*-hex-2-enopyranoside 15. A solution of 1.37 g (4.47 mmol) of phenyl 2,3-dideoxy-4,6-di-*O*-acetyl-α-D-*erythro*-hex-2-enopyranoside **14** in methanol (80 mL) containing 15 mg (0.33 mmol) of CH_3ONa was stirred at 25 °C for 30 min. The solution was treated with Amberlite IR-120 H^+, and the methanol evaporated under vacuum. The crude diol obtained was dissolved in DMF (8 mL), and imidazole (0.77 g, 11.3 mmol) and *t*-$BuMe_2SiCl$ (0.81 g, 5.43 mmol) were added. The mixture was stirred at room temperature for 48 h and then partitioned between water (70 mL) and chloroform (20 mL). The aqueous layer was washed with additional chloroform (3 x 20 mL), and the combined extracts were dried over sodium sulfate. After solvent evaporation, the crude product was chromatographed on silica gel, eluting with EtOAc/hexane (1/3) (R_f 0.37) to afford the product **15** as an oil. Yield 85 %; $[\alpha]_D^{25}$ + 88.6° (*c* 2.5, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.08 (s, 6H, $SiCH_3$), 0.88 (s, 9H, $SiCMe_3$), 3.18 (bs, 1H, OH), 3.78 (dd, 1H, $J_{6,5}$ = 3.2 Hz, $J_{6,6'}$ = 9.0 Hz, H-6), 3.83-3.92 (m, 2H, H-5, H-6'), 4.28 (ddd, 1H, $J_{4,2}$ = 1.2 Hz, $J_{4,3}$ = 2.7 Hz, $J_{4,5}$ = 7.3 Hz, H-4), 5.62 (bs, 1H, H-1), 5.87 (ddd, 1H, $J_{3,1}$ = 2.2 Hz, $J_{3,2}$ = 10.2 Hz, $J_{3,4}$ = 2.7 Hz, H-3), 6.08 (ddd, 1H, $J_{2,1}$ = 1.2 Hz, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 1.2 Hz, H-2), 7.0-7.3 (m, 5H, Ph); ^{13}C NMR δ - 5.54 and - 5.47 ($SiCH_3$), 18.22 ($SiCMe_3$), 25.84 ($SiCMe_3$), 65.07 (C-6), 66.49 (C-4), 70.94 (C-5), 92.88 (C-1), 125.06 (C-2), 133.76 (C-3), 116.94, 122.13, 129.43 and 157.42 (Ph).

Anal. Calcd for $C_{18}H_{28}SiO_4$: C, 64.44; H, 8.11. Found: C, 64.35; H, 8.16.

Phenyl 2,3-Dideoxy-4,6-di-*O*-*t*-butyldimethylsilyl-α-D-*erythro*-hex-2-enopyranoside 16. The crude diol obtained using the above mentioned method was dissolved in DMF (8 mL) and imidazole (1.13 g, 19 mmol) and *t*-BuMe$_2$SiCl (2.5 g, 16.5 mmol) were added. The mixture was stirred at room temperature for 48 h and after usual work-up, the crude product was chromatographed on silica gel, eluting with EtOAc/hexane (1/3) (R_f 0.83) to afford the product **15** as an oil. Yield 85 %; $[\alpha]_D^{25}$ + 13.0° (*c* 1.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 3H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$), 0.11 (s, 3H, $SiCH_3$), 0.12 (s, 3H, $SiCH_3$), 0.86 (s, 9H, $SiCMe_3$), 0.90 (s, 9H, $SiCMe_3$), 3.67-3.95 (m, 3H, H-5, H-6, H-6'), 4.32 (ddd, 1H, $J_{4,2}$ = 1.2 Hz, $J_{4,3}$ = 2.7 Hz, $J_{4,5}$ = 8.5 Hz, H-4), 5.63 (dd, 1H, $J_{1,2}$ = 1.2 Hz, $J_{1,3}$ = 2.0 Hz, H-1), 5.83 (ddd, 1H, $J_{3,1}$ = 2.0 Hz, $J_{3,2}$ = 10.1 Hz, $J_{3,4}$ = 2.7 Hz, H-3), 6.00 (ddd, 1H, $J_{2,1}$ = $J_{2,4}$ = 1.2 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 6.95-7.31 (m, 5H, Ph); ^{13}C NMR δ - 5.38, - 5.12, - 4.90 and - 4.33 ($SiCH_3$), 18.61 ($SiCMe_3$), 25.72 and 25.91 ($SiCMe_3$), 62.10 (C-6), 63.39 (C-4), 73.29 (C-5), 93.05 (C-1), 124.64 (C-2), 135.60 (C-3), 116.96, 121.85, 129.28 and 157.58 (Ph).

Anal. Calcd for $C_{24}H_{42}Si_2O_4$: C, 63.95; H, 9.39. Found : C, 63.60; H, 9.44.

Phenyl 2,3-Dideoxy-4-*O*-benzyl-α-D-*erythro*-hex-2-enopyranoside 18. Compound **15** (1.26 g, 4.78 mmol) was dissolved in DMSO (20 mL) in the presence of KOH (1.07 g, 19.1 mmol). The mixture was stirred for 15 min at 0 °C, and benzyl chloride (1.83 g, 14.5 mmol) was added slowly. The reaction was stirred at room temperature for 14 h and then partitioned between water (80 mL) and chloroform (3 x 30 mL). Usual work-up and chromatography on silica gel, eluting with EtOAc/hexane (1/3) (R_f 0.26) afforded the product **18** as an oil. Yield 70 %; ^{1}H NMR ($CDCl_3$) δ 1.90 (s, 1H, OH), 3.74 (dd, 1H, $J_{6,5}$ = 4.2 Hz, $J_{6,6'}$ = 11.9 Hz, H-6), 3.81 (dd, 1H, $J_{6',5}$ = 2.6 Hz, $J_{6',6}$ = 11.9 Hz, H-6'), 3.98 (ddd, 1H, $J_{5,4}$ = 9.6 Hz, $J_{5,6}$ = 4.2 Hz, $J_{5,6'}$ = 4.2 Hz, H-5), 4.16 (ddd, 1H, $J_{4,2}$ = 1.0 Hz, $J_{4,3}$ = 2.7 Hz, $J_{4,5}$ = 9.6 Hz, H-4), 4.58 and 4.70 (2 x d, 2H, J = 11.6 Hz, OCH_2Ph), 5.67 (bs, 1H, H-1), 5.91 (ddd, 1H, $J_{3,1}$ = 2.0 Hz, $J_{3,2}$ = 10.2 Hz, $J_{3,4}$ = 2.7 Hz, H-3), 6.22 (ddd, 1H, $J_{2,1}$ = 1.0 Hz, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 1.0 Hz, H-2), 7.2-7.4 (m, 10 H, Ph); ^{13}C NMR δ 61.89 (C-6), 69.71 (C-4), 70.53 (C-5), 71.05 (OCH_2Ph), 92.86 (C-1), 125.48 (C-2), 131.36 (C-3), 116.53, 122.11, 127.53, 128.33, 129.38, 137.59 and 156.99 (Ph).

Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found : C, 72.91; H, 6.42.

Phenyl 2,3-Dideoxy-4-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-α-D-*erythro*-hex-2-enopyranoside 2. A solution of 0.5 g (1.6 mmol) of **18**, 0.4 g (5.2 mmol) of imidazole and 0.78 g (5.2 mmol) of *t*-BuMe$_2$SiCl in DMF (6 mL) was stirred for 48 h at room temperature. After usual work-up, chromatography on silica gel, eluting with EtOAc/hexane (1/4) (R_f 0.76), afforded compound **2** as an oil. Yield 80 %; $[\alpha]_D^{20}$ +38.0 (*c* 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) 0.03 (s, 6H, $SiCH_3$), 0.85 (s, 9H, $SiCMe_3$), 3.81 (dd,

1H, $J_{6,5}$ = 4.0 Hz, $J_{6,6'}$ = 11.5 Hz, H-6), 3.86 (dd, 1H, $J_{6',5}$ = 2.3 Hz, $J_{6',6}$ = 11.5 Hz, H-6'), 3.94 (ddd, 1H, $J_{5,4}$ = 9.2 Hz, $J_{5,6}$ = 4.0 Hz, $J_{5,6'}$ = 2.3 Hz, H-5), 4.19 (dddd, 1H, $J_{4,1} = J_{4,2} = J_{4,3}$ = 1.7 Hz, $J_{4,5}$ = 9.2 Hz, H-4), 4.59 and 5.69 (2 x d, 2H, J = 11.6 Hz, OC*H*$_2$Ph), 5.64 (bs, 1H, H-1), 5.89 (ddd, 1H, $J_{3,1}$ = 2.1 Hz, $J_{3,2}$ = 10.1Hz, $J_{3,4}$ = 1.7 Hz, H-3), 6.18 (ddd, 1H, $J_{2,1}$ = 2.3 Hz, $J_{2,3}$ = 10.1 Hz, $J_{2,4}$ = 1.7 Hz, H-2), 7.2-7.4 (m, 10H, Ph); ^{13}C NMR δ - 5.4 and - 5.3 (SiCH$_3$), 18.62 (Si*C*Me$_3$), 25.67 (SiC*Me*$_3$), 62.19 (C-6), 69.53 (C-4), 70.96 (O*C*H$_2$Ph), 71.20 (C-5), 92.85 (C-1), 125.51 (C-2), 131.69 (C-3), 116.74, 121.67, 127.49, 128.15, 129.07, 138.33 and 157.72 (Ph).

Anal. Calcd for $C_{25}H_{34}SiO_4$: C, 70.38; H, 9.03. Found : C, 70.55; H, 8.12.

Phenyl 2,3-Dideoxy-6-*O*-trityl-α-D-*erythro*-hex-2-enopyranoside 17. To the crude diol (2 g, 9.0 mmol) obtained from phenyl 2,3-dideoxy-4,6-di-*O*-acetyl-α-D-*erythro*-hex-2-pyranoside and dissolved in C_5H_5N (60 mL) was added TrCl (5.0g, 18.1 mmol). After stirring at room temperature for 24 h, the mixture was partitioned between water (100 mL) and dichloromethane (200 mL). After usual work-up, the product **17** was obtained by chromatography on silica gel eluting with EtOAc/hexane (1/3) (R_f 0.31). Yield 80 %. $[\alpha]_D^{25}$ + 51.6° (*c* 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 2.22 (bs, 1H, OH), 3.34 (dd, 1H, $J_{6,5}$ = 4.7 Hz, $J_{6,6'}$ = 9.7 Hz, H-6), 3.42 (dd, 1H, $J_{6',5}$ = 5.2 Hz, $J_{6',6}$ = 9.7 Hz, H-6'), 3.92 (ddd, 1H, $J_{5,4}$ = 9.3 Hz, $J_{5,6}$ = 4.7 Hz, $J_{5,6'}$ = 5.2 Hz, H-5), 4.21 (ddd, 1H, $J_{4,3}$ = 2.0 Hz, $J_{4,2}$ = 1.3 Hz, $J_{4,5}$ = 9.3 Hz, H-4), 5.67 (bs, 1H, H-1), 5.91 (ddd, 1H, $J_{3,1}$ = 2.3 Hz, $J_{3,2}$ = 10.0 Hz, $J_{3,4}$ = 2.0 Hz, H-3), 6.06 (ddd,1H, $J_{2,1}$ = 2.3 Hz, $J_{2,3}$ = 10.0 Hz, $J_{2,4}$ = 1.3 Hz, H-2), 7.1-7.4 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 64.43 (C-6), 65.34 (C-4), 71.05 (C-5), 87.10 (*C*Ph$_3$), 92.75 (C-1), 125.43 (C-2), 133.94 (C-3), 115.3-157.3 (Ph).

Anal. Calcd for $C_{31}H_{28}O_4$: C, 80.15; H, 6.08. Found : C, 79.41; H, 6.10.

Phenyl 2,3-Dideoxy-4-*O*-benzyl-6-*O*-trityl-α-D-*erythro*-hex-2-enopyranoside 3. A solution of compound **17** (2.0 g, 4.31 mmol) was dissolved in DMSO (30 mL) in the presence of KOH (1.45 g, 25.8 mmol). The mixture was stirred for 15 min at 0 °C, and benzyl chloride (1.09 g, 8.62 mmol) was added. After stirring for 24 h and usual work-up, column chromatography on silica gel eluting with AcOEt/hexane (1/3) (R_f 0.31) afforded pure **3**. Yield 62 %; $[\alpha]_D^{25}$ + 40.4° (*c* 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 3.19 (dd, 1H, $J_{6,5}$ = 4.7 Hz, $J_{6,6'}$ = 10.2 Hz, H-6), 3.44 (dd, 1H, $J_{6',5}$ = 1.6 Hz, $J_{6',6}$ = 10.2 Hz, H-6'), 4.08 (ddd, 1H, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 4.7 Hz, $J_{5,6'}$ = 1.6 Hz, H-5), 4.26 (dddd, 1H, $J_{4,1}$ = 1.5 Hz, $J_{4,2} = J_{4,3}$ = 1.8 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 4.49 and 4.34 (2 x d, 2H, J = 11.5 Hz, OC*H*$_2$Ph), 5.75 (bs, 1H, H-1), 5.91 (ddd, 1H, $J_{3,1}$ = 2.7 Hz, $J_{3,2}$ = 10.2 Hz, $J_{3,4}$ = 1.8 Hz, H-3), 6.18 (ddd, 1H, $J_{2,1}$ = 1.4 Hz, $J_{2,3}$ = 10.2 Hz, $J_{2,4}$ = 1.8 Hz, H-2), 7.1-7.3 (m, 25H, Ph); ^{13}C NMR ($CDCl_3$) δ 61.55 (C-6), 68.58 (C-4), 71.29 (*C*H$_2$Ph), 71.31 (C-5), 86.90 (*C*Ph$_3$), 92.7 (C-1), 125.85 (C-2), 131.87 (C-3), 117.2-157.5 (Ph).

Anal. Calcd for $C_{38}H_{34}O_4$: C, 82.28; H, 6.18. Found : C, 82.56; H, 6.03.

Methyl 2-(2',3'-Dideoxy-4',6'-di-*O*-benzyl-D-*erythro*-hex-2'-enopyranosyl)-2,2-(diacetyl) acetate 7.

α Anomer: oil; yield 64%; R_f 0.27 (20% AcOEt/hexane); $[\alpha]_D^{20}$ + 53.5° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 2.30 (3H, s, $COCH_3$), 2.37 (3H, s, $COCH_3$), 3.48 (1H, dd, $J_{6",6'}$ = 10.3, $J_{6",5'}$ = 7.8, H-6"), 3.61 (1H, m, $J_{4',5'}$ = 4.4, H-4'), 3.67 (1H, dd, $J_{6',6"}$ = 10.3, $J_{6',5'}$ = 5.7, H-6'), 3.75 (1H, s, OCH_3), 4.32 (1H, ddd, $J_{1',4'}$ = 2.0, $J_{1',3'}$ = 1.7, $J_{1',2'}$ = 1.1, H-1'), 4.37 (1H, bt, H-5'), 4.53 and 4.51 (2 x 2H, 2 x s, OCH_2Ph), 6.02 (1H, ddd, $J_{3',2'}$ = 10.7, $J_{3',4'}$ = 4.0, $J_{3',1'}$ = 2.2, H-3'), 6.10 (1H, dd, $J_{2',3'}$ = 10.7, $J_{2',1'}$ = 1.1, H-2'), 7.20-7.40 (10H, m, Ph); ^{13}C NMR δ 28.98 and 29.49 ($COCH_3$), 52.88 (OCH_3), 67.68 (C-6'), 67.91 (C-4'), 69.51 (C-1'), 70.45 (OCH_2Ph), 73.13 (OCH_2Ph), 74.17 (C-5'), 79.37 (C-2), 125.67 (C-2'), 129.56 (C-3'), 127.57, 127.62, 127.68, 127.80, 128.39, 128.41, 137.69 and 137.99 (Ph), 167.35 (OC=O), 201.61 (C=O).

Anal. Calcd for $C_{27}H_{30}O_7$: C, 69.51; H, 6.48. Found: C, 69.70; H, 6.64.

β Anomer: oil; yield 70%; R_f 0.30 (20% AcOEt/hexane); $[\alpha]_D^{20}$ + 104.3° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 2.22 (3H, s, $COCH_3$), 2.32 (3H, s, $COCH_3$), 3.60-3.80 (3H, m, H-5', H-6' and H-6"), 3.75 (3H, s, OCH_3), 4.07 (1H, ddd, $J_{4',5'}$ = 8.7, $J_{4',1'}$ = 2.8, $J_{2',4'}$ = 1.7, H-4'), 4.54 (2H, s, OCH_2Ph), 4.49 and 4.46 (2 x 1H, 2 x d, J =11.5, OCH_2Ph), 5.02 (1H, ddd, $J_{1',4'}$ = 2.8, $J_{1',3'}$ = 2.2, $J_{1',2'}$ = 1.5, H-1'), 5.95 (1H, ddd, $J_{2',3'}$ = 10.6, $J_{2',4'}$ = 1.7, $J_{2',1'}$ = 1.5, H-2'), 6.04 (1H, ddd, $J_{3',2'}$ = 10.6, $J_{3',1'}$ = 2.2, $J_{3',4'}$ = 1.7, H-3'), 7.2-7.4 (10H, m, Ph); ^{13}C NMR δ 29.04 and 29.15 ($COCH_3$), 52.94 (OCH_3), 69.30 (C-6'), 69.55 (C-4'), 71.31 (OCH_2Ph), 73.08 (OCH_2Ph), 74.77 (C-1'), 77.74 (C-5'), 79.91 (C-2), 127.64 (C-2'), 129.15 (C-3'), 127.28, 127.50, 127.84, 127.89, 128.35, 128.44, 137.74 and 138.30 (Ph), 167.51 (OC=O), 200.12 and 201.73 (C=O).

Anal. Calcd for $C_{27}H_{30}O_7$: C, 69.51; H, 6.48. Found: C, 69.76; H, 6.51.

Ethyl 2-(2',3'-Dideoxy-4',6'-di-*O*-benzyl-D-*erythro*-hex-2'-enopyranosyl)-2-(*R,S*)-nitro-2-(*R,S*)-allyl acetate 11.

α Anomer: oil; yield 90%; R_f 0.5 (30% AcOEt/hexane); $[\alpha]_D^{20}$ + 25.8° (*c* 1.9, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.24 and 1.27 (2 x 2 s, 0.37 x 3H and 0.63 x 3H, J = 7.2 Hz, CH_3), 2.98 (dd, 0.37 H, J = 11.5 Hz, J = 7.5 Hz, CH_2-CH=), 2.98 (dd, 0.63 H, J = 13.7 Hz, J = 7.6 Hz, CH_2-CH=), 3.26 (dd, 0.37 H, J = 11.5 Hz, J = 6.9 Hz, CH_2-CH=), 3.38 (dd, 0.63 H, J = 13.7Hz, J = 7.2 Hz, CH_2-CH=), 3.57 (dd, 1H, $J_{6",6'}$ = 10.5 Hz, $J_{6",5'}$ = 4.9 Hz, H-6"), 3.64 (dd, 1H, $J_{6',6"}$ = 10.5 Hz, $J_{6',5'}$ = 5.2 Hz, H-6'), 3.81 (ddd, 0.63 H, ddd, $J_{5',4'}$ = $J_{5',6'}$ = $J_{5',6"}$ = 5.2 Hz, H-5'), 3.89 (m, 1H, H-4'), 4.01 (ddd, 0.37 H, $J_{5',4'}$ = $J_{5',6'}$ = $J_{5',6"}$ = 4.9 Hz, H-5'), 4.22 (m) and 4.25 (M) (2 x q, 0.37 x

2H and 0.63 x 2H, CH_2), 4.45 and 4.53 (2 x d, 2H, J = 11.8 Hz, OC*H*$_2$Ph), 4.51 and 4.57 (2 x d, 2H, J = 12.1 Hz, OC*H*$_2$Ph), 4.86 (ddd, 0.63 H, $J_{1',4'} = J_{1',3'} = J_{1',2'}$ = 2.1 Hz, H-1'), 4.98 (ddd, 0.37H, $J_{1',4'} = J_{1',3'} = J_{1',2'}$ = 2.1 Hz, H-1'), 5.10-5.25 (m, 2H, CH=C*H*$_2$), 5.65-5.85 (m, 1H, C*H*=CH_2), 6.08 (ddd, 1H, $J_{3',2'}$ = 10.6 Hz, $J_{3',4'}$ = 4.8 Hz, $J_{3',1'}$ = 2.2 Hz, H-3'), 6.17 (ddd, 1H, $J_{2',3'}$ = 10.6 Hz, $J_{2',4'}$ = 3.2 Hz, $J_{2',1'}$ = 2.2 Hz, H-2'), 7.20-7.40 (m, 10H, Ph); ^{13}C NMR δ 13.81 (CH_3), 36.90 and 37.24 (0.37 and 0.63 *C*H_2-CH=), 62.72 and 62.78 (0.63 and 0.37 CH_2), 68.58 (C-6'), 68.70 (C-4'), 70.21 and 70.63 (0.63 and 0.37 OCH_2Ph), 71.26 (C-1') 73.15 (OCH_2Ph), 73.25 and 73.58 (0.37 and 0.63 C-5'), 92.00 (C quat.), 121.14 and 121.25 (0.37 and 0.63 *C*H=CH_2), 126.37 and 126.78 (0.63 and 0.37 C-2'), 129.86 and 130.22 (0.63 and 0.37 C-3'), 127.66, 127.79, 128.34, 128.41, 128.76, 129.86, 130.22, 137.92 and 138.06 (CH=*C*H_2 and Ph), 164.5 and 165.7 (C=O).

Anal. Calcd for $C_{27}H_{31}NO_7$: C, 67.34; H, 6.49; N, 2.90. Found: C, 66.90; H, 6.23: N, 2.75.

β Anomer: oil; yield 98%; R_f 0.44 (25% AcOEt/hexane); $[\alpha]_D^{20}$ + 75.0° (*c* 0.9, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.24 and 1.27 (2 x s, 0.37 x 3H and 0.63 x 3H, J = 7.1 Hz, CH_3), 2.90 (dd, 0.63 H, J = 14.6 Hz, J = 7.3 Hz, C*H*$_2$-CH=), 2.99 (dd, 0.37 H, J = 13.7 Hz, J = 6.7 Hz, C*H*$_2$-CH=), 3.14 (dd, 0.63 H, J = 14.6 Hz, J = 7.3 Hz, C*H*$_2$-CH=), 3.28 (dd, 0.37 H, J = 13.7 Hz, J = 6.7 Hz, C*H*$_2$-CH=), 3.58-3.75 (m, 3H, H-5', H-6', H-6"), 3.92 and 4.04 (2 x dd, 0.37 H and 0.63 H, $J_{4',1'}$ = 2.9 Hz, $J_{4',5'}$ = 8.5 Hz, H-4'), 4.23 and 4.27 (2 x q, 0.63 x 2H and 0.37 x 2H, J = 7.1 Hz, CH_2), 4.42 and 4.52 (2d, 2H, J = 12.0 Hz, OC*H*$_2$Ph), 4.50 and 4.53 (2d, 2H, J = 12.5 Hz, OC*H*$_2$Ph), 4.53 and 4.55 (2d, 2H, J = 11.2 Hz, OC*H*$_2$Ph), 4.61 and 4.63 (2d, 2H, J = 11.5 Hz, OC*H*$_2$Ph), 4.82 and 5.01 (2 x d, 0.37 H and 0.63 H, $J_{1',4'}$ = 2.9 Hz, H-1'), 5.10-5.25 (m, 2H, CH=C*H*$_2$), 5.65-5.85 (m, 1H, C*H*=CH_2), 6.06 and 6.08 (2 x s, 0.37 x 2H and 0.63 x 2H, H-2', H-3'), 7.20-7.40 (m, 10H, Ph); ^{13}C NMR δ 13.84 and 14.23 (0.63 and 0.37 CH_3), 35.91 and 36.72 (0.63 and 0.37 *C*H_2-CH=), 62.68 and 62.72 (0.63 and 0.37 CH_2), 69.12 and 69.50 (0.63 and 0.37 C-6'), 69.72 and 69.82 (0.63 and 0.37 C-4'), 71.35 and 71.45 (0.37 and 0.63 OCH_2Ph), 73.35 (OCH_2Ph), 74.64 and 75.77 (0.37 and 0.63 C-1'), 77.99 and 78.38 (0.63 and 0.37 C-5'), 96.56 and 96.78 (0.63 and 0.37 C quat.), 120.75 and 121.40 (0.63 and 0.37 *C*H=CH_2), 126.04 and 126.18 (0.63 and 0.37 C-2'), 130.05 and 130.51 (0.37 and 0.63 C-3'), 127.6, 127.8, 128.3, 128.4, 128.8, 129.8,130.2, 137.8 and 138.4 (CH=*C*H_2 and Ph), 164.51 (C=O).

Anal. Calcd for $C_{27}H_{31}NO_7$: C, 67.34; H, 6.49; N, 2.90. Found: C, 67.26; H, 6.26: N, 3.00.

Procedure for Pd(0)-Catalyzed Alkylation of Compound 6. To a solution of 20.7 mg (0.0226 mmol) of $Pd_2(dba)_3$ and 19.3 mg (0.045 mmol) of 1,4-bis(diphenyl-

phosphino)butane in 5 mL of THF at 25 °C was added 200 mg (0.453 mmol) of compound **6**. To the above mixture was added 128.7 mg (0.906 mmol) of diallyl carbonate in 2 mL of THF and the mixture was stirred at room temperature for 0.5 h. Concentration and column chromatography furnished the allylated glycosides **11**, only as the β anomer starting from **6**β, and as a mixture of α and β anomers in a ratio 60/40 starting from **6**α. **11** α was obtained by alkylation of the phenyl glycoside using the usual procedure.

Ethyl 2-(2',3'-Dideoxy-4'-*O*-benzyl-6'-*O*-*t*-butyldimethylsilyl-α-D-*erythro*-hex-2'-enopyranosyl)-2(*R,S*)-nitroacetate 12. Oil; yield 78 %; R_f 0.57 (20 % AcOEt-hexane); $[\alpha]_D^{20}$ + 33.9° (*c* 1, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.06 (s, 6H, $SiCH_3$), 1.29 and 1.31 (2 t, 0.75 x 3H and 0.25 x 3H, J = 7.2 Hz, CH_3), 1.90 (s, 9H, CMe_3), 3.61 (m, 1H, H-5'), 3.74 (dd, 0.25 H, $J_{6',5'}$ = 3.0 Hz, $J_{6',6''}$ = 11.6 Hz, H-6'), 3.76 (dd, 0.75 H, $J_{6',5'}$ = 3.0 Hz, $J_{6',6''}$ = 11.6 Hz, H-6'), 3.76 (dd, 0.75 H, $J_{6',5'}$ = 2.6 Hz, $J_{6',6''}$ = 11.1 Hz, H-6'), 3.82 (dd, 0.75 H, $J_{6'',5'}$ = 4.8 Hz, $J_{6'',6'}$ = 11.1 Hz, H-6''), 3.85 (dd, 0.25 Hz, $J_{6'',5'}$ = 4.3 Hz, $J_{6'',6'}$ = 11.6 Hz, H-6''), 4.09 (dddd, 1H, $J_{4',1'}$ = 2.1 Hz, $J_{4',2'}$ = 1.7 Hz, $J_{4',3'}$ = 2.1 Hz, $J_{4',5'}$ = 7.7 Hz, H-4'), 4.28 and 4.29 (2 x q, 2H, OCH_2CH_3), 4.57 and 4.64 (2 x d, 0.25 x 2H, J = 11.6 Hz, OCH_2Ph), 4.59 and 4.65 (2 x d, 0.75 x 2H, J = 11.6 Hz, OCH_2Ph), 4.97-5.03 (m, 1H, H-1'), 5.27 (d, 0.25 H, $J_{2,1'}$ = 8.1 Hz, H-2), 5.33 (d, 0.75 H, $J_{2,1'}$ = 10.3 Hz, H-2), 5.88 (ddd, 1H, $J_{2',1'}$ = 2.1 Hz, $J_{2',3'}$ = 10.8 Hz, $J_{2',4'}$ = 1.7 Hz, H-2'), 6.14 (ddd, 1H, $J_{3',1'}$ = 2.1 Hz, $J_{3',2'}$ = 10.8 Hz, $J_{3',4'}$ = 2.1 Hz, H-3'), 7.3-7.4 (m, 5H, Ph); ^{13}C NMR δ - 5.48 and - 5.36 ($SiCH_3$), 13.76 (-CH_2-CH_3), 18.31 ($SiCMe_3$), 25.86 ($SiCMe_3$), 62.24 (C-6'), 63.22 (CH_2-CH_3), 68.50 and 68.99 (0.75 and 0.25 C-4'), 70.03 and 70.85 (0.75 and 0.25 C-1'), 71.13 and 71.52 (0.25 and 0.75 OCH_2Ph), 73.48 and 74.49 (0.75 and 0.25 C-5'), 88.4 (C-2), 124.26 and 124.87 (0.75 and 0.25 C-2'), 130.15 and 130.98 (0.25 and 0.75 C-3'), 127.81, 128.43 and 137.80 (Ph), 162.02 (C=O).

Anal. Calcd for $C_{23}H_{35}SiNO_7$: C, 59.33; H, 7.58; N, 3.01. Found : C, 59.62; H, 7.57; N, 2.79.

Ethyl 2-(2',3'-Dideoxy-4'-*O*-benzyl-6'-*O*-trityl-α-D-*erythro*-hex-2'-enopyranosyl)-2(*R,S*)-nitroacetate 13. Oil; yield 87 %; $[\alpha]_D^{20}$ + 33.9° (*c* 1, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.19 and 1.28 (2 x t, 0.25 x 3H and 0.75 x 3H, CH_3), 3.18 (dd, 0.25 H, $J_{6',5'}$ = 4.2 Hz, $J_{6',6''}$ = 10.2 Hz, H-6'); 3.23 (dd, 0.75 H, $J_{6',5'}$ = 4.7 Hz, $J_{6',6''}$ = 10.2 Hz, H-6'), 3.35 (dd, 0.25 H, $J_{6'',5'}$ = 2.5 Hz, $J_{6'',6'}$ = 10.2 Hz, H-6''), 3.39 (dd, 0.75 H, $J_{6'',5'}$ = 2.2 Hz, $J_{6'',6'}$ = 10.2 Hz, H-6''), 3.73 (m, 1H, $J_{5',4'}$ = 8.2 Hz, H-5'), 4.12 (dddd, 1H, $J_{4',1'}$ = 2.3 Hz, $J_{4',2'}$ = 1.3 Hz, $J_{4',3'}$ = 1.3 Hz, $J_{4',5'}$ = 8.2 Hz, H-4'), 4.28 (m, 2H, OCH_2-CH_3), 4.33 and 4.35 (2 x d, 0.75 H and 0.25 H, J = 11.3 Hz, OCH_2Ph), 4.48 and 4.50 (2 x d, 0.75 H and 0.25 H, J = 11.3 Hz, OCH_2Ph), 5.07 (dddd, 0.25 H, $J_{1',2'}$ = 2.5 Hz, $J_{1',3'}$ = 2.1 Hz, $J_{1',4'}$ = 2.3 Hz, $J_{1',2}$ = 8.7 Hz, H-1'), 5.12

(dddd, 0.75 Hz, $J_{1',2'}$ = 2.5 Hz, $J_{1',3'}$ = 2.1 Hz, $J_{1',4'}$ = 2.3 Hz, $J_{1',2}$ = 10.1 Hz, H-1), 5.28 (d, 0.25 H, $J_{2,1'}$ = 8.7 Hz, H-2), 5.38 (d, 0.75 H, $J_{2,1'}$ = 10.1 Hz, H-2), 5.89 (ddd, 1H, $J_{2',1'}$ = 2.5 Hz, $J_{2',3'}$ = 10.5 Hz, $J_{2',4'}$ = 1.9 Hz, H-2'), 6.13 (ddd, 1H, $J_{3',1'}$ = 2.1 Hz, $J_{3',2'}$ = 10.5 Hz, $J_{3',4'}$ = 1.9 Hz, H-3'), 7.1-7.4 (m, 20H, Ph); ^{13}C NMR δ 13.83 (C-1), 62.64 and 62.79 (0.25 and 0.75 C-6'), 63.22 and 63.31 (0.25 and 0.75 CH_2-CH_3), 69.27 and 69.61 (0.25 and 0.75 C-4'), 70.32 and 71.14 (0.25 and 0.75 C-1'), 71.38 and 71.74 (0.25 and 0.75 OCH_2Ph), 72.63 and 73.55 (0.75 and 0.25 C-5'), 86.51 (CPh_3), 88.35 and 88.46 (0.25 and 0.75 C-2), 124.18 and 124.85 (0.75 and 0.25 C-2'), 130.69 and 131.47 (0.25 and 0.75 C-3'), 127.03, 127.10, 127.86, 127.92, 128.04, 128.19, 128.46, 128.63, 128.82, 129.04, 129.67, 137.56 and 143.86 (Ph), 162.14 and 162.36 (0.75 and 0.25 C=O).

Anal. Calcd for $C_{36}H_{35}NO_7$: C, 72.83; H, 5.94; N, 2.36. Found : C, 72.90; H, 6.00; N, 2.16.

Ethyl 2-(2',3'-Dideoxy-4',6'-di-*O*-benzyl-α-D-*erythro*-hex-2'-enopyranosyl)-2-(ethoxycarbonyl)-2-methyl acetate 8. Oil; yield 88 %; R_f 0.5 (25 % AcOEt/hexane); $[\alpha]_D^{20}$ + 24.9° (*c* 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.21 and 1.22 (2 x t, 2 x 3H, CH_2-CH_3), 1.48 (s, 3H, CH_3), 3.58 (dd, 1H, $J_{6',5'}$ = 5.1 Hz, $J_{6',6''}$ = 10.2 Hz, H-6'), 3.63 (dd, 1H, $J_{6'',5'}$ = 5.2 Hz, $J_{6'',6'}$ = 10.2 Hz, H-6''), 3.87 (ddd, 1H, $J_{4',1'}$ = 2.0 Hz, $J_{4',2'}$ = 0 Hz, $J_{4',3'}$ = 2.0 Hz, $J_{4',5'}$ = 4.3 Hz, H-4'), 4.05 (ddd, 1H, $J_{5',4'}$ = 4.3 Hz, $J_{5',6'}$ = 5.1 Hz, $J_{5',6''}$ = 5.2 Hz, H-5'), 4.17 (q, 2H, J = 7.0 Hz, CH_2-CH_3), 4.19 (q, 2H, J = 7.0 Hz, CH_2-CH_3), 4.49 and 4.57 (2 x d, 2H, J = 11.9 Hz, OCH_2Ph), 4.85 (bs, 1H, H-1'), 6.02 (ddd, 1H, $J_{3',1'}$ = 1.8 Hz, $J_{3',2'}$ = 10.7 Hz, $J_{3',4'}$ = 2.0 Hz, H-3'), 6.07 (d, 1H, $J_{2',3'}$ = 10.7 Hz, H-2'), 7.17-7.55 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.05 and 14.09 (CH_3-CH_2), 16.33 (CH_3-), 57.81 (C quat.), 61.47 and 61.57 (CH_3-CH_2-), 68.87 (C-6'), 68.90 (C-4'), 70.48 and 73.31 (OCH_2Ph), 72.36 (C-1'), 73.65 (C-5'), 126.60 (C-2'), 129.04 (C-3'), 127.70, 127.76, 127.90, 128.43, 129.62, 132.50, 138.19 and 138.41 (Ph), 170.14 and 170.63 (OC=O).

Anal. Calcd for $C_{28}H_{34}O_7$: C, 69.69; H, 7.10. Found : C, 69.70; H, 7.13.

Ethyl 2-(2',3'-Dideoxy-4',6'-di-*O*-benzyl-α-D-*erythro*-hex-2'-enopyranosyl)-2-(ethoxycarbonyl)-2-allyl acetate 9. Oil; yield 95 %; R_f 0.54 (25 % AcOEt/hexane); $[\alpha]_D^{20}$+ 28.9° (*c* 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.20 and 1.22 (2 x t, 2 x 3H, CH_3), 2.72 (dd, 1H, J = 14.1 Hz, J = 7.5 Hz, CH_2-CH=), 3.04 (dd, 1H, J = 14.1 Hz, J = 7.4 Hz, CH_2-CH=), 3.58 (dd, 1H, $J_{6',5'}$ = 4.4 Hz, $J_{6',6''}$ = 10.4 Hz, H-6'), 3.63 (dd, 1H, $J_{6'',5'}$ = 5.9 Hz, $J_{6'',6'}$ = 10.4 Hz, H-6''), 3.87 (m, 1H, H-4'), 3.93 (ddd, 1H, $J_{5',4'}$ = 4.2 Hz, $J_{5',6'}$ = 4.4 Hz, $J_{5',6''}$ = 5.9 Hz, H-5'), 4.12 and 4.18 (2 x q, 2 x 2 H, -CH_2-CH_3), 4.48 and 4.56 (2 x d, 2 x 1H, J = 11.8 Hz, OCH_2Ph), 4.50 and 4.56 (2 x d, 2 x 1H, J = 12.1 Hz, OCH_2Ph), 4.72 (bs, 1H, H-1'), 5.05 (d, 1H, J = 10.1 Hz,

=CH_2), 5.11 (d, 1H, J = 16.9 Hz, =CH_2), 5.74-5.88 (m, 1H, -CH=), 5.98 (ddd, 1H, $J_{2',1'}$ = 2.1 Hz, $J_{2',3'}$ = 10.7 Hz, $J_{2',4'}$ = 2.6 Hz, H-2'), 6.22 (ddd, 1H, $J_{3',1'}$ = 2.0 Hz, $J_{3',2'}$ = 10.7 Hz, $J_{3',4'}$ = 2.0 Hz, H-3'), 7.18-7.33 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$) δ 13.96 and 13.99 (2 x CH_3), 35.99 (*C*H_2-CH=), 61.14 and 61.20 (2 x OCH_2), 61.53 (C quat.), 68.78 (C-6'), 69.02 (C-4'), 70.14 and 73.13 (O*C*H_2Ph), 71.22 (C-1'), 73.18 (C-5'), 118.92 (CH_2=), 125.49 (C-2'), 129.69 (C-3'), 127.47, 127.50, 127.61, 128.23, 128.26, 128.30, 133.01, 138.12 and 138.41 (-*C*H=CH_2 and Ph), 169.57 and 169.38 (OC=O).

Anal. Calcd for $C_{30}H_{36}O_7$: C, 70.84; H, 7.12. Found : C, 71.02; H, 7.28.

Methyl 2-(2',3'-Dideoxy-4',6'-di-*O*-benzyl-α-D-*erythro*-hex-2'-eno-pyranosyl)-2-(methoxycarbonyl)-2-propargyl acetate 10. Oil; yield 92 %; R_f 0.32 (20 % AcOEt/hexane); $[\alpha]_D^{20}$ + 21.8° (*c* 1.4, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.98 (dd, 1H, J = 2.5 Hz, J = 2.6 Hz, C≡CH), 2.87 (dd, 1H, J = 2.5 Hz, J = 17.1 Hz, C*H*$_2$-C≡C), 3.21 (dd, 1H, J = 2.6 Hz, J = 17.1 Hz, C*H*$_2$-C≡C), 3.56 (dd, 1H, $J_{6',5'}$ = 4.9 Hz, $J_{6',6''}$ = 10.5 Hz, H-6'), 3.61 (dd, 1H, $J_{6'',5'}$ = 5.5 Hz, $J_{6'',6'}$ = 10.5 Hz, H-6''), 3.68 and 3.71 (2 x s, 2 x 3H, CH_3-), 3.85 (m, 1H, H-4'), 3.94 (ddd, 1H, $J_{5',4'}$ = 4.9 Hz, $J_{5',6'}$ = 5.5 Hz, $J_{5',6''}$ = 4.9 Hz, H-5'), 4.50 and 4.52 (2 x d, 2 x 1H, J = 12.0 Hz, OC*H*$_2$Ph), 4.49 and 4.56 (2 x d, 2 x 1H, J = 11.7 Hz, OC*H*$_2$Ph), 4.89 (ddd, 1H, $J_{1',2'}$ = 2.5 Hz, $J_{1',3'}$ = 1.3 Hz, $J_{1',4'}$ = 2.1 Hz, H-1'), 5.99 (ddd, 1H, $J_{2',1'}$ = 2.5 Hz, $J_{2',3'}$ = 10.6 Hz, $J_{2',4'}$ = 3.5 Hz, H-2'), 6.30 (ddd, 1H, $J_{3',1'}$ = 1.3 Hz, $J_{3',2'}$ = 10.6 Hz, $J_{3',4'}$ = 1.3 Hz, H-3'), 7.22-7.32 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$) δ 21.48 (-*C*H_2-C≡), 52.54 and 52.81 (2 x CH_3), 61.02 (C quat.), 68.80 (C-6'), 68.90 (C-4'), 70.18 and 73.22 (O*C*H_2Ph), 70.96 (C-1'), 71.43 (≡CH), 73.65 (C-5'), 79.63 (-*C*≡CH), 125.84 (C-2'), 129.37 (C-3'), 127.46, 127.59, 127.63, 127.77, 128.35, 138.20 and 138.40 (Ph), 168.91 and 168.99 (OC=O).

Anal. Calcd for $C_{28}H_{30}O_7$: C, 70.27; H, 6.32. Found : C, 70.21; H, 6.20

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