Pergamon

Tetrahedron Vol. 50, No. 18, pp. 5369-5380, 1994

0040-4020/94 $6.00+0.00

0040-4020(94)E0214-E

Stereocontrol in Radical Cyclizations on Sugar Templates

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Abstract : The radical cyclization of alkyl hex-2-enopyranosides provides a stereocontrolled route to fused furanopyranes. The intermediate radical is generated either *via* the reduction of the appropriate halide by tin hydride or *via* sulfonyl radical addition to allyl hex-2-enopyranosides. The two methodologies are compared with respect to diastereoselectivity. Stereocontrol is discussed on the basis of conformational preference in the transition state.

Radical cyclizations on sugar templates have drawn a considerable interest over the past five years.[1-6] Most of these studies, undertaken for synthetic purpose, have not only opened new ways for the synthesis of optically pure compounds but also provided a lot of original mechanistic information. During the course of general studies on sulfonyl radical induced cyclizations of 1,6-dienes,[7] the addition of tosyl bromide and allylic sulfones to hexenopyranoside-derived dienes has been explored.[7c] Carbohydrates constitute a potential source of substituted dienes of well defined spatial arrangement and thus formally allow a detailed insight of stereocontrol in radical cyclizations leading to polysubstituted compounds. Because of their reversible addition to alkenes, sulfonyl radicals,[7d,8] like trialkyl stannyl radicals,[4k,9] are especially suited for the chemoselective functionalization of unsymmetrical dienes. In the typical cases of dienes **5a-d** described herein, tosyl radical adds selectively to the terminal double bond anchored to the carbohydrate ring. Other reactions which similarly involve the intramolecular addition of a radical located on the sugar side chain to a double bond internal to the carbohydrate ring, were simultaneously investigated by other research groups[5-6] who generated the radical *via* the reduction of a halide by tributyl tin hydride. This topic is developed hereafter *via* the reduction of halides **1a-d**.

This paper is devoted to the stereochemical outcome of the cyclizations of closely related prochiral radicals that were generated by both methods and compares data gathered from two different research groups.

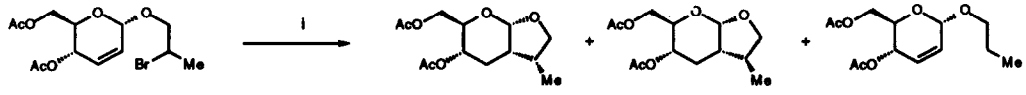
Results

Secondary radicals bearing substituents of gradually increasing steric bulk were produced through the reduction of bromides **1a-c** and of chloride **1d**. The results are summarized in Tables I-IV respectively. Halides **1a-d** were used as 10:1 mixture of α and β anomers. However, only the results concerning the major α isomers will be discussed here.

The reduction of **1a** (Table I) led to a mixture of bicyclic products **2a** and **3a** together with side products arising from the β anomer. Their ratio was determined from 500 MHz ^{1}H NMR analysis of the mixture of isolated products. The stereoselectivity appeared not to be sensitive to the dilution when the reaction was conducted on 0.01 M to 0.05 M solutions. Since under this last dilution a significant amount of uncyclized reduced product (**4a**) was formed - especially at low temperature - no attempts were made to use more concentrated solutions. Lowering the temperature slightly enhances the stereoselectivity of the cyclization.

Similar observations apply to the reduction of **1b** (Table II). The experiments were systematically conducted on 0.01 M solutions. They led to endo:exo (**2b**:**3b**) ratios that were in all cases lower than the ratios obtained from **1a**.

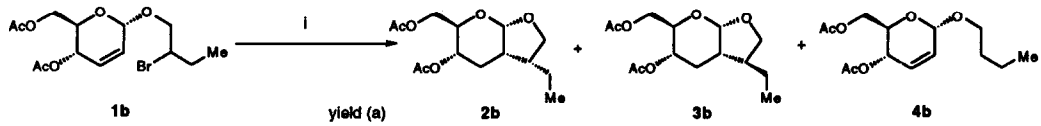
Table I. Experimental Conditions and Relative Ratio of 2a, 3a, 4a for the Radical Reduction of 1a



1a	yield (a)	2a	3a	4a
PhH (0.01 M) ; 80°C ; 24h	88%	64.5%	35.5%	not detected
$PhCH_3$ (0.05 M) ; 0°C ; 2h	86%	58%	32%	10%
$PhCH_3$ (0.01 M) ; 0°C ; 3h	95%	64%	34%	2%
$PhCH_3$ (0.05 M) ; -78°C ; hv ; 4h	47%	36%	16%	48%
$PhCH_3$ (0.01 M) ; -78°C ; hv ; 3h	75%	58%	26%	16%

i : *n*-Bu_3SnH (1.3 equiv) ; AIBN (0.1 equiv). a) yield of isolated 2a+3a

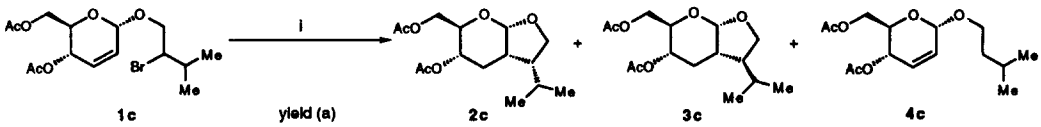
Table II. Experimental Conditions and Relative Ratio of 2b, 3b, 4b for the Radical Reduction of 1b



1b	yield (a)	2b	3b	4b
PhH (0.01 M) ; 80°C ; 20h	96%	51%	49%	not detected
$PhCH_3$ (0.01 M) ; 0°C ; 3h	93%	53%	45%	2%
$PhCH_3$ (0.01 M) ; -78°C ; 3h	94%	38%	33%	29%

i : *n*-Bu_3SnH (1.4 equiv) ; AIBN (0.1 equiv). a) yield of isolated 2b+3b

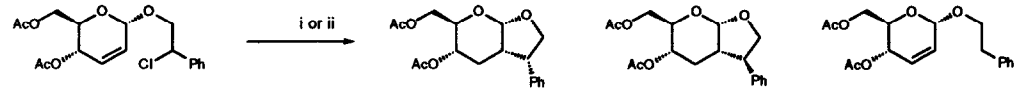
Table III. Experimental Conditions and Relative Ratio of 2c, 3c, 4c for the Radical Reduction of 1c



1c	yield (a)	2c	3c	4c
PhH (0.01 M) ; 80°C ; 24h	95%	55%	45%	not detected
$PhCH_3$ (0.01 M) ; 0°C ; hv ; 3 h	92%	49%	49%	2%

i : *n*-Bu_3SnH (1.4 equiv) ; AIBN (0.1 equiv). a) yield of isolated 2c+3c

Table IV. Experimental Conditions and Relative Ratio of 2d, 3d, 4d for the Radical Reaction of 1d



1d	Conditions / yield (a)	2d	3d	4d
PhH (0.01 M) ; 80°C ; 20h	i / 77%	16%	84%	not detected
PhH (0.01 M) ; 25°C ; hv ; 7h	i / 69%	12%	76%	12%
PhH (0.01 M) ; 80°C ; 20h	ii / 70%	7%	93%	not detected

i : *n*-Bu_3SnH (1.4 equiv) ; AIBN (0.1 equiv) ; ii : $(Me_3Si)_3SiH$ (1.2 equiv) ; AIBN (0.1 equiv). a) yield of isolated 2d+3d+4d

The compounds **2c** and **3c**, isolated from the reduction of **1c** (Table III), could not be separated chromatographically. Their ratio were determined from the NMR spectrum of the mixture, but their identification could not be established from these data. In any case, it is evident from these results that the

ratio **2c:3c** is very close to 50:50.

Chloride **1d** exhibited a very special behaviour compared to the other members in the series, since the endo:exo (**2d:3d**) ratio was totally reversed, the exo isomer being very largely predominant (Table IV). When the reaction was conducted with tris trimethylsilyl silane as the reducing agent instead of tributyl tin hydride, not only was the formation of the reduced uncyclized product totally avoided, but the exo:endo selectivity was raised from 5.3:1 to 13.3:1.

The second part of the experimental data deals with the addition of tosyl bromide and methyl 2-tosylmethyl-2-propenoate (**12**) to the unsaturated α-glucosides **5a-c**, bearing different hydroxyl protecting groups - either acetates, benzyl ethers or a methylene ketal -, and the galactopyranoside **5d**. These results are reported in Table V for the addition of TsBr and in Table VII for the addition of methyl 2-tosylmethyl-2-propenoate. The addition of TsCl to **5a** has also been investigated (Table VI.)

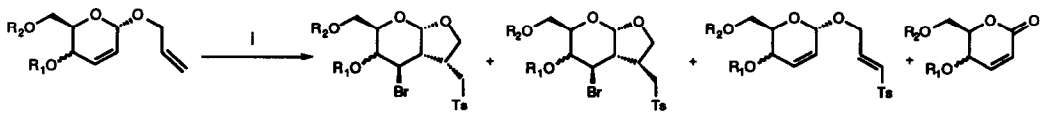
The addition of TsBr was conducted at 18°C, in a pyrex vessel, on 0.016 M solutions of the reactants in methylene chloride or acetonitrile. The photochemical initiation was achieved by an external irradiation with a high pressure mercury lamp. In some experiments, traces of the dehydrohalogenated 1,2-adducts **8a-d** were detected together with the cyclized adducts **6a-d** and **7a-d**, and variable amounts the hex-2-enono-1,5-lactone **9a** were also formed. It was difficult to separate this by-product, arising from the oxidative degradation of the starting material, from the major endo adduct. This led us to overestimate the stereoselectivity in our very first experiments on **5a**.[7c] The formation of **9a** was very sensitive to the solvent and to the quality of the sample of TsBr used in the experiment and it could be avoided in methylene chloride when using acid free, freshly prepared and carefully dried tosyl bromide. It appeared that when starting from the gluco derivative **5a** the endo stereoisomer was favored over the exo isomer (72:28). The ratio was similar in the case of the galacto derivative **5d**, the selectivity being 70:30. The stereochemistry was assigned from NOE difference spectroscopy. Whereas the configuration of C4 does not change the endo:exo ratio, the selectivity is influenced by the nature of the protective groups. A lower selectivity was obtained with the methylene ketal. The selectivity was nearly unchanged when TsCl was used as the reagent instead of TsBr (Table VI).

The addition of methyl 2-tosylmethyl-2-propenoate (**12**) was conducted under different conditions (Table VII), but only the experiments performed at 80°C in the presence of a large excess of sulfone gave satisfying yields in cyclized adducts. This is in agreement with the experimental conditions recommended independently by Witham[8c-d] - who first initiated the use of this reagent - and by Chuang.[8f,g] We observed that a photochemical initiation at room temperature was inefficient. When the reaction was conducted in CCl_4, an important amount of **10** - previously isolated from the addition of TsCl and resulting from a chlorine atom transfer from the solvent - was formed in addition to the expected adducts **13-14** ; therefore this solvent was discarded. The use of a catalytic amount of TsCl in benzene led to a significant enhancement of the yield in adducts **13+14**.

Discussion

The tin hydride reduction of bromides **1a-c**, like the cyclization of dienes **5a-d**, gives the endo isomer as the major product. Both reactions proceed *via* the intramolecular addition of closely related prochiral 5-alkenyl radicals. Due to exclusive *cis* ring junction and to exclusive equatorial transfer of the bromine atom or of the alkenyl chain -the latter *via* an addition elimination sequence -, one or two stereogenic centres are totally controlled, depending on which method is used. On the other hand, the endo:exo selectivity is in agreement with the generally preferred 1,5-*cis* ring closure observed with 1-mono-substituted 5-hexenyl radicals.[10] However, the 1,5-*cis:trans* ratio is slightly but significantly lower than the 80:20 ratio reported for the cyclization of comparable acyclic radicals.[7a,f]

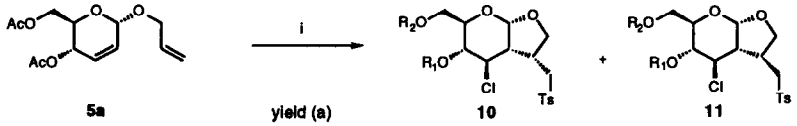
Table V. Products Relative Ratio for the Radical Addition of TsBr to 5a-d



	yield (a)	solvent	6	7	8	9
5a: R_2=Ac R_1=Ac (eq)	70%	(b)	72%	28%	traces	not detected
		(c)	62%	24%	traces	14%
5b: R_2=Bn R_1=Bn (eq)	42%	(b)	71%	29%	not detected	not detected
5c: R_2=R_1= -CH_2- (eq)	50%	(b)	65%	35%	not detected	not detected
5d: R_2=Ac R_1=Ac (ax)	50%	(b)	70%	30%	traces	not detected

I : TsBr (1 eq.) ; CH_2Cl_2 (b) or CH_3CN (c) (0.016 M) ; hv ; 7 - 24h . a) yield of isolated 6+7

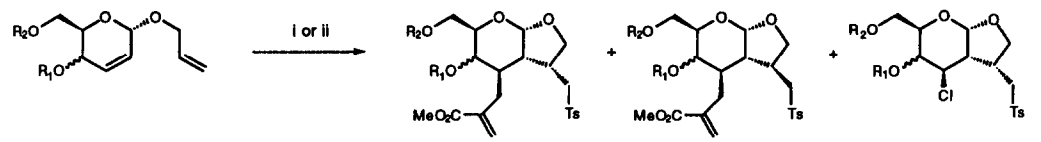
Table VI. Relative Ratio of 10, 11 for the Radical Addition of TsCl to 5a



5a	yield (a)	10	11
	55%	75%	25%

i : TsCl (5equiv) ; CH_2Cl_2 (0.016 M) ; hv ; 28h. a) yield of isolated 10+11

Table VII. Relative Ratio of 13, 14, 10 for the Radical Addition of 12 to 5a and 5d



	Conditions /yield (a)	13	14	10
5a : R_2=Ac R_1=Ac (eq)	i / 97%	33%	25%	42%
	ii / 77%	70%	30%	-
5d : R_2=Ac R_1=Ac (ax)	ii / 62%	66%	34%	-

i : $TsCH_2C(CH_2)CO_2Me$ 12 (3 equiv) ; BPO ; CCl_4 . ii : $TsCH_2C(CH_2)CO_2Me$ 12 (2 equiv) ; BPO; TsCl ; PhH. a) yield of isolated 13+14+10

With simple models, the 1,5-*cis* control is well explained on the basis of the preferred "chair-like" conformation of the transition state, where the substituent on the radical centre occupies a pseudo-equatorial position.[10a,b] As pointed out by Houk,[10c] "boat-like" conformations may be only slightly destabilized with respect to chair-like ones and they have to be considered in order to quantitatively correctly predict the stereoselectivity for many systems.[10c-e] The exclusive involvement of boat conformers has been elegantly demonstrated by Rajanbabu in the cyclization of polysubstituted radicals derived from glucose.[4a]

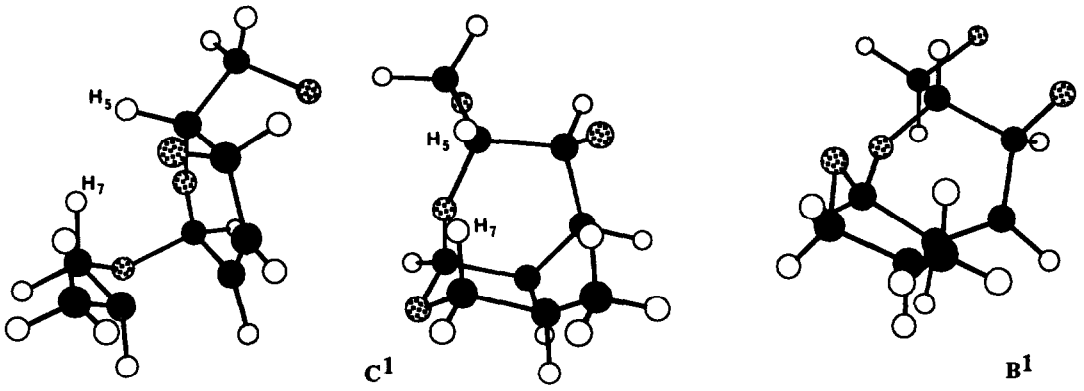


Figure 1. Transition states leading to endo products*

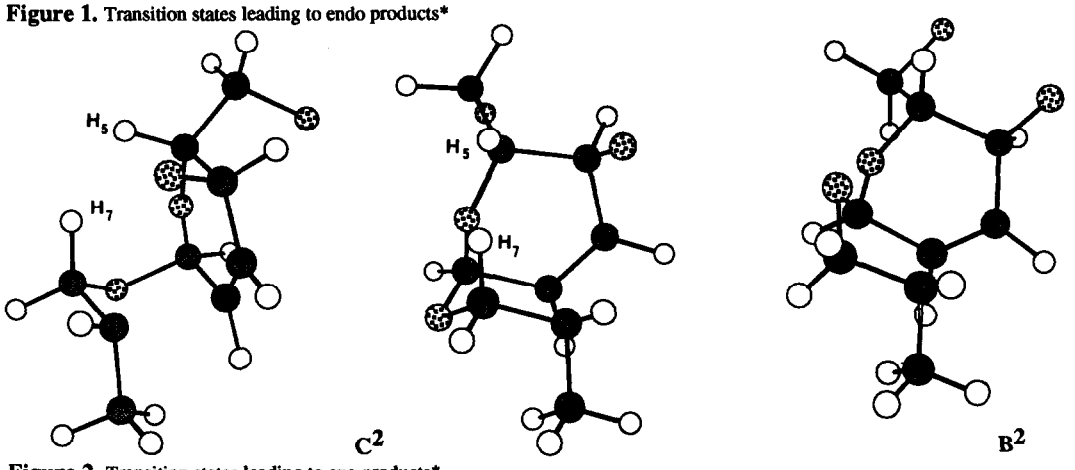


Figure 2. Transition states leading to exo products*

*CSC Chem 3D models of transition states; forming bond 2.27Å; the protections of OH functions have been omitted for clarity; the substituent on the radical centre is CH_3.

If one looks at the possible conformations of the axial side chain in the transition states leading to the endo products (Figure. 1), it appears that the chair-like transition states $\mathbf{C}^1$, though bearing the alkyl or tosylmethyl substituent on the radical centre in a pseudo-equatorial position, is highly destabilized by non-bonded interactions between the endo H5 and the pseudo-axial H7. The same interaction is present in the chair conformer $\mathbf{C}^2$ bearing the substituent on the radical centre in a pseudo-axial position. Neither $\mathbf{C}^1$ nor $\mathbf{C}^2$ can be invoked to explain the formation of the major endo product and the minor exo epimer, respectively. This leads to the conclusion that the relative stability of the boat conformations $\mathbf{B}^1$ leading to the endo product - where the alkyl substituent occupies a pseudo-equatorial position - and $\mathbf{B}^2$ leading to the exo epimer - bearing the substituent in a pseudo-axial position - are likely to control the **2:3** and **6:7** ratios, in other words the 1,5-*cis:trans* selectivity (Figure 2). It must be emphasized that, due to the eno-pyranoside moiety, the chair-like and boat like transition states differ by the conformation around the side chain pivots. In most cases, the two boat conformers bearing the substituent on the radical center in axial or equatorial position are less energetically different than the corresponding chair conformers. When both conformers can participate in the overall selectivity, it has been shown from theoretical calculations on other radical cyclizations[7e,10c] that taking into account only chair-like conformers lead to overestimate the 1,5-*cis-trans* ratio. This probably accounts for the reduced selectivity in the cases described herein where the examination of models strongly

suggests that only boat conformers should contribute to the transition state.

The endo:exo selectivity observed from the reduction of bromides **1a-c** decreases in the series as the size of the substituent on the radical centre increases. The involvement of additional steric effects that destabilize the "endo transition state" ($\mathbf{B}^1$) with respect to the "exo transition state" ($\mathbf{B}^2$) where the substituent on the radical centre cannot have any interaction with the α substituents on the sugar skeleton is conceivable. This could be the case for **1c** (R=iPr) but it is less evident in the case for **1b** (R=Et).

We were not expecting a difference in selectivity between the two cyclization protocols. The functionalization of dienes with tosyl derivatives exhibits a higher selectivity; this is particularly striking if one compares the results obtained from the reduction of **1b** to the addition of any of the tosyl derivatives to **5a** and the differences are not consistent with temperature effects. No satisfying explanation can be put forward to account for these variations which rely on small differences in transition states energies.

When the substituent on the radical centre is a phenyl group (**1d**), not only does the selectivity favor the exo isomer but it is strongly influenced by the rate of hydrogen abstraction in the final propagation step. The rate constant for the hydrogen transfer from tributyl tin hydride to a secondary radical is 1.5×10^6 mol^{-1} s^{-1}at 25°C,[11a] and from bis trimethylsilylsilane only 1.4×10^5.[11b] Radical cyclizations of stabilized radicals such as benzylic radicals is well known to be reversible.[12] Under experimental conditions where the final reduction is slow compared to the reversal of the intramolecular addition, the thermodynamic product is favored. This is likely to be the case with the benzylic radical derived from **1d**. The tenfold decrease in the rate of hydrogen abstraction when going from the tin hydride to the silane allows the exclusive formation of the thermodynamic exo product.

Conclusion

Carbohydrates can provide a variety of precursors for 5-hexenyl radicals of well defined stereochemistry which lead with a good regio and stereoselectivity to polysubstituted cyclopentanes. However, the rationalization of these experiments on the basis of the conformational analysis of the transition states involved in the cyclization step cannot simply rely on the concept of "chair-like transition state" generally satisfying for monosubstituted radicals. The radical cyclizations reported therein of α-anomeric sugar derivatives provide new examples where only boat conformers are involved in the transition state.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded using $CDCl_3$ as solvent. Column chromatographies were carried out on silica gel 60 (Merck 7734). HPLC analyses were conducted on Waters Nova-Pak Silica (4 μ) column (3.9 mm x 15 cm) coupled to a UV detector (254 nm) or a refractometer, using ethyl acetate:*iso*-octane mixtures as eluent. Sulfonyl bromide was prepared according to known procedures and was dried under vacuum before use. For ^{13}C spectra the sign * indicates that assignments may be reversed.

Preparation of the halides 1a-d. These compounds were prepared according to the procedure of Ferrier[14]. The reaction was performed under argon atmosphere. In a typical experiment (preparation of **1a**) 3,4,6-tri-*O*-acetyl-D-glucal (1.152 g, 4.23 mmol) and 2-bromo-1-propanol (1 g, 7.19 mmol) were dissolved in 20 mL of acetonitrile. The mixture was cooled to 0°C and BF_3:OEt_2 (0.18 g, 1.26 mmol) was added. After 10 min, the reaction was quenched with aqueous NaH_2PO_4. After extraction with CH_2Cl_2, the organic layer was washed successively with aqueous NaH_2PO_4. and brine and then dried over Na_2SO_4. Evaporation of the solvent, followed by chromatography (toluene:EtOAc, 50:1 to 40:1), afforded **1a** (1.257 g, 3.59 mmol, 85%) as a 91:9 mixture of α: β anomers.

1a (α–anomer, mixture of epimers) : ^1H NMR (500 MHz): 5.92 (m, 1H) (H2), 5.86 (ddd, J = 10.5, 3.0, 1.2, 0.5H) (H3), 5.85 (ddd, J = 10.5, 3.0, 1.2, 0.5H) (H3), 5.32 (ddd, J = 9.8, 3.0, 1.5, 0.5H) (H4), 5.31 (ddd, J = 9.5, 3.0, 1.5, 0.5H) (H4), 5.09 (m, 0.5H) (H_1), 5.08 (m, 0.5H) (H1), 4.29-4.18 (m, 3H) (H6a, H6b, H8), 4.16 (m, 1H) (H5), 3.97 (dd, J = 10.9, 6.2, 0.5H) (H7b), 3.88 (dd, J = 11.0, 6.0, 0.5H) (H7b), 3.77 (dd, J = 11.0, 6.8, 0.5H) (H7a), 3.77 (dd, J = 10.9, 6.8, 0.5H) (H7a), 2.12 (s, 3H) (CH_3CO), 2.10 (s, 3H)

(CH_3CO), 1.72 (d, J = 7.0, 1.5H), (CH_3), 1.71 (d, J = 7.0, 1.5H) (CH_3). CI MS (NH_3) : 370 and 368 : $[M + NH_4]^+$; 230 : $[M+NH_3 - (CH_3CHBrCH_2O)]^+$; 213 $[M - (CH_3CHBrCH_2O)]^+$.

1b (yield 95%), (α–anomer, mixture of epimers) : ^1H NMR (500 MHz) : 5.92 (m, 1H) (H2), 5.85 (ddd, J = 10.0, 4.3, 2.2, 1H) (H3), 5.31 (m, 1H) (H4), 5.08 (m, 1H) (H1), 4.26-4.18 (m, 2H) (H6b, H6a), 4.18-4.08 (m, 2H) (H5, H8), 4.02 (dd, J = 10.6, 6.0, 0.5H) (H7b), 3.98 (dd, J = 10.8, 6.0, 0.5H) (H7b), 3.80 (dd, J = 10.8, 6.4, 0.5H) (H7a), 3.76 (dd, J = 10.6, 6.2, 0.5H) (H7a), 2.13 (s, 1.5H) (CH_3CO), 2.12 (s, 1.5H) (CH_3CO), 2.10 (s, 3H) (CH_3CO), 2.00 (m, 1H) (H9a), 1.80 (m, 1H) (H9b), 1.07 (t, J = 7.5, 3H) (CH_3). FD MS : 366 and 364 : M^+ ; 264 and 262 ; 213.

1c (yield 85%), (α–anomer, mixture of epimers) : ^1H NMR (500 MHz) 5.92 (d, J = 10.0, 1H) (H2), 5.84 (ddd, J = 10.0, 5.0, 2.2, 0.5H) (H3), 5.83 (ddd, J = 10.0, 5.0, 2.2, 0.5H) (H3), 5.32 (m, 1H) (H4), 5.07 (br s, 0.5H) (H1), 5.05 (br s, 0.5H) (H1), 4.27-4.14 (m, 3.5H) (H6a, H6b, H8, H5), 4.12 (ddd, J = 9.8, 5.8, 2.2, 0.5H) (H5), 4.04 (dd, J = 10.8, 7.0, 0.5H) (H7b), 4.03 (dd, J = 11.0, 6.2, 0.5H) (H7b), 3.81 (dd, J = 10.8, 6.4, 0.5H) (H7a), 3.79 (dd, J = 11.0, 6.8, 0.5H) (H7a), 2.06 (s, 1.5H) (CH_3CO), 2.05 (s, 1.5H) (CH_3CO), 2.04 (s, 3H) (CH_3CO), 2.02 (m, 1H) (H9), 1.06 (d, J = 7.0, 1.5H) (CH_3), 1.04 (d, J = 7.0, 1.5H) (CH_3), 1.00 (d, J = 7.0, 1.5H) (CH_3), 0.98 (d, J = 7.0, 1.5H) (CH_3) ; FD MS : 380 and 378 : M^+ ; 379 and 377 ; 337 and 335 ; 278 and 276 ; 213.

1d (yield 88%), (α–anomer, mixture of epimers) : ^1H NMR (500 MHz) 7.22-7.17 (m, 5 H) (HAr), 5.91-5.88 (m, 1H) (H2), 5.85 (ddd, J = 10.0, 2.6, 1.8, 0.5H) (H3), 5.77 (ddd, J = 10.2, 2.6, 2.0, 0.5H) (H3), 5.31 (ddd, J = 9.8, 2.6, 1.4, 0.5H) (H4), 5.29 (ddd, J = 9.8, 2.6 1.4, 0.5H) (H4), 5.13 (br s, 0.5H) (H1), 5.12 (dd, J = 8.0, 5.4, 0.5H) (H8), 5.04 (dd, J = 7.6, 5.8, 0.5H) (H_8), 4.98 (br s, 0.5H) (H1), 4.23 (dd, J = 12.0, 5.2, 0.5H) (H6a), 4.18 (dd, J = 10.4, 7.6, 0.5H) (H7a), 4.13 (superimposed m, 1H) (H5, H6a), 4.11 (dd, J = 12.0, 2.2, 0.5H) (H6b), 4.08 (dd, J = 10.6, 5.4, 0.5H) (H7a), 3.99 (dd, J = 10.6, 8.0, 0.5H) (H7b), 3.95 (dd, J = 10.4, 5.8, 0.5H) (H7b), 3.96 (superimposed m, 1H) (H5, H6b), 2.12 (s, 1.5H) (CH_3CO), 2.10 (s, 1.5H) (CH_3CO), 2.08 (s, 1.5H) (CH_3CO), 2.05 (s, 1.5H) (CH_3CO). FD MS ; 370 and 368 : M^+; 332 : $[M-HCl]^+$.

Tin Hydride reductions of 1a-d. The reactions were performed under argon atmosphere. In a typical experiment *n*-Bu_3SnH (273 mg, 0.939 mmol) and AIBN (7 mg, 0.042.mmol) were added, at room temperature, to a 0.01 M solution of **1a** (0.3 g, 0.85 mmol) in degassed benzene (85 mL). The mixture was heated under reflux. After 6 h, additional amounts of *n*-Bu_3SnH (50 mg, 0.171 mmol) and of AIBN (7 mg. 0.042 mmole) were added. After refluxing during 24 h, the reaction mixture was cooled at room temperature and the solvent was evaporated under reduced pressure. The residual oil was dissolved in acetonitrile (50 mL). The solution was extracted five times with hexane (50 mL). After evaporation the residue was flash-chromatographed (*n*-hexane:EtOAc, 6:1). The minor products arising from the β anomer were separated from the major compounds **2a** and **3a** (combined isolated yields : 205 mg, 0.752 mmol, 88%). The reaction was performed similarly at 0°C and -78°C in toluene, using photochemical initiation with a medium pressure mercury lamp.

2a : ^1H NMR (500 MHz) 5.37 (d, J = 4.0, 1H) (H1), 4.86-4.76 (m, 1H) (H4), 4.33 (dd, J = 12.0, 5.0, 1H) (H6a), 4.13 (dd, J = 12.0, 2.0, 1H) (H6b), 3.99-3.94 (m, 1H) (H5), 3.98 (dd, J = 8.2, 8.0, 1H) (H7a), 3.65 (dd, J = 10.3, 8.0, 1H) (H7b), 2.56 (m, 1H) (H8), 2.23-2.14 (m, 1H) (H2), 2.08 (s, 3H) (CH_3CO), 2.07 (s, 3H) (CH_3CO), 2.03 (ddd, J = 12.2, 6.2, 4.2, 1H) (H3eq), 1.38 (ddd, J = 12.2, 12.0, 1H) (H3ax), 0.95 (d, J = 7.0, 3H) (CH_3) ; ^{13}C NMR (75 MHz) 170.98 (C=O), 170.10 (C=O), 102.00 (C1), 71.40 (C7), 69.70 (C5), 66.90 (C4), 62.70 (C6), 38.70 (C2*), 35.00 (C8*), 25.70 (C3), 21.13 (CH_3CO), 21.10 (CH_3CO), 10.9 (CH_3).

3a : ^1H NMR (500 MHz) 5.43 (d, J = 4.7, 1H) (H1), 4.84-4.76 (m, 1H) (H4), 4.28 (superimposed dd , J = 8.4, 1H) (H7a), 4.27 (dd, J = 12.0, 5.6, 1H) (H6a), 4.15 (dd, J = 12.0, 2.2, 1H) (H6b), 3.99-3.94 (m, 1H) (H5), 3.46 (dd, J = 8.4, 4.4, 1H) (H7b), 2.23-2.14 (m, 2H) (H8, H3eq), 2.09 (s, 3H) (CH_3CO), 2.06 (s, 3H) (CH_3CO), 1.95 (m, 1H) (H2), 1.54 (ddd, J = 13.8, 8.2, 8.0, 1H) (H3ax), 1.06 (d, J = 7.0, 3H) (CH_3) ; ^{13}C NMR (75 MHz) 170.95 (C=O), 170.10 (C=O), 100.60 (C1), 73.10 (C7), 69.40 (C5), 66.50 (C4), 63.10 (C6), 42.10 (C2*) 37.70 (C8*), 29.00 (C3), 21.10 (CH_3CO), 20.90 (CH_3CO), 18.10 (CH_3).: FD MS **2a** + **3a** : 272 : M^+; 271. Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34 ; H, 7.40. Found : C, 57.43 ; H, 7.48.

Reduction of 1b. The reduction of **1b** (200 mg, 0.547 mmol) , performed at 80°C, led to 150 mg (0.525 mmol, 96%) of cyclized products. The minor products arising from the β anomer were separated from the major compounds **2b** and **3b** by flash chromatography (*n*-hexane:EtOAc, 6:1).

2b : ^1H NMR (500 MHz) 5.36 (d, J = 3.8, 1H) (H1), 4.83-4.76 (m, 1H) (H4), 4.33 (dd, J = 12.0, 4.8, 1H) (H6a), 4.12 (dd, J = 12.0, 2.1, 1H) (H6b), 4.02-3.95 (m, 2H) (H5, H7a), 3.69 (dd, J = 10.4, 8.1, 1H) (H7b), 2.41-2.33 (m, 1H) (H8), 2.29-2.23 (m, 1H) (H2), 2.08 (s, 3H) (CH_3CO), 2.06 (s, 3H) (CH_3CO), 2.02 (ddd, J = 12.2, 6.7, 4.5, 1H) (H3eq), 1.40 (q, J = 12.2, 1H) (H3ax), 1.50-1.30 (superimposed m, 2H) (H9a, H9b), 0.95 (t, J = 7.5, 3H) (CH_3); ^{13}C NMR (100 MHz) 170.90 (C=O), 170.00 (C=O), 101.90 (C1), 71.30 (C7), 69.60 (C5), 66.80 (C4), 62.70 (C6), 42.60 (C2*), 37.20 (C8*), 25.40 (C3), 21.10 (CH_3CO), 20.80 (CH_3CO), 19.80 (C9), 12.50 (CH_3).

3b : ^1H NMR (500 MHz) 5.37 (d, J = 4.5, 1H) (H1), 4.83-4.76 (m, 1H) (H4), 4.26 (superimposed m, 1H) (H7a), 4.27 (dd, J = 12.2, 4.8, 1H) (H6a), 4.15 (dd, J = 12.2, 2.7, 1H) (H6b), 4.02-3.95 (m, 1H) (H5), 3.53 (dd, J = 8.9, 4.5, 1H) (H7b), 2.16 (ddd, J = 13.2, 6.3, 5.2, 1H) (H3eq), 2.10.1.99 (m, 1H) (H2), 2.08 (s, 3H) (CH_3CO), 2.05 (s, 3H) (CH_3CO), 1.98-1.93 (m, 1H) (H8), 1.55 (dt, J =

13.2, 6.4, 1H) (H3ax), 1.50-1.30 (m, 2H) (H9a, H9b), 0.98 (t, J = 7.2, 3H) (CH_3); ^{13}C NMR (100 MHz) 170.90 (C=O), 170.00 (C=O), 100.60 (C1), 70.10 (C7), 69.50 (C5), 66.60 (C4), 63.10 (C6), 45.30 (C2*), 40.30 (C8*), 29.70 (C3), 26.30 (C9), 21.10 (CH_3CO), 20.80 (CH_3CO), 12.40 (CH_3).

Reduction of 1c. The similar reduction of **1c** (300 mg, 0.791 mmol) at 80°C led to 225 mg (0.751 mmol, 95%) of cyclized products. The minor products arising from the β anomer were separated from the major compounds **2c** and **3c** by flash chromatography (*n*-hexane:EtOAc, 6:1).The identities of **2c** and **3c** could not be established from NMR data; their ratio 45:55 was determined from ^{1}H NMR. In the following, the signals assigned to the major and the minor isomers are identified by M and m respectively whenever they are distinct.

2c, 3c : ^{1}H NMR (500 MHz) 5.35 (d, J = 4.0, 1H) (H1m), 5.30 (d, J = 4.8, 1H) (H1M), 4.85-4.77 (m, 2H) (H4), 4.33 (dd, J = 12.0, 4.6, 1H) (H6a), 4.27 (dd, J = 12.2, 5.8, 1H) (H6a), 4.22 (dd, J = 8.6, 8.0, 1H) (H7am), 4.15 (dd, J = 12.0, 2.4, 1H) (H6b), 4.12 (dd, J = 12.2, 2.0, 1H) (H6b), 4.02-3.96 (m, 5H) (H5, H7b, H7aM), 2.25 (m, 1H) (H8M), 2.22-2.04 (m, 4H) (H8m, H2, H3eqm), 2.08 (s, 6H) (CH_3CO), 2.05 (s, 6H) (CH_3CO), 1.82 (m, 1H) (H3eqM), 1.63-1.55 (m, 3H) (H9, H3axm), 1.42 (q, J = 10.3, 1H) (H3axM), 0.96 (m, 6H) (CH_3), 0.88 (d, J = 7.2, 3H) (CH_3M), 0.82 (d, J = 6.6, 3H) (CH_3m).

Reduction of 1d. The reduction of **1d** (104 mg, 0.28 mmol) at 80°C led to 72 mg (0.215 mmol, 77%) of cyclized products. The major isomers **2d** and **3d** were isolated by flash chromatography (*n*-hexane:AcOEt, 4:1). Analytical pure samples of **3d** and enriched **2d** were obtained by preparative HPLC.

3d : ^{1}H NMR (500 MHz) : 7.40-7.10 (m, 5H) (HAr), 5.56 (d, J = 5.5, 1H) (H1), 4.90 (ddd, J = 8.0, 5.8, 5.6, 1H) (H4), 4.49 (dd, J = 9.0, 7.5, 1H) (H7a), 4.28 (dd, J = 12.0, 5.8, 1H) (H6a), 4.21 (dd, J = 12.0, 3.2, 1H) (H6b), 4.10 (ddd, J = 8.0, 5.8, 3.2, 1H) (H5), 3.92 (dd, J = 9.0, 7.2, 1H) (H7b), 3.46 (ddd, J = 7.6, 7.5, 7.2, 1H) (H8), 2.41 (dddd, J = 7.5, 5.8, 5.6, 5.5, 1H) (H2), 2.19 (dt, J = 14.4, 5.6, 1H) (H3eq), 2.13 (s, 3H) (CH_3 CO), 2.10 (s, 3H) (CH_3CO), 1.72 (dt, J = 14.4, 5.8, 1H) (H3ax). (The stereochemistry is confirmed by NOE experiments). FD MS : 334 : M^+; 274 : $[M\text{-}CH_3CO_2H]^+$; Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66, H, 6.63. Found : C, 64.65 ; H, 6,85.

2d : ^{1}H NMR (500 MHz) 5.57 (d, J = 3.8, 1H) (H1), 5.00 (ddd, J = 10.0, 9.3, 5.1, 1H) (H4), 4.78 (dd, J = 10.0, 4.8, 1H) (H7a), 3.69 (ddd, J = 9.0, 4.8, 3.8, 1H) (H8), 2.12 (s, 3H) (CH_3CO), 2.09 (s, 3H) (CH_3CO). The signals of the major isomer overlapped the others signals.

Allyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5a). This compound was prepared according to known procedures,[14] in 75 % yield, from 3,4,6-tri-*O*-acetyl-D-glucal, *via* a Ferrier reaction. mp 42-43°C (pentane). ^{1}H NMR (400 MHz) 6.00-5.83 (m, 3H) (H2, H3, H8), 5.38-5.28 (m, 2H) (H4, H9b), 5.22 (dq, J = 10.4, 1.2, 1H) (H9a), 5.09 (s large, 1H) (H1), 4.30-4.02 (m, 5H) (H5, H6a, H6b, H7a, H7b), 2.13 (s, 3H) (CH_3), 2.08 (s, 3H) (CH_3); ^{13}C NMR (100 MHz) 170.75 (C=O), 170.26 (C=O), 134.05 (C8), 129.21 (C2*), 127.71 (C3*), 117.51 (C9), 93.60 (C1), 69.25 (C7), 66.91 (C5), 65.23 (C4), 62.91 (C6), 20.93 (CH_3), 20.75 (CH_3). Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.78 ; H, 6.71. Found : C, 57.82 ; H, 6.74.

Addition of TsBr to 5a. In a typical experiment, **5a** (0.54 g, 2 mmol) was allowed to react with TsBr (0.46 g, 2 mmol) in 125 mL of dried and degassed CH_2Cl_2. The pyrex vessel, was placed in a thermostatic bath at 15°C under inert atmosphere and was submitted to external irradiation with a high pressure mercury lamp. The reaction was monitored by TLC. After 24 h the solvent was evaporated under reduced pressure at room temperature and the residual syrup was immediately chromatographed ($CHCl_3$:Et_2O, 6:4) to avoid further degradation. This led to 480 mg of **6a** and **9a** (R_f 0.52), 120 mg of a mixture containing **6a**, **9a** and **7a** and 100 mg of **7a** (R_f 0.48) (70% overall yield), in that order of elution. The presence of **9a** was detected by ^{1}H NMR, and an authentic sample was synthetized according to a literature protocol[15] to confirm identification. An accurate measurement of the products ratio was made possible by HPLC analysis of a prefiltrated crude reaction mixture using *iso*Octane:EtOAc (7:3) and a flow rate of 2 mL/min.

Acetic acid 6-acetoxymethyl-4-bromo-3-(toluene-4-sulfonylmethyl)-hexahydro-furo[2,3-b]pyran-5-yl-ester (6a, 7a).

6a : ^{1}H NMR (400 MHz) 7.80 (d, J = 8.2, 2H) (HAr), 7.40 (d, J = 8.2, 2H) (HAr), 5.33 (d, J = 4.1, 1H) (H1), 5.17 (t, J = 10.3, 1H) (H4), 4.36 (dd, J = 9.8, 7.1, 1H) (H7S), 4.30 (dd, J = 12.5, 4.4, 1H) (H6a), 4.01 (dd, J = 12.5, 2.3, 1H) (H6b), 3.97 (ddd, J = 10.3, 4.4, 2.3, 1H) (H5), 3.88 (t, J = 9.8, 1H) (H7R), 3.87 (t, J = 10.3, 1H) (H3), 3.75 (dd, J = 13.8, 2.7, 1H) (H9S), 3.20 (dd, J = 13.8, 11.8, 1H) (H9R), 3.07 (m, 1H) (H8), 2.73 (ddd, J = 9.9, 5.7, 4.1, 1H) (H2), 2.45 (s, 3H) (CH_3Ph), 2.18 (s, 3H) (CH_3CO), 2.10 (s, 3H) (CH_3CO); ^{13}C NMR (100 MHz) 170.74 (C=O), 169.30 (C=O), 145.39 (=C), 135.99 (=C), 130.23 (=CH), 127.90 (=CH), 101.25 (C1), 69.79 (C5*), 69.52 (C4*), 69.33 (C7), 62.04 (C6), 55.91 (C9), 48.01 (C2*), 47.49 (C3*), 35.14 (C8), 21.68 (CH_3Ph), 20.77 (CH_3), 20.66 (CH_3). Anal. Calcd for $C_{20}H_{25}O_8SBr$: C, 47.53; H, 4.99. Found : C, 47.09; H, 5.06.

7a : ^{1}H NMR (400 MHz) 7.80 (d, J = 8.2, 2H) (HAr), 7.40 (d, J = 8.2, 2H) (HAr), 5.29 (d, J = 4.5, 1H) (H1), 5.13 (t, J = 9.5, 1H) (H4), 4.32 (dd, J = 12.4, 4.6, 1H) (H6a), 4.30 (m, 1H) (H7S), 4.04 (dd, J = 12.4, 2.4, 1H) (H6b), 3.95 (ddd, J = 9.5, 4.6, 2.4, 1H) (H5), 3.86 (t, J = 9.8, 1H) (H3), 3.81 (dd, J = 10.0, 3.8, 1H) (H7R), 3.18 (ABpart of a ABX spectrum, J_{AB} = 14.0, 2H) (H9S,H9R), 2.83 (m, 1H) (H8), 2.57 (ddd, J = 9.8, 4.5, 2.2, 1H) (H2), 2.42 (s, 3H) (CH_3Ph), 2.08 (s, 3H) (CH_3CO), 2.05 (s, 3H) (CH_3CO); ^{13}C

NMR (100 MHz) 170.56 (C=O), 169.17 (C=O), 145.27 (=C), 136.12 (=C), 130.12 (=CH), 128.04 (=CH), 99.95 (C1), 70.84 (C7), 69.73 (C5), 69.36 (C4), 62.05 (C6), 59.37 (C9), 51.30 (C2), 50.75 (C3), 37.65 (C8), 21.59 (CH_3Ph), 20.59 (CH_3). Anal. Calcd for $C_{20}H_{25}O_8S$: C, 47.53; H, 4.99. Found: C, 48.55; H, 5.45.

Addition of Methyl 2-tosylmethyl-2-propenoate (12) to 5a.

Method (a)[8c] : a solution containing **5a** (195 mg, 0.73 mmol) and **12** (550 mg, 3 eq) in 20 mL of carbon tetrachloride was heated at reflux, under argon, in the presence of benzoyl peroxide (0.2 eq added by successive portions). After 15 h, separation by column chromatography ($CHCl_3$:Et_2O; 6:4) led to 140 mg of **10** (R_f 0.55), 120 mg of **13a** (R_f 0.43) and 90 mg of **14a** (R_f 0.38).

Method (b)[8f] : a solution containing **5a**, (270 mg, 1 mmol), **12** (510 mg, 2 eq) and TsCl (48 mg, 0.25 eq) in 10 mL of benzene was heated under argon in the presence of benzoyl peroxide (0.2 eq). The reaction, monitored by thin layer chromatography, was refluxed for 12.5 h. After the addition of 50 mL of ethyl acetate, the solution was washed twice with 10 mL of water and then dried over Na_2SO_4. The residue was separated by chromatography ($CHCl_3$:Et_2O, from 9:1 to 6:4). This led to 250 mg of **13a**, 100 mg of a mixture of **13a** and **14a** and 50 mg of **14a** (77% overall yield). The ratio **13a**:**14a** (70:30) was determined by HPLC analysis of the crude reaction mixture (*iso*octane:EtOAc, 6:4, 2 mL/mn)

13a : ^{1}H NMR (400 MHz) 7.82 (d, J = 8.1, 2H) (HAr), 7.37 (d, J = 8.1, 2H) (HAr), 5.98 (s, 1H) (H12a), 5.54 (s, 1H) (H12b), 5.42 (d, J = 4.2, 1H) (H1), 4.83 (t, J = 9.3, 1H) (H4), 4.18 (dd, J = 8.7, 7.5, 1H) (H7S), 4.15 (dd, J = 12.3, 5.0, 1H) (H6a), 3.98 (dd, J = 12.3, 2.5, 1H) (H6b), 3.89 (dd, J = 10.4, 8.7, 1H) (H7R), 3.83 (ddd, J = 9.3, 5.0, 2.5, 1H) (H5), 3.77 (s, 3H) (OCH_3), 3.74 (dd, J = 14.1, 5.3, 1H) (H9S), 3.56 (dd, J = 14.1, 9.2, 1H) (H9R), 3.08-2.97 (m, 1H) (H8), 2.72-2.65 (m, 1H) (H10b), 2.46 (s, 3H) (CH_3Ph), 2.17-1.97 (m, 3H) (H10a, H2, H3), 2.06 (s, 3H) (CH_3CO), 1.91 (s, 3H) (CH_3CO); ^{13}C NMR (25 MHz) 170.65 (C=O), 169.92 (C=O), 166.99 ($COOCH_3$), 144.91 (=C), 137.38 (C11), 136.36 (=C), 129.92 (=CH), 127.72 (=CH), 125.99 (C12), 100.81 (C1), 69.92 (C5), 69.91 (C7), 68.28 (C4), 62.39 (C6), 54.03 (C9), 51.83 (OCH_3), 43.01 (C2), 39.07 (C10), 35.98 (C8), 34.32 (C3), 21.52 (CH_3Ph), 20.72 (CH_3CO). HRMS $[M\text{-}CH_2OCOCH_3]^+$ calcd for $C_{22}H_{27}O_8S$: 451.1426, found : 451.1413.

14a : ^{1}H NMR (400 MHz) 7.79 (d, J = 8.1, 2H) (HAr), 7.38 (d, J = 8.1, 2H) (HAr), 6.14 (s, 1H) (H12a), 5.58 (s, 1H) (H12b), 5.42 (d, J = 5.6, 1H) (H1), 4.79 (dd, J = 9.1, 6.3, 1H) (H4), 4.35 (dd,J = 9.5, 6.6, 1H) (H7S), 4.18 (dd, J = 12.2, 5.1, 1H) (H6a), 4.07 (dd, J = 12.2, 2.6, 1H) (H6b), 3.90 (ddd, J = 9.1, 5.1, 2.6, 1H) (H5), 3.77 (s, 3H) (OCH_3), 3.58 (dd, J = 9.5, 5.0, 1H) (H7R), 3.16-3.08 (m, 2H) (H9S, H9R), 3.04 (m, 1H) (H8), 2.58 (dd, J = 14.2, 5.2, 1H) (H10a), 2.46 (s, 3H) (CH_3Ph), 2.40 (dd, J = 14.2, 8.7, 1H) (H10b), 2.15 (m, 1H) (H3), 2.08 (s, 3H) (CH_3CO), 2.05 (m, 1H) (H2), 1.91 (s, 3H) (CH_3CO); ^{13}C NMR (25MHz) 170.55 (C=O), 169.93 (C=O), 166.61 ($COOCH_3$), 144.97 (=C), 137.81 (C11), 136.26 (=C), 129.92 (=CH), 127.73 (=CH), 126.60 (C12), 99.58 (C1), 70.93 (C7), 69.45 (C5), 68.41 (C4), 62.99 (C6), 58.87 (C9), 51.77 (OCH_3), 45.41 (C2), 37.69 (C8), 36.70 (C10), 36.56 (C3), 21.45 (CH_3Ph), 20.70 (CH_3CO), 20.69 (CH_3CO). HRMS $[M\text{-}CH_3CO_2H]^+$ calcd for $C_{23}H_{28}O_8S$: 464.1505, found : 464.1489; $[M\text{-}CH_2OCOCH_3]^+$ calcd for $C_{22}H_{27}O_8S$: 451.1426, found : 451.1426.

10 : ^{1}H NMR 7.81 (d, J = 8.1, 2H) (HAr), 7.39 (d, J = 8.1, 2H) (HAr), 5.41 (d, J = 3.9, 1H) (H1), 5.15 (t, J = 10.0, 1H) (H4), 4.41 (dd, J = 9.3, 7.9, 1H) (H7S), 4.36 (dd, J = 12.5, 4.3, 1H) (H6a), 4.03 (dd, J = 12.5, 2.0, 1H) (H6b), 4.04-3.99 (m, 1H) (H5), 3.91 (t, J = 10.0, 1H) (H3), 3.89 (t, J = 9.3, 1H) (H7R), 3.71 (dd, J = 13.5, 2.4, 1H) (H9S), 3.21 (dd, J = 13.5, 11.7, 1H) (H9R), 3.10-3.00 (m, 1H) (H8), 2.56 (ddd, J = 10.0, 5.4, 4.1, 1H) (H2), 2.46 (s, 3H) (CH_3Ph), 2.08 (s, 3H) (CH_3CO), 2.07 (s, 3H) (CH_3CO); ^{13}C NMR (25 MHz) 170.68 (C=O), 169.87 (C=O), 145.36 (=C), 135.98 (=C), 130.21 (=CH), 127.93 (=CH), 100.91 (C1), 69.60 (C5), 69.40 (C4), 69.19 (C7), 61.27 (C6), 56.80 (C3), 55.96 (C9), 47.76 (C2), 34.99 (C8), 21.67 (CH_3Ph), 20.76 (CH_3CO), 20.59 (CH_3CO). HRMS see **10+11**.

Addition of TsCl of 5a. A solution containing **5a**, as a 9:1 mixture of α and β anomers, (540 mg, 2 mmol), TsCl (1.95 g, 5 eq) and AIBN (65 mg 0.2 eq) was irradiated for 25 h. A flash chromatography (pentane:EtOAc, 4:1 to 1:1) led to 470 mg of **10+11** (in a 75:25 ratio determined by ^{1}H NMR) and 45mg of a minor product arising from the β anomer.

11 : ^{1}H NMR (400 MHz) 7.75 (d, J = 8.4, 2H) (HAr), 7.33 (d, J = 8.4, 2H) (HAr), 5.32 (d, J = 4.4, 1H) (H1), 5.04 (t, J = 9.5, 1H) (H4), 4.27 (dd, J = 12.5, 4.5, 1H) (H6a), 4.26 (dd, J = 9.9, 7.0, 1H) (H7S), 4.01 (dd, J = 12.5, 2.4, 1H) (H6b), 3.94 (ddd, J = 9.5, 4.5, 2.4, 1H) (H5), 3.79 (t, J = 9.5, 1H) (H3), 3.78 (dd, J = 9.9, 3.7, 1H) (H7R), 3.13 (AB part of a ABX spectrum, J_{AB} = 13.9, 2H) (H9S, H9R), 2.90-2.81 (m, 1H) (H8), 2.44-2.38 (superpimposed ddd, J = 4.4, 2.2, 1H) (H2), 2.41 (s, 3H) (CH_3Ph), 2.04 (s, 3H) (CH_3CO), 2.02 (s, 3H) (CH_3CO); ^{13}C NMR (50 MHz) 170.85 (C=O), 169.53 (C=O), 145.49 (=C), 135.96 (=C), 130.28 (=CH), 128.18 (=CH), 100.03 (C1), 70.51 (C5), 70.01 (C7), 69.63 (C4), 62.22 (C6), 59.89 (C9), 59.27 (C3), 50.61 (C2), 36.82 (C8), 21.79 (CH_3Ph), 20.87 (CH_3CO), 20.75 (CH_3CO). HRMS (**10+11**) $[M\text{-}OCOCH_3\text{-}HCl]^+$ calcd for $C_{18}H_{21}O_6S$: 365.1059, found : 365.1049.

Allyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5b). This compound was prepared from **5a** according to the protocol developed by Szeja.[16] Benzyl chloride (0.87 mL, 4 eq) was added slowly at 50°C, over 6 h , to a mixture of **5a** (0.51 g, 1.9 mmol), 3.8 mL of 50% NaOH, 0.1 mL of *tert* butanol and 0.12 g of tetrabutyl ammonium hydrogenosulfate in 4 mL of benzene, vigorously stirred at 50°C,. Stirring was continued at 50°C for 4 h after the end of addition; the solution was diluted with 10 mL of benzene and the aqueous layer was extracted with two portions of 15 mL of benzene. The combined organic layers were washed

with a saturated solution of NaCl and dried over Na_2SO_4. Purification by chromatography (pentane:Et_2O, 75:25) led to 550 mg (80%) of Allyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (R_f 0.61) and 80 mg (15%) of Allyl 6-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (R_f 0.12).

5b : ^{1}H NMR (200 MHz) 7.32-7.20 (m, 10H) (HAr), 6.04 (d, J = 10.2, 1H) (H3), 6.02-5.78 (m, 1H) (H8), 5.74 (d, J = 10.2, 1H) (H2), 5.32 (dq, J = 18.5, 1.7, 1H) (H9a), 5.12 (m, 1H) (H9b), 5.04 (s, 1H) (H1), 4.60-4.35 (m, 4H) (CH_2Ph), 4.32-3.95 (m, 4H) (H7a, H7b, H4, H5), 3.72-3.66 (m, 2H) (H6a, H6b); ^{13}C NMR (50 MHz) 138.03 (=C), 137.93 (=C), 134.36 (C8), 130.64 (C3*), 128.21-127.48 (=CH), 126.39 (C2*), 116.96 (C9), 93.73 (C1), 73.18 (C4), 70.86 (C7), 70.20 (C5), 69.06 (CH_2Ph), 68.88 (CH_2Ph), 68.70 (C6). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found : C, 75.57; H, 7.12.

Addition of TsBr to 5b. Addition of TsBr (470 mg, 2 mmol) to **5b** (733 mg, 1 eq) led, after flash chromatography on silicagel (pentane:EtOAc, 10:1 to 6:1) to 150 mg of **6b**, 180 mg of a mixture containing **6b**, **7b** and 170 mg of **7b**. ^{1}H NMR (400 MHz) of a sample of the crude reaction mixture, filtered on a short pad of silica, revealed a 71:29 ratio for **6b**:**7b**.

6b : ^{1}H NMR (400 MHz) 7,78 (d, J = 8.2, 2H) (HAr), 7.48-7.15 (m, 12 H) (HAr), 5.34 (d, J = 4.2, 1H) (H1), 4.86 (d, J = 10.2, 1H) (CH_2Ph), 4.68 (d, J = 12.1, 1H) (CH_2Ph), 4.57 (d, J = 10.2, 1H) (CH_2Ph), 4.52 (d, J = 12.1, 1H) (CH_2Ph), 4.30 (dd, J = 9.2, 7.8, 1H) (H7a), 3.92 (m, 2H) (H3, H4), 3.86 (dd, J = 10.8, 2.6, 1H) (H6b), 3.85 (m, 2H) (H5, H7b), 3.81 (dd, J = 13.9, 5.2, 1H) (H9S), 3.67 (dd, J = 10.8, 2.0, 1H) (H6a), 3.20 (dd, J = 13.9, 11.6, 1H) (H9R), 3.11-3.01 (m, 1H) (H8), 2.85 (ddd, J = 9.8, 5.7, 4.2, 1H) (H2), 2.47 (s, 3H) (CH_3Ph); ^{13}C NMR (100 MHz) 145.24 (=C), 137.57 (=C), 137.51 (=C), 136.28 (=C), 130.19 (=CH), 128.50, 128.43, 128.16, 128.10, 128.02, 127.92 (=CH), 101.55 (C1), 77.25 (C5*), 75.51 (CH_2Ph), 73.79 (CH_2Ph), 72.18 (C4*), 69.49 (C7**), 68.42 (C6**), 55.92 (C9), 51.38 (C3), 48.59 (C2), 35.33 (C8), 21.68 (CH_3Ts).

7b : ^{1}H NMR (400 MHz) 7.80 (d, J = 8.2, 2H) (HAr), 7.40-7.10 (m, 12H) (HAr), 5.34 (d, J = 4.6, 1H) (H1), 4.85 (d, J = 10.4, 1H) (CH_2Ph), 4.63 (d, J = 12.0, 1H) (CH_2Ph), 4.51 (d, J = 10.4, 1H) (CH_2Ph), 4.50 (d, J = 12.0, 1H) (CH_2Ph), 4.26 (dd, J = 9.8, 6.8, 1H) (H7a), 3.91 (t, J = 9.1, 1H) (H3), 3.81 (t, J = 9.1, 1H) (H4), 3.80-3.65 (m, 4H) (H7b, H6a, H6b, H5), 3.20 (AB part of a ABX spectrum, J_{AB} = 14.0, 2H) (H9R, H9S), 2.85-2.78 (m, 1H) (H8), 2.58 (ddd, J = 9.2, 4.6, 2.3, 1H) (H2), 2.48 (s, 3H) (CH_3Ph); ^{13}C NMR (50 MHz) 145.10 (=C), 137.33 (=C), 137.32 (=C), 135.81 (=C), 130.01-127.53 (=CH), 100.20 (C1), 76.36 (C5*), 76.43 (CH_2Ph), 73.52 (CH_2Ph), 73.20 (C4*), 69.72 (C7**), 66.53 (C6**), 59.25 (C9), 54.07 (C3), 51.56 (C2), 37.71 (C8), 21.57 (CH_3Ph). HRMS **6a+7b** calcd for $C_{15}H_{21}O_4{}^{79}Br$: 344.0623 found : 344.0630; m/z (%) 91 (100), 113 (3.41), 114 (3.88), 129 (4.21), 131 (2.46), 159 (4.13), 205 (5.01), 219 (2.80) 344 (0.49), 346 (0.48).

Allyl 4,6-*O*-methylene-α-D-*erythro*-hex-2-enopyranoside (5c). 3-*O*-acetyl-1,5-anhydro-2-deoxy-4,6-O-methylene-D-*ribo*-hex-1-enytol was prepared in five steps from methyl α-D-glucopyranoside, according to procedures previously described for related compounds.[17a-d] In the ultimate step this compound was converted into **5c** *via* a Ferrier reaction (cf **5a**).

5c : ^{1}H NMR (200 MHz) 6.13 (d, J = 10.0, 1H) (H2), 6.10-5.90 (m, 1H) (H10), 5.83 (dt, J = 10.0, 2.4, 1H) (H3), 5.50-5.20 (m, 2H) (H9a, H9b), 5.20 (two superimposed d, J = 6.1, 6.4, 2H) (H1,H7e), 4.74 (d, J = 6.1, 1H) (H7a), 4.40-4.00 (m, 3H), 4.00-3.40 (m, 3H).

Addition of TsBr to 5c. According to the previously described protocol, **5c** (160 mg, 0.8 mmol) was allowed to react with TsBr (190 mg, 1 eq). After 7 h, chromatography ($CHCl_3$:Et_2O, 6:4) led to 95 mg of **8c** (R_f 0.67), 20 mg of a mixture of **6c** and **7c** and 40 mg of **7c** (R_f 0.57).

6c : ^{1}H NMR (400 MHz) 7.78 (d, J = 8.2, 2H) (HAr), 7.38 (d, J = 8.2, 2H) (HAr), 5.26 (d, J = 4.2, 1H) (H1), 5.08 (d, J = 6.4, 1H) (H7eq), 4.62 (d, J = 6.4, 1H) (H7ax), 4.34 (dd, J = 9.2, 7.7, 1H) (H8S), 4.12 (dd, J = 10.6, 5.2, 1H) (H6eq), 3.84 (t, J = 9.9, 1H) (H3), 3.84 (superimposed m, 1H) (H8R), 3.81 (dd, J = 13.9, 2.8, 1H) (H10S), 3.73 (dt, J = 10.0, 5.2, 1H) (H5), 3.43 (t, J = 10.0, 1H) (H6ax), 3.36 (t, J = 10.3, 1H) (H4), 3.19 (dd, J = 13.8, 11.6, 1H) (H10R), 3.07 (m, 1H) (H9), 2.74 (ddd, J = 9.9, 5.8, 4.2, 1H) (H2), 2.44 (s, 3H) (CH_3Ph); ^{13}C NMR (100 MHz) 145.31 (=C), 136.08 (=C), 130.19 (=CH), 127.86 (=CH), 101.49 (C1), 94.07 (C7), 80.23 (C4), 69.57 (C8), 68.18 (C6), 65.17 (C5), 55.61 (C10), 48.09 (C2), 46.09 (C3), 35.26 (C9), 21.65 (CH_3Ph).

7c : ^{1}H NMR (400 MHz) 7.76 (d, J = 8.2, 2H) (HAr), 7.35 (d, J = 8.2, 2H) (HAr), 5.27 (d, J = 4.4, 1H) (H1), 5.11 (d, J = 6.4, 1H) (H7eq), 4.68 (d, J = 6.4, 1H) (H7ax), 4.32 (dd, J = 10.0, 6.6, 1H) (H8S), 4.16 (dd, J = 10.6, 5.1, 1H) (H6eq), 3.87 (dd, J = 10.0, 2.8, 1H) (H8R), 3.80 (t, J = 10.3, 1H) (H3), 3.75 (dt, J = 9.6, 5.1, 1H) (H5), 3.42 (superimposed m, 1H) (H6ax), 3.44 (t, J = 10.3, 1H) (H4), 3.26-3.18 (AB part of a ABX spectrum, 2H) (H10R, H10S), 2.80 (m, 1H) (H9), 2.68 (m, 1H) (H2), 2.48 (s, 3H) (CH_3Ph); ^{13}C NMR (100 MHz) 145.34 (=C), 135.77 (=C), 130.15 (=CH), 127.88 (=CH), 100.55 (C1), 93.99 (C7), 79.62 (C4), 69.69 (C8), 68.19 (C6), 66.46 (C5), 59.15 (C10), 51.19 (C2), 50.48 (C3), 38.09 (C9), 21.66 (CH_3Ph.

Allyl 4,6-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (5d). This compound was prepared in 52% yield from 3,4,6-tri-*O*-acetyl-D-galactal, according to the procedure previously applied to the synthesis of **5a**.

5d : ^{1}H NMR (200 MHz) 6.15-6.01 (AB part of a ABX spectrum, J_{AB} = 10.1, 2H) (H2, H3), 5.90 (m, 1H) (H8), 5.32-5.17 (m, 2H) (H9a, H9b), 5.10 (d, J = 3.6, 1H) (H1), 5.01 (dd, J = 5.1, 2.4, 1H) (H4), 4.33 (m, 1H) (H5), 4.29-4.01 (m, 4H) (H6a, H6b, H7a, H7b), 2.06 (s, 6H) (CH_3CO); ^{13} C NMR (25 MHz) 170.30 (C=O), 170.29 (C=O), 134.07 (C8), 130.59 (C3), 125.30 (C2), 117.69

(C9), 93.07 (C1), 68.90 (C7), 66.83 (C5), 62.81 (C4), 62.80 (C6), 20.77 (CH_3CO). Anal. Calcd for $C_{13}O_6H_{18}$: C, 57.77 ; H, 6.71. Found: C, 57.66 ; H, 6.72.

Addition of TsBr to 5d. Addition of TsBr (235 mg, 1 mmol) to **5d** (270 mg, 1 eq) led, after chromatography ($CHCl_3$:Et_2O, from 9:1 to 3:7), to 30 mg of unreacted **5d**, 80 mg of **6d** (R_f 0.45 ($CHCl_3$:Et_2O, 6:4)), 90 mg of a mixture containing **6d** and **7d**, together with traces of the dihydrohalogenated 1,2-adduct **8d** (detected by ^1H NMR by the presence of two dt, at 6.75 and 7.10 ppm respectively, characteristic of the ethylenic protons in the α-β unsaturated sulfone) and finally 40 mg of **7d** (R_f 0.40 ($CHCl_3$:Et_2O; 6:4)). The ratio of **6d**:**7d** was determined by HPLC analysis (*iso*octane:EtOAc; 6:4; 2 mL/min) of a sample of the crude reaction mixture, filtered on a short pad of silica.

6d : ^1H NMR (400 MHz) 7.79 (d, *J* = 8.2, 2H) (HAr), 7.40 (d, *J* = 8.2, 2H) (HAr), 5.38 (d, *J* = 3.9, 1H) (H1), 5.35 (br d, *J* = 3.5, 1H) (H4), 4.35 (dd, *J* = 9.3, 8.2, 1H) (H7S), 4.27 (br t, *J* = 6.7, 1H) (H5), 4.13 (dd, *J* = 10.8, 3.5, 1H) (H3), 4.11 (dd, *J* = 11.5, 6.0, 1H) (H6a), 3.99 (dd, *J* = 11.5, 6.7, 1H) (H6b), 3.86 (dd, *J* = 10.5, 9.3, 1H) (H7R), 3.74 (dd, *J* = 13.9, 2.8, 1H) (H9S), 3.26 (dd, *J* = 13.9, 11.9, 1H) (H9R), 3.14-3.05 (m, 1H) (H8), 2.68-2.62 (ddd, *J* = 10.8, 5.8, 3.9, 1H) (H2), 2.46 (s, 3H) (CH_3Ph), 2.17 (s, 3H) (CH_3CO), 2.05 (s, 3H) (CH_3CO); ^{13}C NMR (25 MHz) 170.37 (C=O), 169.75 (C=O), 145.22 (=C), 135.95 (=C), 130.11 (=CH), 127.78 (=CH), 101.26 (C1), 68.73 (C5), 68.40 (C7), 67.55 (C4), 62.46 (C6), 56.17 (C9), 45.04 (C2), 43.14 (C3), 34.66 (C8), 21.56 (CH_3Ph), 20.62 (CH_3CO), 20.50 (CH_3CO).

7d : ^1H NMR (400 MHz) 7.81 (d, *J* = 8.2, 2H) (HAr), 7.38 (d, *J* = 8.2, 2H) (HAr), 5.35 (d, *J* = 1.3, 1H) (H1), 5.32 (d, *J* = 4.3, 1H) (H4), 4.29 (dd, *J* = 10.1, 7.3, 1H) (H7S), 4.25 (t, *J* = 6.3, 1H) (H5), 4.11 (dd, *J* = 11.5, 5.9, 1H) (H6a), 4.01 (dd, *J* = 11.5, 7.0, 1H) (H6b), 4.02 (dd, *J* = 11.0, 4.3, 1H) (H3), 3.82 (dd, *J* = 10.1, 3.6, 1H) (H7R), 3.26 (dd, *J* = 14.0, 6.6, 1H) (H9S), 3.21 (dd, *J* = 14.0, 6.9, 1H) (H9R), 2.81-2.73 (m, 1H) (H8), 2.52 (ddd, *J* = 11.0, 4.1, 1.3, 1H) (H2), 2.46 (s, 3H) (CH_3Ph), 2.16 (s, 3H) (CH_3CO), 2.05 (s, 3H) (CH_3CO); ^{13}C NMR (100 MHz) 170.43 (C=O), 169.72 (C=O), 145.32 (=C), 136.09 (=C), 130.21 (=CH), 128.14 (=CH), 100.21 (C1), 69.90 (C5), 68.98 (C7), 67.51 (C4), 62.40 (C6). 59.63 (C9), 49.51 (C2), 46.84 (C3), 37.40 (C8), 21.67 (CH_3Ph), 20.62 (CH_3CO), 20.55 (CH_3CO).

Addition of methyl 2-tosylmethyl-2-propenoate to 5d. Reaction of **5d** (100 mg, 0,4 mmol) with **12** (190 mg, 2 eq) in the presence of TsCl (0.25 eq) and benzoyl peroxide (0.20 eq) at reflux in benzene led after chromatography ($CHCl_3$:Et_2O, 9:1 to 4:6) to 30 mg of recovered **5d**, 15 mg of **13d** (R_f 0.43 ($HCCl_3$:Et_2O; 6:4)), 50 mg of a mixture of **13d** and **14d**, and 15 mg of **14d** (R_f 0.40 ($CHCl_3$:Et_2O; 6:4)) - 63% overall yield -.The 66:34 ratio of **13d**:**14d** was determined by HPLC analysis of the crude reaction mixture (*iso*octane:EtOAc; 6:4; 2 mL/min).

13d : ^1H NMR (400 MHz) 7.84 (d, *J* = 8.0, 2H) (HAr), 7.37 (d, *J* = 8.0, 2H) (HAr), 6.29 (s, 1H) (H12a), 5.55 (s, 1H) (H12b), 5.40 (d, *J* = 4.2, 1H) (H1), 5.05 (t, *J* = 2.06, 1H) (H4), 4.11 (dd, *J* = 11.0, 4.9, 1H) (H6a), 4.07 (dd, *J* = 8.0, 6.8, 1H) (H7S), 4.05 (superimposed m, 1H) (H5), 3.95 (t, *J* = 8.4, 1H) (H7R), 3.93 (dd, *J* = 11.0, 7.0, 1H) (H6b), 3.76 (s, 3H) (OCH_3), 3.75 (dd, *J* = 13.7, 4.3, 1H) (H9S), 3.53 (dd, *J* = 13.7, 10.1, 1H) (H9R), 3.07-2.98 (m, 1H) (H8), 2.53 (d, *J* = 14.6, 1H) (H10a), 2.46 (s, 3H) (CH_3Ph), 2.19-1.97 (m, 3H) (H2, H3, H10b), 2.14 (s, 3H) (CH_3CO), 2.04 (s, 3H) (CH_3CO); ^{13}C NMR (100 MHz) 170.70 (C=O), 170.14 (C=O), 167.23 (COOMe), 144.91 (=C), 136.86 (C_{11}), 135.65(=C), 129.98 (=CH), 129.84 (C_{12}), 128.01 (=CH), 100.49 (C1), 70.64 (C5), 69.94 (C7), 66.03 (C4), 62.67 (C6), 55.00 (C9), 52.08 (OCH3), 41.42 (C2), 34.89 (C8), 34.26 (C3), 33.70 (C10), 21.66 (CH_3Ph), 20.81 (CH_3CO), 20.79 (CH_3CO). HRMS $[M\text{-}CH_2OCOCH_3\text{-}CH_3CO_2H]^+$ calcd for $C_{20}H_{23}O_6S$: 391.1215, found : 391.1214.

14d : ^1H NMR (400 MHz) 7.81 (d, *J* = 7.8, 2H) (HAr), 7.37 (d, *J* = 7.8, 2H) (HAr), 6.28 (s, 1H) (H12a), 5.59 (s, 1H) (H12b), 5.42 (d, *J* = 3.8, 1H) (H1), 5.01 (s br, 1H) (H4), 4.25 (dd, *J* = 9.3, 5.8, 1H) (H7S), 4.12 (dd, *J* = 10.9, 4.7, 1H) (H6a), 4.05 (dd, *J* = 7.2, 4.7, 1H) (H5), 3.93 (dd, *J* = 10.9, 7.2, 1H) (H6b), 3.77 (s, 3H) (OCH_3), 3.66 (d, *J* = 9.3, 1H) (H7R), 3.21 (AB part of a ABX spectrum, J_{AB} = 13.9, J_{AX} = 7.9, J_{BX} = 3.2, 2H) (H9S, H9R), 3.07 (m, 1H) (H8), 2.59 (d, *J* = 13.9, 1H) (H10a), 2.46 (s, 3H) (CH_3Ph), 2.14 (s, 3H) (CH_3CO), 2.17-2.00 (m, 3H) (H2, H3, H10b), 2.04 (s, 3H) (CH_3CO); ^{13}C NMR (100 MHz) 170.73 (C=O), 170.38 (C=O), 167.15 ($COOCH_3$), 145.16 (=C), 136.78 (C_{11}), 136.35 (=C), 130.20 (=CH), 129.06 (C12), 128.09 (=CH), 100.25 (C1), 70.11 (C7), 70.06 (C5), 65.05 (C4), 63.30(C6), 60.06 (C9), 52.06 (OCH_3), 42.58 (C2), 38.31 (C8), 36.64 (C3), 32.51 (C10), 21.72 (CH_3Ph), 20.89 (CH_3CO), 20.85 (CH_3CO). HRMS $[M\text{-}CH_3CO_2H]^+$ calcd for $C_{23}H_{28}O_8S$: 464.1505, found : 464.1489.

References and notes

1 - *For the cyclization of radicals located on the carbohydrate ring leading to bicyclic compounds or spiro ketals see:* a) Gröninger, K. S.; Jäger, K. F.; Giese, B. *Liebigs Ann. Chem.* **1987**, *8*, 731. b) Stork, G.; Suh, H. S.; Kim, G. *J. Am. Chem. Soc.* **1991**, *113*, 7054. c) Vite, G. D.; Alonso, R. A.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 2271. d) Alonso, R. A.; Vite, G. D.; Mc Devitt, R. E.; Fraser-Reid, B. *Ibid.* **1992**, *57*, 573. e) Lopez, J. C.; Gomez, A.H.; Valverde, S. *J. Chem. Soc., Chem. Commun.* **1992**, 613.

2 - *For the cyclization of radicals located on the carbohydrate ring leading to fused rings see:* a) Audin, C.; Lancelin, J.-M.; Beau, J.-M. *Tetrahedron Lett.* **1988**, *29*, 3691. b) Hashimoto, H.; Furuichi, K.; Miwa, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1002. c) Vapachedu, S. R.; Sharma, G. V. M. *Tetrahedron Lett.* **1990**, *31*, 4931. d) Lee, J.; Teng, K.; Marquez, V. E. *Ibid.* **1992**, *33*,

1539. e) Velasquez, S.; Huss, S.; Camarasa, M. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1263.See also ref. 6b and 6g.

3 - *For radical cyclization involving two chains (one bearing the radical precursor, the other bearing the radical acceptor) anchored to the carbohydrate ring see:* a) Haudrechy, A.; Sinäy, P. *Carbohydr. Res.* **1991**, *216*, 375. b) Rama Rao, A.V.; Yadav, J. S.; Rao, C. S.; Chandrasekhar, S. *J. Chem. Soc., Perkin Trans. I* **1990**, 1211. c) Contelles, J. M.; Martinez-Grau, A. *Tetrahedron* **1991**, *47*, 7663. d) Contelles, J. M.; Ruiz, P.; Sanchez, B.; Jimeno, M. L. *Tetrahedron Lett.* **1992**, *33*, 5261. e) Contelles, J. M.; Martinez-Grau, A.; Ripoll, M. M.; Cano, H.; Foces-Foces, C. *J. Org. Chem.* **1992**, *57*, 403. f) Araki, Y.; Endo, T.; Arai, Y.; Tanji, M.; Ishido, Y. *Tetrahedron Lett.* **1989**, *30*, 2829. g) Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1991**, *113*, 5791. h) Dickson, J. K.; Tsang, Jr. R.; Llera, J. H.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 5350. i) Yeung, B. W. A.; Alonso, R. A.; Vite, G. D.; Fraser-Reid, B. *J. Carbohydr. Chem.* **1989**, *8*, 413.

4 - *For radical cyclization involving precursors prepared from carbohydrates see:* a) Rajanbabu, T. V. *Acc. Chem. Res.* **1991**, *24*, 139. b) Wilcox, S. C.; Thomasco, L. M. *J. Org. Chem.* **1985**, *50*, 546. c) Wilcox, S. C.; Gaudino, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3102. d) *Ibid.* **1990**, *112*, 4374. e) Bartlett, P.A.; Mc Laren, K.L.; Ting, P.C. *J. Am. Chem. Soc.* **1988**, *100*, 1633. f) Contelles, J.M.; Pozuelo, C.; Jimeno, M.L.; Martinez, L.; Martinez-Grau, A. *J. Org. Chem.* **1992**, *57*, 2625. g) *Ibid. Tetrahedron Lett.* **1991**, *32*, 6437. h) Contelles, J.M.; Sanchez, B.; Pozuelo, C. *Tetrahedron Asym.* **1992**, *3*, 689. i) Rochigneux, I.; Fontanel, M.L.; Malanda, J.-C.; Doutheau, A. *Tetrahedron Lett.* **1991**, *32*, 2017. j) Enholm, E.J.; Satici, H.; Trivellas, A. *J. Org. Chem.* **1989**, *54*, 5841. k) Hanessian, S.; Léger, R. *J. Am. Chem. Soc.* **1992**, *114*, 3115. l) Redlich, H.; Sudav, W.; Szardenings, A.K.; Vollerthun, R.*Carbohydr. Res.* **1992**, *226*, 57.

5 - *For radical cyclization on a double-bond internal to the carbohydrate ring see:* a) Ferrier, R. J.; Petersen, P. M. *Tetrahedron*, **1990**, *46*, 1. b) Lopez, J.-C.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1989**, *111*, 3450. c) Moufid, N.; Chapleur, Y.; Mayon, P. *J. Chem. Soc., Perkin Trans. I* **1992**, 991. d) *Ibid.* **1992**, 999. d) Mc Donald, C. E.; Dugger, R. W. *Tetrahedron Lett.* **1988**, *29*, 2413. e) Wee, A .G. H. *Tetrahedron* **1990**, *46*, 5065.

6 - a) De Mesmaeker, A.; Hoffmann, P.; Ernst, B. *Tetrahedron Lett.* **1988**, *29*, 6585. b) *Ibid.* **1989**, *30*, 57. c) De Mesmaeker, A.; Hoffmann, P.; Winkler, T.; Waldner, A. *Synlett.* **1990**, 201. d) De Mesmaeker, A.; Hoffman, P.; Ernst, B.; Huy, P.; Winkler, T. *Tetrahedron Lett.* **1989**, *30*, 6307. e) *Ibid.* **1989**, *30*, 6311. f) De Mesmaeker, A.; Waldner, A.; Hoffmann, P.; Mindt, T.; Hug, P.; Winkler, T. *Synlett.* **1990**, 687. g) De Mesmaeker, A.; Waldner, A.; Hoffmann, P.; Hug, P.; Winkler, T. *Ibid.* **1992**, 285.

7 - a) De Riggi, I.; Surzur, J.-M.; Bertrand, M. P. *Tetrahedron* **1988**, *44*, 7119. b) De Riggi. I.; Surzur, J.-M.; Bertrand, M. P.; Archavlis, A.; Faure, R. *Ibid.* **1990**, *46*, 5285. c) Nouguier. R.; Lesueur, C.; De Riggi, I.; Bertrand, M. P.; Virgili, A. *Tetrahedron Lett.* **1990**, *31*, 3541. d) De Riggi, I.; Gastaldi, S.; Surzur, J.-M.; Bertrand, M. P.; Virgili, A. *J. Org. Chem.* **1992**, *57*, 6118. e) De Riggi, I.; Nouguier, R.; Surzur, J.-M.; Bertrand, M.P.; Jaime, C.; Virgili, A. *Bull. Soc. Chim. Fr.* **1993**, *130*, 229. f) The cyclization of ethyl 4-*O*-allyl-hex-2-enopyranoside, where no steric hindrance precludes chair transition states, exhibits the same endo:exo selectivity as the cyclization of diallylether (80:20) (C. Lesueur, thesis, Marseille, 1993 - unpublished results).

8 - *For evidence and synthetic applications of the reversibility of sulfonyl radical addition to double bond see:* a) Skell, P. S.; Woodworth, R. C.; Mc Namara, J. H. *J. Am. Chem. Soc.* **1957**, *79*, 1253. b) b) Ueno, Y.; Aoki, S.; Okawara, M. *Ibid.* **1979**, *101*, 5414. c) Harvey, L. W.; Philips, E. D.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1990**, 481. d) Smith, T. A. K.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1985**, 897. e) Padwa, A.; Murphree, S. S.; Yeske, P. E. *Tetrahedron Lett.* **1990**, *31*, 2983. f) Chuang, C.-P. *Synlett.* **1990**, 527. g) Chuang, C.-P.; Hou, S. S.; Wu, R. R. *Synthetic Commun.* **1992**, *22*, 467. h) Russel, G. A.; Tashtoush, H.; Ngoviwatchai, P. *J. Am. Chem. Soc.*, **1984**, *106*, 4622. i) Ueno, Y.; Aoki, S.; Okawara, M. *J. Chem. Soc., Chem. Commun.* **1980**, 683. j) Ueno, Y.; Sano, H.; Aoki, S.; Okawara, M. *Tetrahedron Lett.* **1981**, *22*, 2675.

9 - Stork, G.; Mook Jr., R. *J. Am Chem. Soc.* **1987**, *109*, 2829.

10 - a) Beckwith, A. L. J. *Tetrahedron*, **1981**, *37*, 3073. b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925. c) Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959. d) Beckwith, A. L. J.; Zimmermann, J. *Ibid.* **1991**, *56*, 5791. e) Beckwith, A. L. J.; Cliff, M. D., Schiesser, C. H. *Tetrahedron* **1992**, *48*, 4641.

11 - a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739. b) Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399.

12 - Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6064.

13 - Da Silva Corrêa, C. M. M.; Oliveira, M. A. *J. Chem. soc., Perkin Trans. II* **1983**, 711.

14 - Panek, J. S.; Sparks, M. A. *Tetrahedron Lett.* **1988**, *29*, 4517.

15 - Jarglis, P.; Lichtenthaler, F. W. *Tetrahedron Lett.* **1982**, *23*, 3781.

16 - Chmielewski, M.; Fokt, I.; Grodner, J.; Grynkiowiez, G.; Szeja, W. *J. Carbohydr. Chem.* **1989**, *8*, 735.

17 - a) Nouguier, R.; Gras, J.-L. *Tetrahedron Lett.* **1989**, *45*, 3423. b) Szeja, W. *Carbohydr. Res.* **1986**, *29*, 4517. c) Whistler, R. L.; Wolfrom, M. L. *"Methods in Carbohydrate Chemistry"* - Academic Press - New-York **1962**, *Vol. 1*, 108. d) Sharma, M.; Brown, R. K. *Can. J. Chem.* **1966**, *44*, 2825.

(*Received in Belgium* 13 *December* 1993; *accepted* 14 *February* 1994)